PHOTOGENERATION AND CHEMISTRY OF α-HYDROXY-SUBSTITUTED ARYLMETHYL CARBANIONS

by

Xigen Xu

B.Sc., Jiangxi University, Nanchang, P.R. China, 1982

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to the required standard

[redacted]

Dr. P. Wan, Supervisor

[redacted]

Dr. T.M. Fyles

[redacted]

Dr. D.A. Harrington

[redacted]

Dr. R.K. Keeler

[redacted]

Dr. R.W. Olafson

Abstract

Supervisor: Dr. P. Wan

The photoretro-aldol reactions of nitrophenyl ethylene glycols and photodecarboxylation of α-hydroxyarylacetate ions and their derivatives have been studied. Both reactions are highly efficient only in aqueous solution. There is strong evidence for the generation of α-hydroxyaryl carbanion intermediates in both reactions.

α-Hydroxy nitroaryl carbanions generated in the photoretro-aldol reaction are not protoned *at all*, but instead lose an electron and a hydrogen atom to give the corresponding nitro arylaldehydes. The nitro arylaldehydes have been found to accept the electron released by the initially photogenerated carbanion intermediate, and are reduced to azoxyaldehydes as final secondary products.

It was discovered that not only α-hydroxy nitroaryl carbanions, but also other nitrobenzyl carbanions, generated either photochemically or thermally, can also reduce nitro arylaldehydes and other nitroaromatic compounds. The enolate ion of *p*-nitroacetophenone (**43**) and derivatives have been found to transfer the electron to unionized **43** and itself are oxidized to *p*-nitrobenzoic acid (**47**). The radical anion of **43** formed is further reduced to give *p*-aminoacetophenone (**59**) so that the net result is a base-catalyzed *disproportionation* of **43** to **59** and **47**.

α-Hydroxy arylacetate ions (**44** and **76-78**) were found to have unusually high quantum yields of photodecarboxylation, in comparison with the parent α-arylacetate ions. The photodecarboxylation is highly pH-dependent; the pH not only affects the reactivity, but also controls the product distribution. Various studies show that α-hydroxyaryl carbanions are the photochemically generated primary intermediates in this reaction.

Examiners:

[redacted]

Supervisor: Dr. P. Wan

[redacted]

Dr. T.M. Fyles

[redacted]

Dr. D.A. Harrington

[redacted]

Dr. R.K. Keeler

[redacted]

Dr. R.W. Olafson

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TO MY FATHER, MOTHER AND HUIPING

CHAPTER ONE

INTRODUCTION

1.1 General

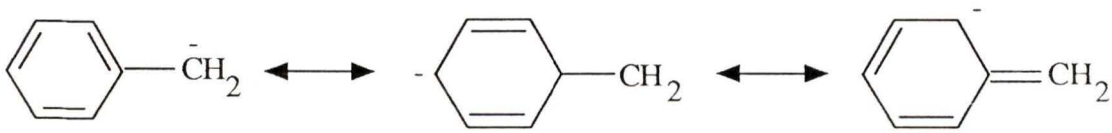
The chemistry of carbanions is an active field of research in ground state chemistry[1]. In the excited state, studies of bond homolyses induced by photolysis are well-documented[2], resulting in radicals. Heterolyses induced by photolysis, resulting in charged intermediates, are much less common[3]. The reason for this is probably because the vast majority of photochemical studies have been performed in the gas phase or in non-polar solvents. These conditions are not favorable for heterolytic bond cleavage[4]. In recent years, photochemical studies carried out in polar solvents, especially in water, have been reported[3,5]. Because of the favorable solvation of ions and ion-pairs in water, heterolytic bond cleavage can become an important or even predominant pathway on photolysis[4,5].

Broadly speaking, a carbanion may be defined as an anion that contains at least one resonance structure in which the negative charge is placed at a carbon. An α-hydroxy aryl-methyl carbanion is a one in which a hydroxyl group is directly linked to the carbon bearing the negative charge. In the ground state, the most useful method for generating carbanions is by deprotonation of the corresponding conjugate acid[6] (eq. 1).

$$RH + B^- \longrightarrow R^- + HB \qquad (1)$$

The ease of deprotonation of the acid, RH, is measured by its acid strength, as determined by its pK_a value. The acidity of RH is related to the relative stabilization associated with the conjugate base, the carbanion R^-. The more stable a carbanion, the stronger the corresponding acid. Shown in Table 1 are the pK_a values of some commonly occurring carbon and oxygen acids in increasing order of acidity. As the acidity increases down the table, the stability of the carbanion so generated increases.

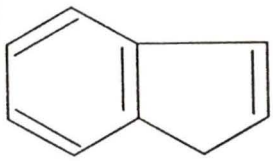
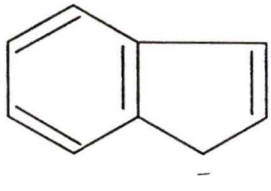
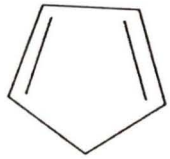
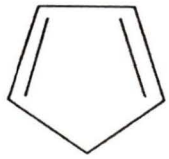
The top part of Table 1 consists of weaker carbon acids ($pK_a > 25$)[7]. Since resonance can stabilize carbanions, benzyl carbanions are much weaker bases than simple hydrocarbon carbanions (eq. 2). The stability of benzyl carbanions, and



(2)

hence their relative ease of generation, is perhaps the most important reason that they are frequently selected as typical carbanions to be studied. Aromaticity can stabilize

Table 1. pK_a Value of Some Carbon and Oxygen Acids

acid	*base*	pK_a	ref.
CH_4	CH_3^-	48	8
$PhCH_3$	$PhCH_2^-$	41	9
Ar_2CH_2	Ar_2CH^-	33.5	10
Ar_3CH	Ar_3C^-	31.5	10
RCH_2CN	$R\bar{C}HCN$	25	11
$RCOCH_2R$	$RCO\bar{C}HR$	19-20	12
		20	13
		16	14
RCH_2OH	RCH_2O^-	16	15
H_2O	HO^-	15.74	16
CH_3OH	CH_3O^-	15.2	14
$(C_6F_5)_3CH$	$(C_6F_5)_3C^-$	16	17
CH_3COCH_2COOR	$CH_3CO\bar{C}HCOOR$	11	11

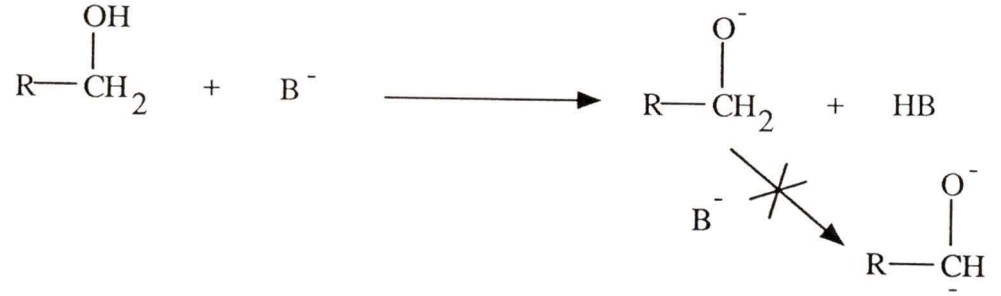
carbanions to a large extent[13,15]. As shown in Table 1, a carbanion can be greatly stabilized when the electron count in a cyclically conjugated array is 4n + 2. Thus, cyclopentadiene (pK_a = 16) is a much stronger acid than acyclic butadienyl systems (pK_a > 30)[15].

Carbanions may be also stabilized by the field effect[17]. In general, a group that withdraws electrons by the field effect increases the acidity of the acid and decreases the basicity of the corresponding carbanion. For example, $(C_6F_5)_3CH$ contains three strongly electron-withdrawing C_6F_5 groups and has a pK_a of 16, in sharp comparison with Ph_3CH, which has a pK_a of 31.5[17].

The acidity of alcohols[14] is much higher than the corresponding hydrocarbons[18]. For example, methanol has a pK_a of 15.2, compared with CH_4, with a pK_a of 48. There are two reasons for this. First, since oxygen is more electronegative than carbon, the proton in the H-O moiety should be more acidic than that in H-C. Second, the ability of H-O to form hydrogen bonds in hydroxylic solvents further enhances its acidity relative to that of H-C. As shown in Table 1, alcohols are much stronger acids than the corresponding hydrocarbons.

Due to the field effect of the hydroxyl group, an α-hydroxy arylmethyl carbanion should be stabilized relative to the parent arylmethyl carbanion. It is conceivable that an α-hydroxy arylmethyl carbanion could be generated by removing a

proton from the carbon of an α-hydroxy-substituted carbon acid. However, because of the higher acidity of the hydroxyl proton, use of any base *will always result in deprotonating the O-H group first*, to give an alkoxide ion. A second deprotonation of the C-H bond, which would generate a dianion, is now unlikely (eq. 3).



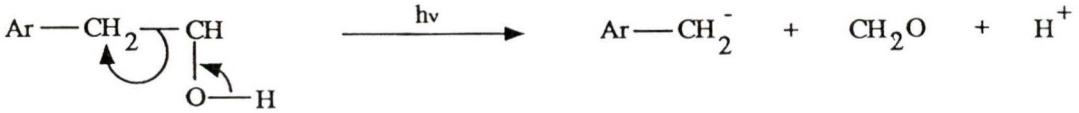
(3)

It is because of the above that there are no experimental reports concerning the generation of α-hydroxy arylmethyl carbanions in the literature. Therefore, the possible generation of these types of carbanions presents a very interesting challenge.

Although not a common method in ground state chemistry, carbanions may also be generated by heterolytic cleavage of a carbon-carbon single bond (eq. 4). Recent progress in

(4)

the study of photochemically induced bond heterolyses[18,19] has provided new routes to photogenerate carbanions. Two such reactions are the photoretro-aldol reaction[3,18] (eq. 5) and photodecarboxylation[19] (eq. 6). Both of these types of



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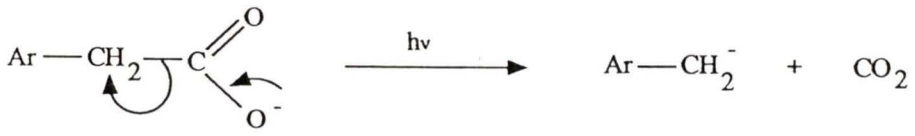
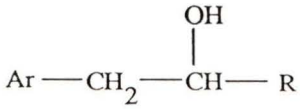


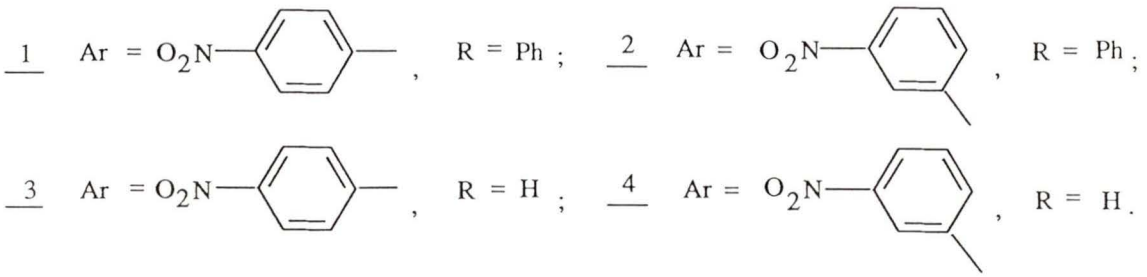
(6)

reactions involve heterolytic cleavage of a carbon-carbon single bond and have proven to be useful methods for carbanion photogeneration. In the following sections, both types of reactions will be reviewed.

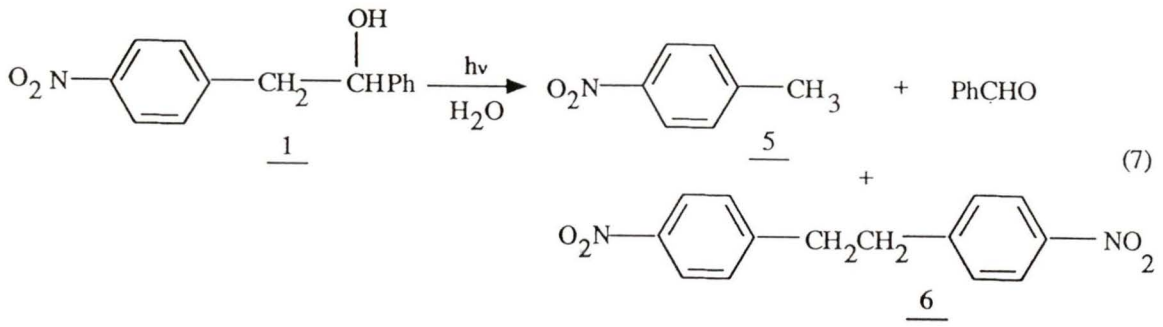
1.2 Photoretro-aldol Reaction.

A number of nitrophenethyl alcohol derivatives, for example **1-4**[3,18,20], undergo photoretro-aldol type reaction in





only aqueous solution and are base and acid catalyzed[3,18,20]. For example, the photoretro-aldol reaction of 2-(*p*-nitrophenyl)-1-phenylethanol[3,20] (**1**) gave *p*-nitrotoluene (**5**) and *p,p*-dinitrobibenzyl (**6**), in addition to benzaldehyde (eq. 7)[3,20]. The ratio of **5** to **6** depends upon



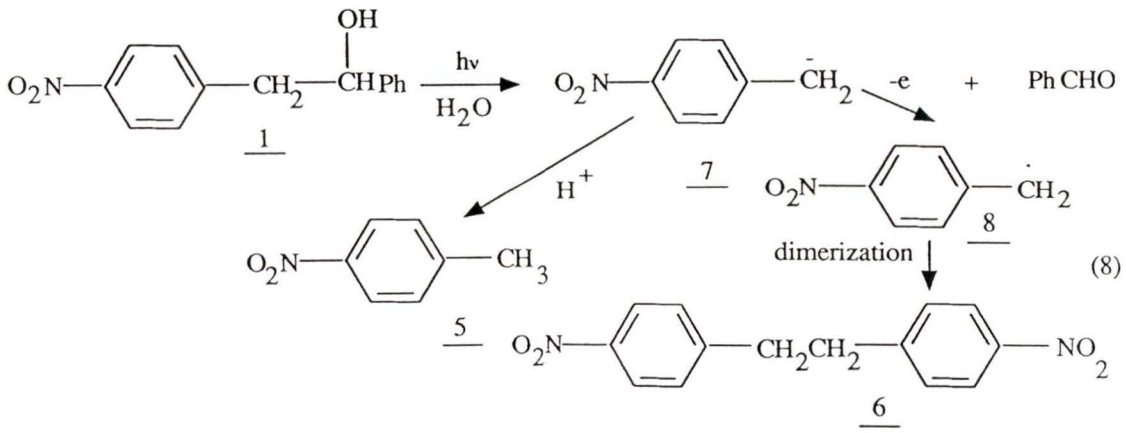
1 5 6 (7)

Table 2. Relative Yields of 5 vs. 6 in Photoretro-aldol Reaction of 1 at Different pH

pH	2	3	4	7	10	11	12	13	14
% **5**	100	90	70	60	50	20	10	5	2
% **6**	0	10	30	40	50	80	90	95	98

the pH of the solution. As shown in Table 2, in acidic and neutral solution, **5** is the major product, while **6** is the minor one. However, in basic solution, the order is reversed; **6** is the major product and **5** the minor one[3,20]. The formation of *p,p'*-dinitrobibenzyl (**6**) is an important piece of evidence

which indicates that the *p*-nitrobenzyl carbanion (**7**) is the intermediate in the photoreaction. This is because **6** is also formed when carbanion **7** is *thermally generated* under strongly basic conditions[21a]. It is believed that carbanion **7** transfers an electron to a molecule of substrate to give *p*-nitrobenzyl radical (**8**), which subsequently dimerizes to give **6**. The radical anion of **5** has been observed by ESR upon reaction of **5** with potassium *t*-butoxide[21a]. It was therefore proposed that the mechanism of the photoretro-aldol reaction involves initial heterolytic cleavage of the benzylic carbon-carbon single bond, yielding carbanion **7** and a carbocation equivalent fragment as primary intermediates. Carbanion **7** can either be protonated to give *p*-nitrotoluene (**5**), or can transfer an electron to substrate to give radical **8**, which will dimerize to give **6** (eq. 8)[3,20]. The radical anion of the substrate **1**



(8)

has been observed by ESR spectrum on photolysis of **1**[21b]. In addition, photolysis of **1** in the presence of a better electron acceptor gives the radical anion of the electron acceptor[21b]. Thus, the radical anion of *p*-nitrobenzoate has been observed by ESR on photolysis of **1** in the presence of *p*-nitrobenzoate (Figure 1)[21b].

1.3 Photoredox Reactions of Nitroaromatic Compounds.

The intramolecular photoredox reaction of a nitroaromatic compound is an oxidation-reduction reaction in which the nitro group is reduced and another group in the molecule is oxidized. Photoredox reductions of *o*-nitroaromatic compounds[22] are typical examples. The mechanism of this type of photoredox reaction[23] involves the abstraction of a hydrogen atom by the excited nitro group--which is believed to be in triplet excited state--to give a biradical as the key intermediate. This biradical can undergo further reaction to give a product with the nitro group reduced and the other substituent oxidized. An example is shown in eq. 9 for the photoredox reaction[23] of *o*-nitrobenzaldehyde (**9**) to *o*-nitrosobenzoic acid (**10**). The primary biradical intermediate recombines to form a five-member heterocyclic product **11**, which is hydrolyzed to furnish the final product, *o*-nitrosobenzoic acid (**10**).

m- And *p*-nitro-substituted isomers can also undergo intramolecular photoredox reaction, although examples are less

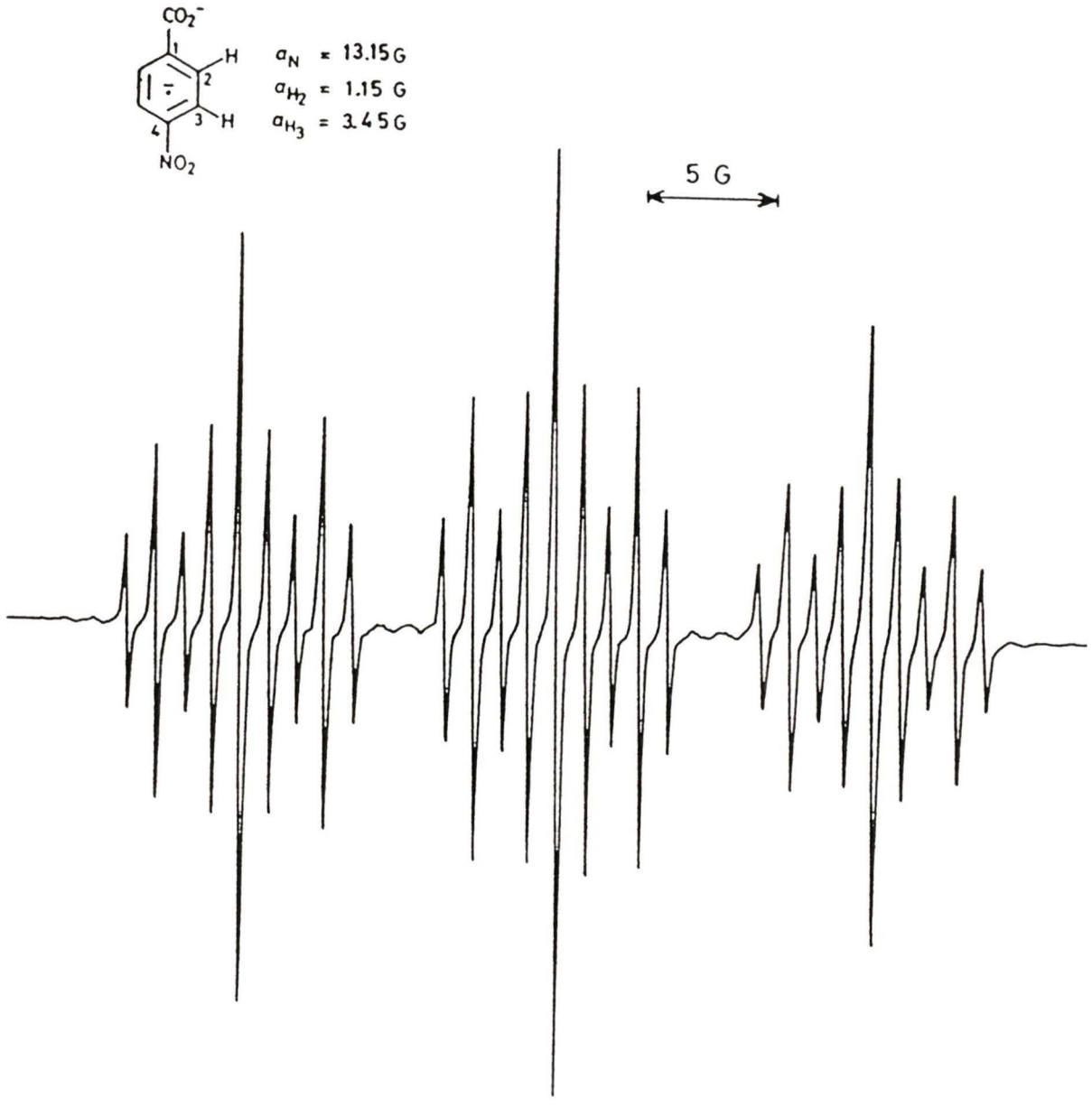
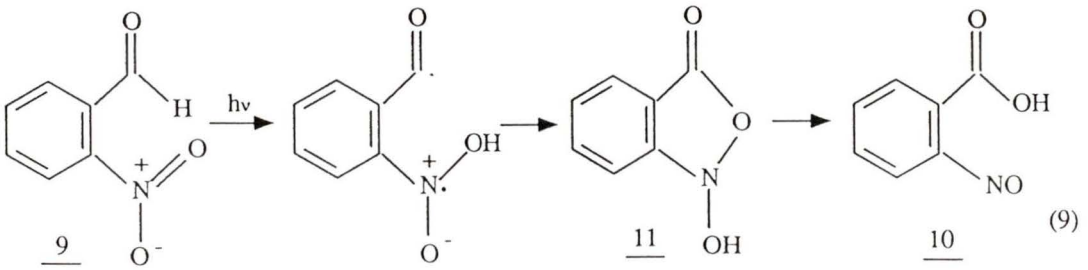


Figure 1 ESR spectrium of the *p*-nitrobenzoate radical anion formed *via* electron transfer from the photogenerated *p*-nitrobenzyl carbanion to *p*-nitrobenzoate in the photoretro-aldol reaction of alcohol **1** in pH 12.



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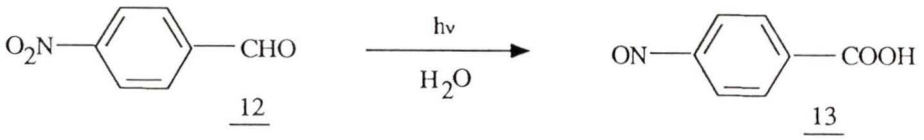
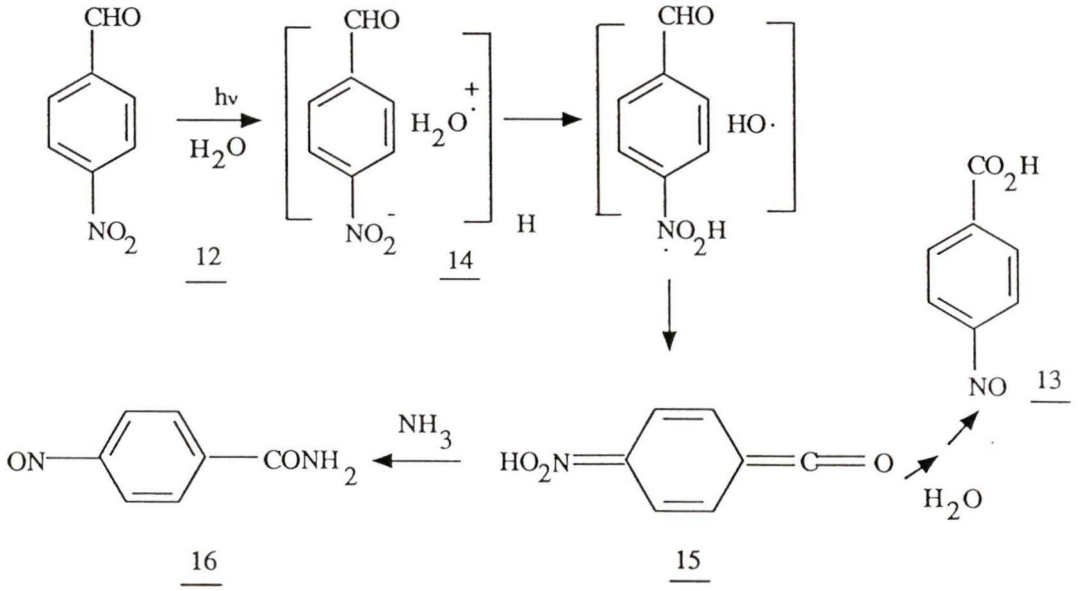
common[24-26]. Photolysis of *p*-nitrobenzaldehyde (**12**) in aqueous solution gave *p*-nitrosobenzoic acid (**13**) as the only product[24,25] (eq. 10). The proposed mechanism[25] involves

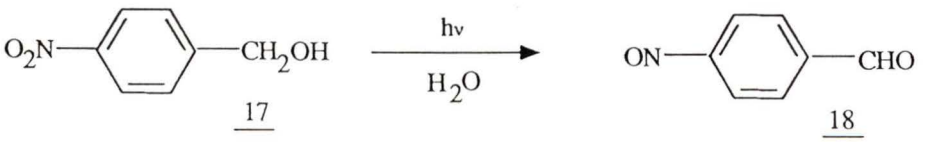


(10)

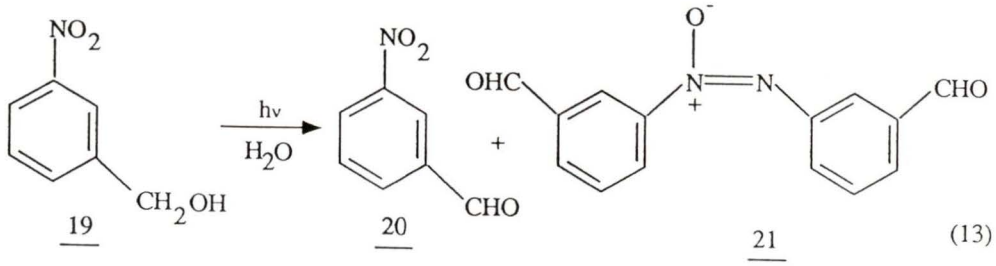
electron transfer from water to the triplet excited state of **12**, to form a radical ion pair **14**. Subsequent proton transfer within **14** and abstraction of the aldehyde hydrogen by the geminate hydroxyl radical gives a quinoid intermediate **15**. Further addition and elimination lead to the product **13**. The presence of ammonia results in formation of *p*-nitrosobenzamide (**16**) (eq. 11). In the paper[25], there was no experimental evidence which would rule out the possibility of the formation of **15** directly from **12**.



Photoredox reactions[26] of *p*- and *m*-nitrobenzyl alcohols (**17** and **19**, respectively) have been reported recently in aqueous solution[26]. Alcohol **17** gave *p*-nitrosobenzaldehyde (**18**) as the only product (eq. 12) in basic solution and alcohol **19**

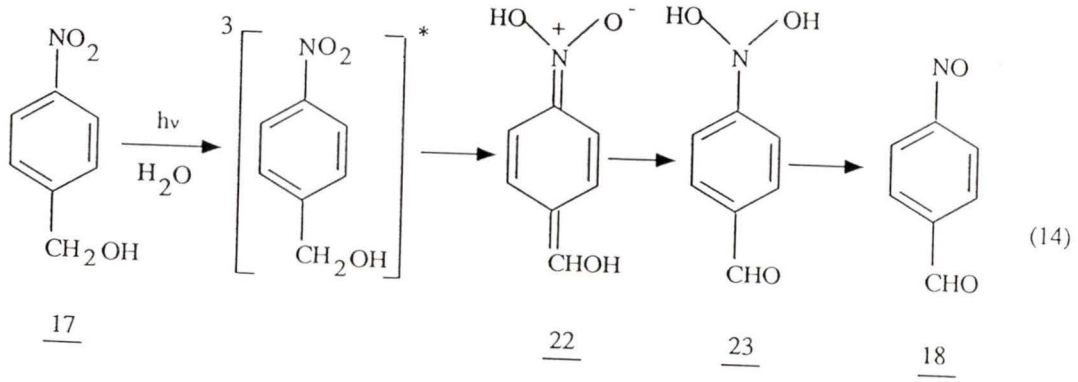


gave *m*-nitrobenzaldehyde (**20**) (major) and *m*-azoxybenzaldehyde (**21**) (minor) as the products (eq. 13).



(13)

The proposed mechanism[26] for the photoredox reaction of **17** involves the key quinoid intermediate **22**, which resembles **15** mentioned above for the photoredox reaction of **12**. Thermal proton transfer of **22** results in hydrated *p*-nitroso-benzaldehyde **23**. Elimination of water leads to formation of *p*-nitrosobenzaldehyde **18** (eq. 14).



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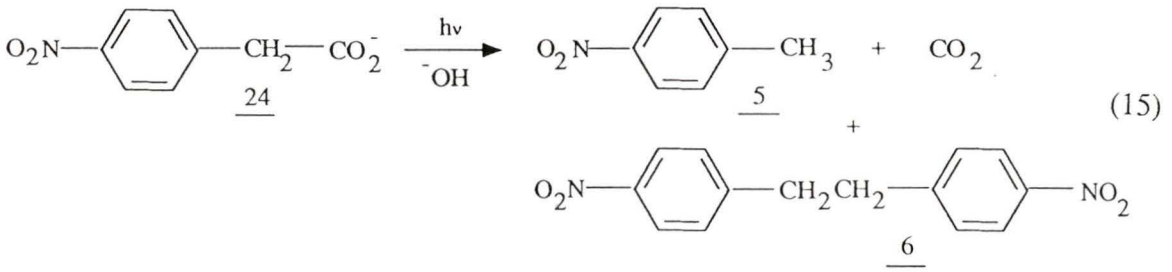
1.4 Photodecarboxylation of Nitrophenyl Acetate Ions

p- And *m*-nitrophenylacetate ions (**24** and **25**,

respectively) were found to undergo irreversible photodecarboxylation in aqueous solution[27] with an approximate quantum yield of 0.6 at λ_{excit}= 367 nm. The isolated products for **24** are *p,p'*-dinitrobibenzyl (**6**) (major) and *p*-nitrotoluene (**5**) (minor) in neutral or basic solution (eq. 15), while the



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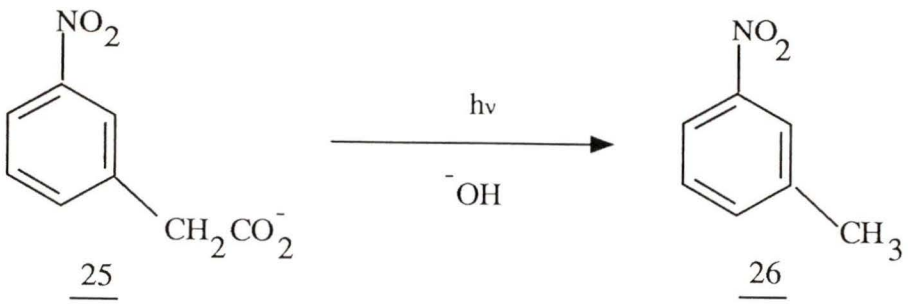
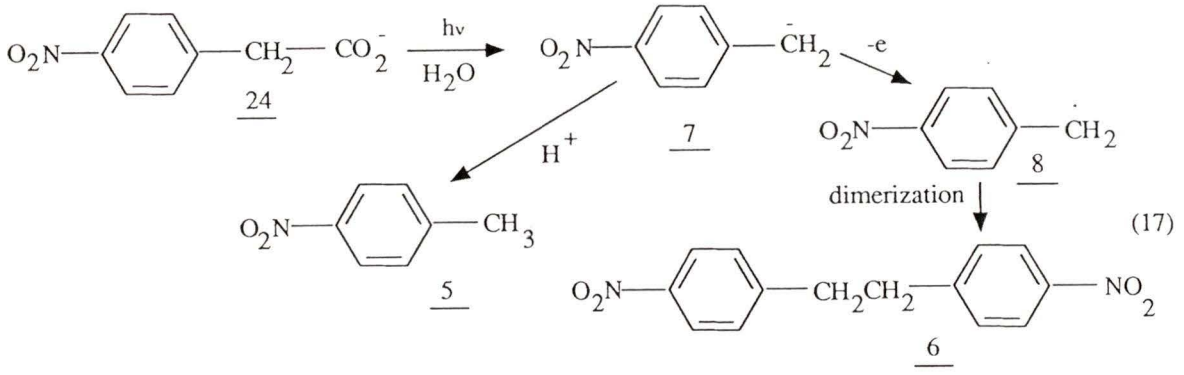
isolated major product for *m*-isomer **25** is *m*-nitrotoluene (**26**) (eq. 16). According to the steady-state product analyses and



(16)

microsecond flash photolysis studies, the mechanism proposed

involves nitrobenzyl carbanions as primary intermediates[3,27]. For example, carbanion **7** is the primary intermediate for the photodecarboxylation of *p*-isomer **24** (eq. 17)[27]. This



(17)

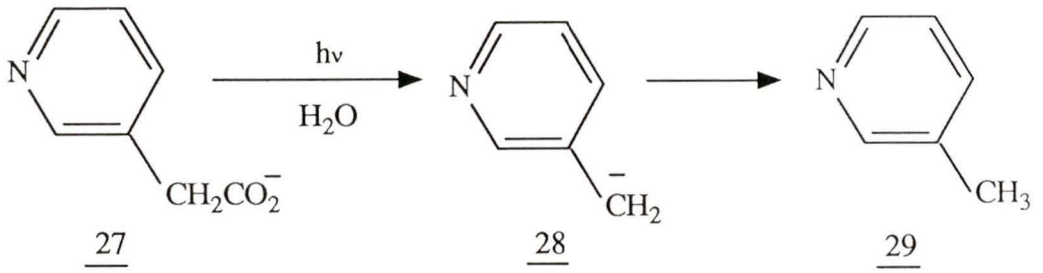
mechanism resembles that proposed for the photoretro-aldol reaction[3]. Strong support for this anionic mechanism is the fact that the protonated forms of both **24** and **25** in either aqueous solution (pH < 4) or nonaqueous solution do not photodecarboxylate[27].

Thermal decarboxylation of **24** and other nitrophenylacetates in non-aqueous solution has also been studied[28] with the conclusion that nitrobenzyl carbaions were also formed as intermediates. Based on the discrepancy in absorption spectra

observed for this thermally generated *p*-nitrobenzyl carbanion **7**[28] with that reported for *photogenerated* **7**[27], it was suggested that the mechanism for photodecarboxylation might involve the initial cleavage to give *p*-nitrobenzyl radical **8** along with carbon dioxide and solvated electron, followed by recombination of the electron with the radical **8** to give **7**, or the radical might recombine to give *p,p'*-dinitrobibenzyl **6**[28]. However, recent studies[29] have shown that nitrobenzyl carbanions suffer substantial solvent-induced spectral shifts in absorption spectra. This solvent effect is the cause of the discrepancy in observed spectra of **7** generated via thermal and photochemical pathways. The radical mechanism[28] can therefore be ruled out. In addition, studies of the photodecarboxylation by picosecond and nanosecond laser flash photolysis[30] have confirmed that the mechanism described in eq. 17 is the dominant cleavage pathway. A long-lived species, assigned to **7**, was detected in the laser flash photolysis of **24**. This experiment confirms that the primary intermediate is the *p*-nitrobenzyl carbanion **7** rather than *p*-nitrobenzyl radical. As in the case of photoretro-aldol reaction of nitrophenethyl alcohols, carbanion **7** transfers an electron to a substrate to give the corresponding radical **8**, which dimerizes to give *p,p'*-dinitrobibenzyl **6** (eq. 6).

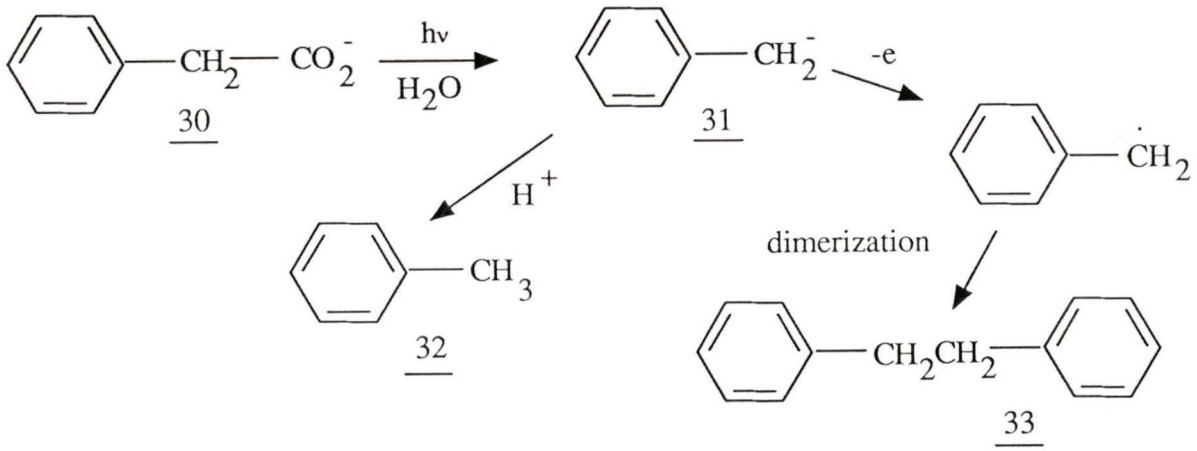
1.5 Photodecarboxylation of Non-nitro-Substituted Aryl Acetate Ions

Photodecarboxylation has been also reported for *o*-, *m*- and *p*-pyridylacetate ions[31]. The mechanism also involves the generation of carbanions as primary intermediates. For example, *m*-pyridylacetate (**27**) photodecarboxylates to give **29** via carbanion **28** (eq. 18)[31]. The pyridyl group is believed to possess enhanced electron-withdrawing ability in the excited state (as a nitrophenyl group). Hence, these reactions are relatively efficient ($\Phi \approx 0.4$-0.6).



27 28 29 (18)

Photodecarboxylation of a number of phenylacetate ions has been studied[32]. The quantum yields of the reaction are generally low ($\Phi < 0.03$)[32,33]. For example, photodecarboxylation[32] of sodium phenylacetate (**30**) in aqueous solution gave toluene (**32**) ($\Phi = 0.03$) and a trace amount of bibenzyl (**33**) ($\Phi = 0.007$), as well as CO_2 ($\Phi = 0.03$) (eq. 19). Based on the results of solvent isotope studies, it was concluded that the primary intermediate for the photodecarboxylation is the benzyl carbanion (**31**)[33]. The major pathway for the reaction of carbanion **31** is protonation, resulting in **32**. The

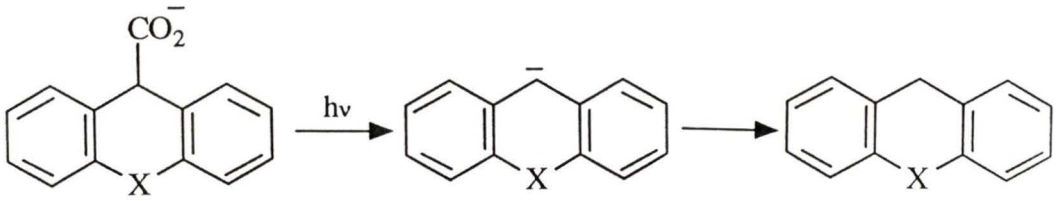


(19)

carbanion may also eject an electron, to give benzyl radical, which dimerizes to give **33**, but this pathway is unimportant[32].

There are no reports in literature about highly efficient photodecarboxylations of non-nitro arylacetate ions until the recent report of the photodecarboxylation of benzannelated acetate ions (**34a-d**)[34] from our laboratory. Thus, a benzannelated acetate ion which can generate a cyclically conjugated carbanion intermediate with 4n electrons undergos much more efficient photodecarboxylation than one which generates 4n + 2 electrons[34]. As shown in Table 3, quantum yield of the photodecarboxylation of **34b**, which generates an 8 electron carbanion intermediate, is very high; while the quantum yield of **34d**, which generates a 6 electron

carbanion intermediate, is very low; quantum yields of **34a** and **34c**, which generate non-cyclically conjugated carbanion intermediates, are in between in quantum efficiency[34]. The proposed mechanism of the reaction is shown by eq. 20[34].



(20)

34 35 36

34a : X = CH_2CH_2 ; 34b : X = CH=CH ;

34c : X = H, H ; 34d :

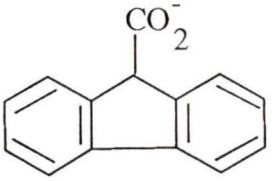


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Table 3. Quantum Yields of Benzannelated Acetate Ions

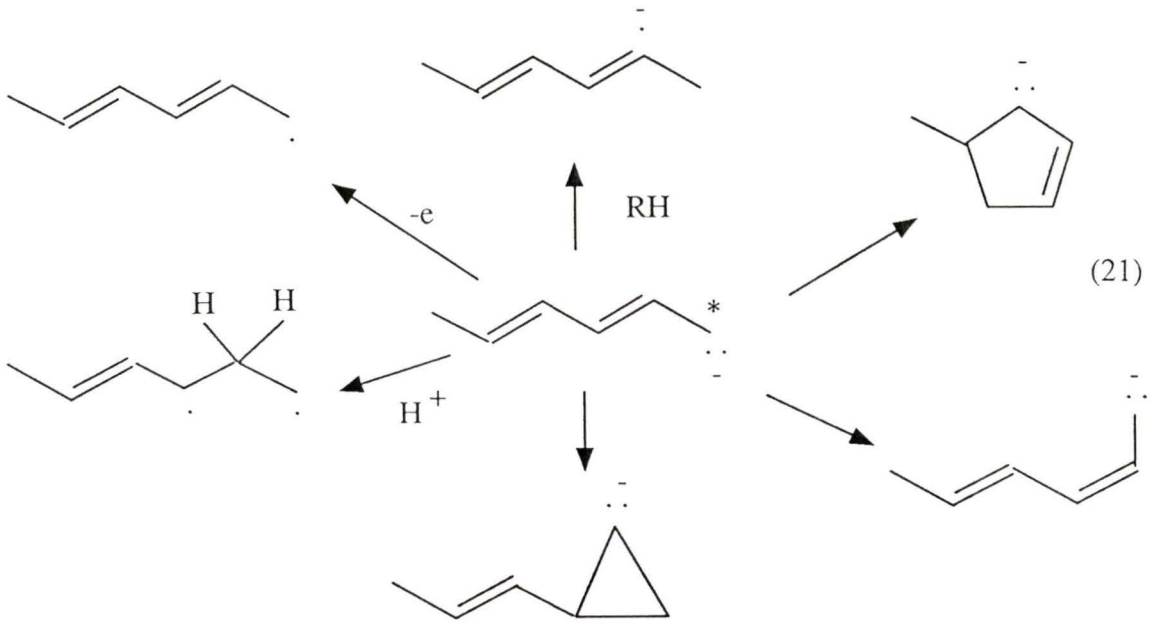
Compound	34a	34b	34c	34d
Φ	0.14	1.0	0.12	< 0.06

The intermediacy of carbanion intermediates **35** was proposed since product studies in D_2O resulted in the incorporation of one deuterium at the dibenzylic position in

the final product **36**[34]. Carbanion **35** was also believed to eject an electron to some extent. The electron could be trapped by externally added *p*-nitrobenzoate, to give the radical anion of *p*-nitrobenzoate, which was observed by ESR spectroscopy. The intensity of the ESR signal observed had a direct dependence on the efficiency of the photodecarboxylation[34]. However, no radical coupling product has yet been isolated, presumably because this electron transfer pathway is a very minor one[34].

1.6 Photochemistry of Carbanions

The photochemistry of carbanions[35,37] has been well studied. Attempts have been made to generalize the photoreaction of carbanions according to the electron density change in the excited states[36]. In practice, the mechanistic behaviour in the photochemistry of carbanions is so diverse that it is impossible to make such generalizations[35a]. An important primary process is electron transfer[37]. For illustrative purposes, the photochemistry of the hexadienyl carbanion (**37**) will be discussed. There are at least six photochemical pathways available (eq. 21)[35a]. The photo-excited carbanion can undergo cis-trans isomerization, or 1,3- and 1,5-cyclization, to give another carbanion isomer. It can also undergo electron ejection to give a radical; protonation to give a 1,3-diradical; and hydrogen abstraction to give a



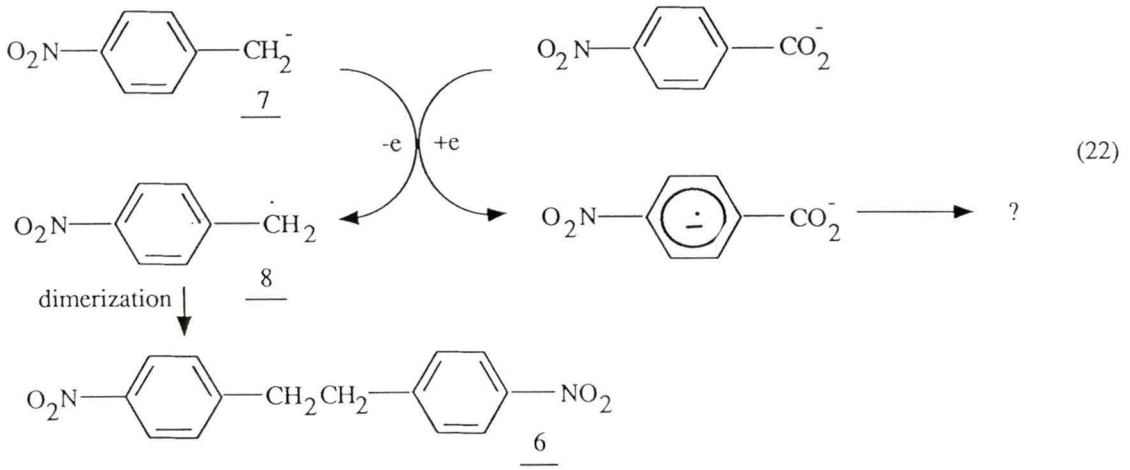
(21)

radical anion[35a] A number of these processes have been observed[35a].

1.7 Reduction of Nitroaromatic Compounds by Carbanions

The nitro group can be reduced by mild reducing agents[22,38] and therefore functions as a mild oxidizing agent. Compounds containing the nitrophenyl group are also good electron acceptors due to the strong electron withdrawing nature of the nitro group[39,40]. Acceptance of one electron by a nitroaromatic compound leads to the generation of the corresponding radical anion, which can be observed and studied by ESR since they have relatively long lifetimes in basic solution[39-41]. Carbanions have been used as electron sources in

strongly basic solution. For example, as mentioned above, carbanion **7** generated in the photoretro-aldol reaction of **1**[3,41] and photodecarboxylation of **24**[20], ejects an electron to an externally added nitroaromatic compound such as *p*-nitrobenzoate, to give the corresponding radical anion (eq. 22). However, the reaction pathway of radical anions generated this way is not known. That is, no reports of stable products from these radical anions have been reported[3].



(22)

1.8 Basis of the Present Studies

As outlined in section 1.1, there are no reports on the generation and chemistry of α-hydroxy arylmethyl carbanions. We have seen that it is impossible to generate such a carbanion by simple deprotonation of the proton at the carbon atom of the corresponding alcohol. Use of C-C bond heterolysis to generate such carbanions in the ground state is

problematic since C-C bond fragmentation is rare at ambient temperature. Because of the added energy in photochemical reaction (60-110 kcal/mol) and the enhanced stabilization of ions or ion pairs in polar solvents[35], it may be possible to design a compound which will undergo heterolytic cleavage to generate an α-hydroxy arylmethyl carbanion on photolysis.

Both photoretrol-aldol reaction of nitrophenethyl alcohols[18] and photodecarboxylation of arylacetate ions[19] described in the previous sections have proved to be excellent methods to photogenerate carbanions, via heterolytic cleavage of a benzylic carbon-carbon bond. The primary goal of the present study is to photogenerate α-hydroxy arylmethyl carbanions based on the above two types of photoreactions.

In Chapter 2, the photochemistry of nitrophenyl ethylene glycols **38-42** will be described. This reaction follows the expected pattern of heterolytic benzylic C-C bond cleavage observed for nitrophenethyl ethanols **1-4**. Evidence is presented to show that *α-hydroxy nitroarylmethyl carbanions are generated as the primary intermediates* on photolysis . A unique property of these α-hydroxy nitroarylmethyl carbanions is that they do not undergo protonation *at all* in the whole pH range (0-14) studied! The only reaction pathway for these carbanions is electron transfer.

We have found that the released electrons from photogenerated *p*-nitrobenzyl carbanion can reduce added nitroaromatic compounds. In Chapter 3, the reduction of some

selected electron acceptors by the electrons released from photodecarboxylation of **24** will be discussed in detail. Studies of these reactions provide indirect evidence for the involvement of electron-tranfer processes in these reactions

Since the enolate ion is a special type of carbanion, it may be possible to use enolate ions as the electron source, to reduce nitroaromatic electron acceptors. In Chapter 3, a novel type of disproportionation reaction initiated by electron tranfer from the enolate ion of *p*-nitroacetophenone (**43**) *via a non-photochemical route* will be also reported.

The photogeneration of non-nitro-substituted α-hydroxy arylmethyl carbanions is also of interest. However, we have so far seen only efficient benzylic C-C heterolysis induced by nitro groups. It would be of interest to test the possibility of photogenerating *unsubstituted* (at the aromatic moiety) α-hydroxyl arylmethyl carbanions. Thus, we started this study by photolyzing the simplest of these compounds, viz., mandelate ion (**44**). The results were surprizing. Photolysis of mandelate ion (**44**) in aqueous solution results in photodecarboxylation with an efficiency almost equal to that of nitrophenylacetate ions **24** and **25**! In Chapter 4, the photochemistry of mandelate ions and other non-nitro-substituted α-hydroxy arylmethyl ions will be reported, which are first examples in which "simple" α-hydroxy arylmethyl carbanions have been photogenerated in solution.

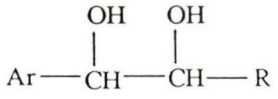
CHAPTER TWO

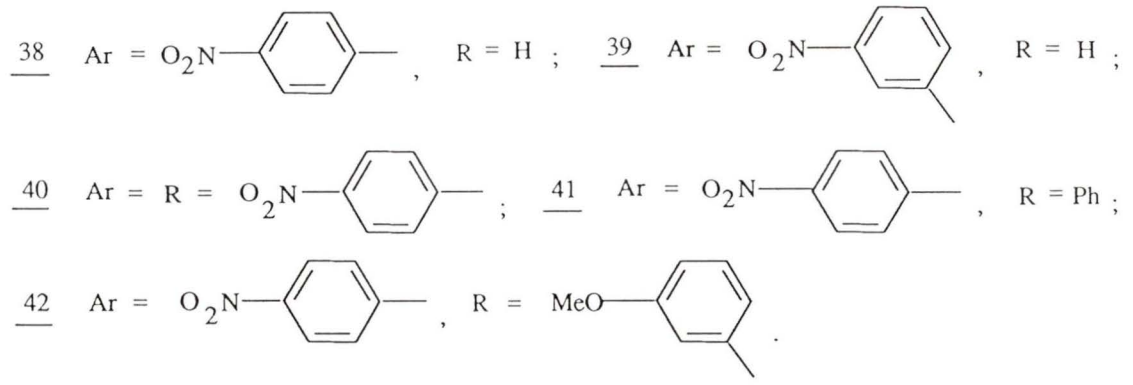
PHOTORETRO-ALDOL TYPE REACTIONS OF NITROPHENYL NITROPHENYL ETHYLENE GLYCOLS

2.1 Introduction

The photochemistry of the nitro group has been a topic of continued interest. Several papers have been published reviewing the progress in the photochemistry of the nitro group in solution[22,38,42,43]. Since the nitro group can stabilize a benzyl carbanion effectively, by both inductive and conjugative effects, nitroaromatic compounds have been widely used to generate carbanions[3,22,27]. Nitroaryl compounds have thus been given special attention in mechanistic studies of heterolytic C-C bond cleavage. It is expected that nitro groups will also stabilize α-hydroxy nitroarylmethyl carbanions. Therefore, the photogeneration of α-hydroxy nitroarylmethyl carbanions can hopefully be carried out readily.

Previous studies[3,18] have shown that the photoretro-aldol reaction of nitrophenethyl alcohols **1-4** involves the formation of primary nitrobenzyl carbanion intermediates via heterolytic bond cleavage. This mechanism is general for all the nitrophenethyl alcohols studied in neutral and basic aqueous solutions[3]. Nitrophenyl ethylene glycols **38-42** are similar to **1-4**, except by the substitution of the α-hydrogen by a hydroxyl group. It is therefore reasonable to assume



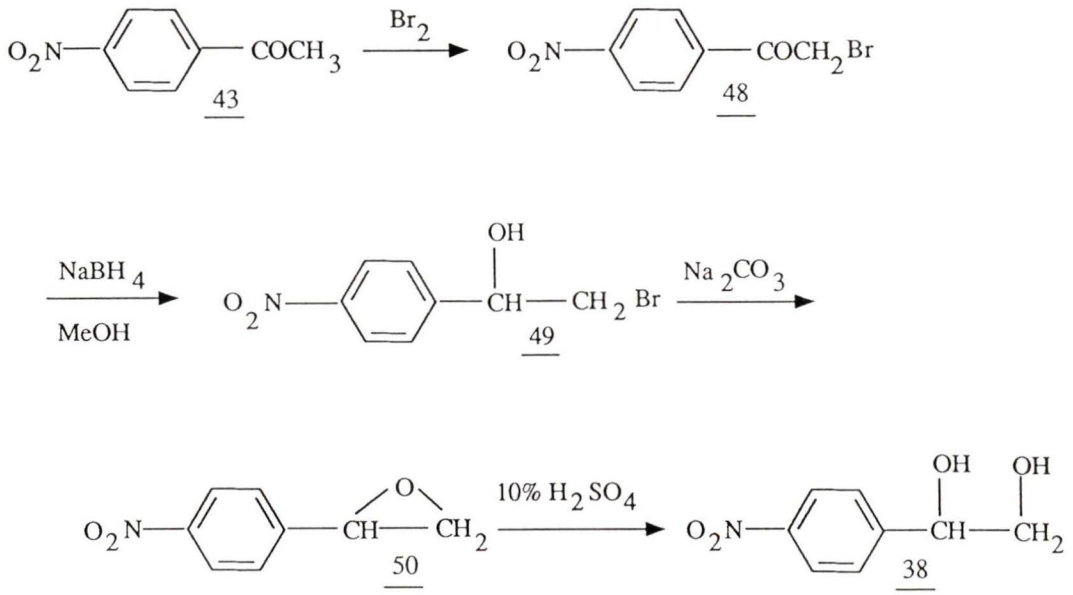


that these nitrophenyl ethylene glycols will also undergo this photoretro-aldol type reaction via the same mechanism. This photoreaction will hopefully lead to the generation of α-hydroxy nitrobenyl carbanions as intermediates so that their chemistry can be studied *in situ*.

2.2 Results and Discussion

2.2.1 Synthesis of Substrates

Glycols **38-42** were selected as the substrates for the photolysis. Synthesis[20] of **38** can be described in Scheme 1. Bromination of **43** gave bromoketone **48** which was reduced by sodium borohydride to the corresponding alcohol **49**.

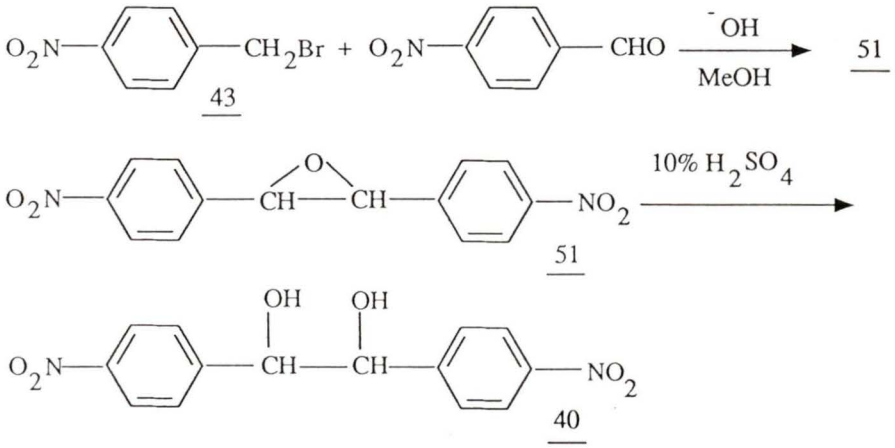


43 48 49 50 38

Scheme 1

Dehydrobromination of **49** under basic conditions gave epoxide **50**, followed by the ring-open hydration to give **38**. These reactions were all carried out with complete conversion. The synthesis of *m*-isomer (**39**) was carried out in a pathway similar to that shown in Scheme 1 for **38**.

For the synthesis of glycol **40**, the method used was different from Scheme 1. Bis(*p*-nitrophenyl) epoxide (**51**) could be synthesized from the reaction of *p*-nitrobenzyl bromide (**51**) with *p*-nitrobenzaldehyde (**12**) in basic ethanol solution (eq. 23)[44]. Ring-open hydration of **52** will lead to



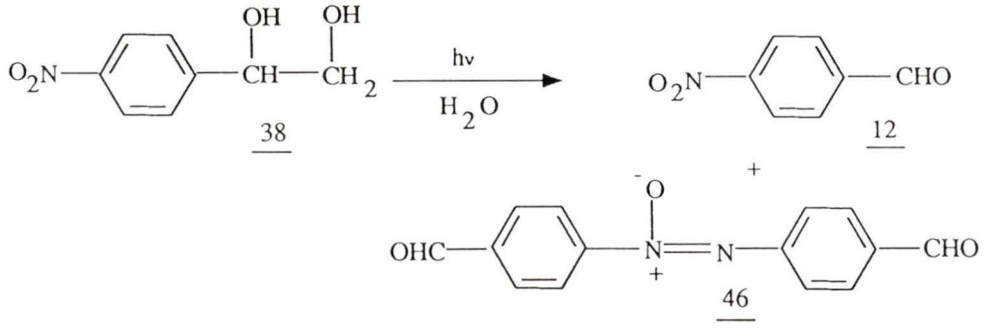
the formation glycol **40** (eq. 24). Syntheses of 1-(*p*-nitrophenyl)-2-phenyl ethylene glycol **41** and 1-(*p*-nitrophenyl)-2-(*m*-methoxy) ethylene glycol **42** were carried out via pathways similar to that shown for the synthesis of **40.**

2.2.2 Solvent Effects

The photoretro-aldol reaction of *p*-NEG (**38**) and *m*-NEG (**39**) was studied in a number of different solvents. No reaction occurred when photolysis was carried out in either pure acetonitrile or methanol. Only in aqueous solution did the photoretro-aldol reaction of both **38** and **39** occur. Aqueous medium was also required for the photoretro-aldol reaction of nitrophenethyl alcohols **1-4**[3,18,20]. These observations suggest that the mechanisms of these reactions involve the formation of ionic intermediates which are stabilized by solvation in water. Less polar solvents are unable to do this, resulting in no photoreaction.

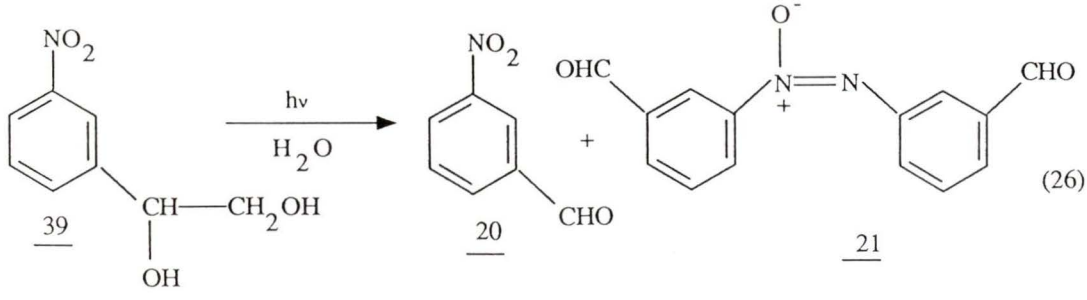
2.2.3 Product Studies

p-NEG (**38**) gave two products in the whole pH range studied (0 - 14). The products were separated and purified by preparative TLC. One product was *p*-nitrobenzaldehyde (**12**), as confirmed by ^{1}H NMR, IR and MS. The other product was *p*-azoxybenzaldehyde (**46**), as determined by ^{1}H NMR, MS, IR and chemical analysis (eq. 25).



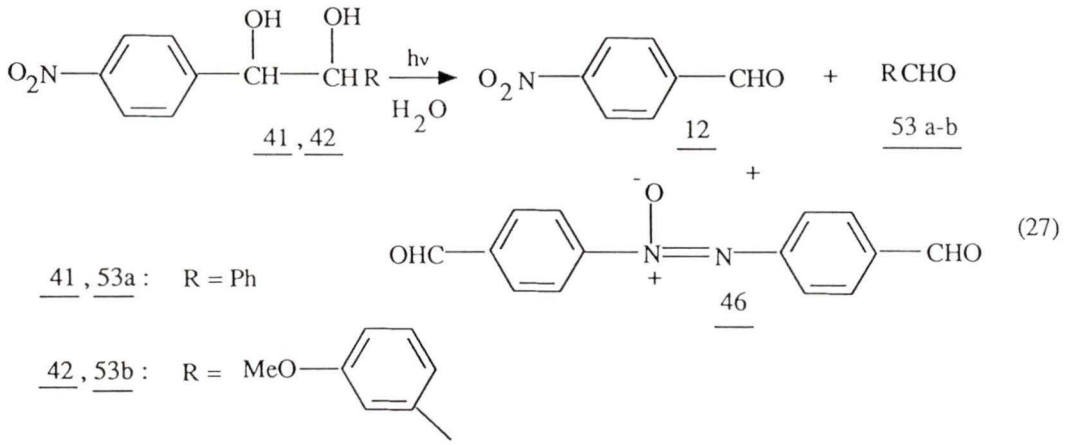
(25)

m-NEG (**39**) also gave two products in the whole pH range studied (0 - 14). The products were separated and purified by preparative TLC, and were *m*-nitrobenzaldehyde (**20**) and *m*-azoxybenzaldehyde (**21**) (eq. 26).



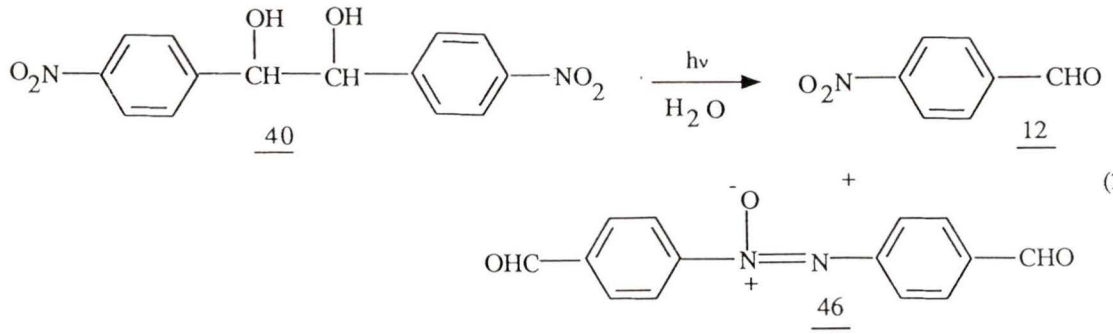
(26)

In a pathway similar to the photoretro-aldol reaction of **38**, photolysis of glycols **41** and **42** in aqueous solution also led to the formation of **12** and **46**. However, benzaldehydes **53a-b** were also formed (eq. 27). It was thus assumed that the



(27)

photoretro-aldol reaction of both **38** and **39** also resulted in the formation of formaldehyde (eqs. 25 and 26), which was lost by evaporation during work-up. For glycol **40**, since the two aryl groups are same, the photoretro-aldol reaction led only to the formation of **12** and **46** (eq. 28).



(28)

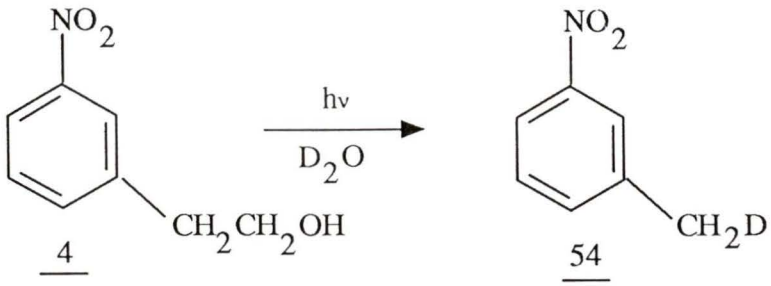
Neither *p*-nitrobenzyl alcohol (**17**) or *m*-nitrobenzyl alcohol (**19**) were obtained from the photolysis of glycol **38** or **39** in any pH. This was rather surprising, since photoretro-aldol reaction of nitrophenethyl alcohols (**1-4**) all resulted in the formation of nitrotoluenes via protonation of the incipient nitroarylmethyl carbanion. One possibility is that **17** or **19** undergoes further photochemical reaction, considering the fact that the photoredox reaction of both **17** and **19** is known[5,26]. However, since the photolysis time for the photoretro-aldol reaction of **38** and **39** is much shorter than the photoredox reaction of **17** and **19**, it is likely that **17** or **19** were not formed at all.

2.2.4 Solvent Isotope Effects

Experiments for the solvent isotope effects of photoretro-aldol reaction of glycols **38** and **39** were carried out by comparing the products and their relative reactivity in H_2O vs. D_2O. There was no significant difference in the reactivity for photoretro-aldol reaction of both **38** and **39**. As indicated by ^1H NMR and MS, deuterium was not incorporated into either nitrobenzaldehydes or azoxybenzaldehydes for both **38** and **39**. There was also no deuterium incorporation in the unreacted substrates. The photoretro-aldol reaction of nitrophenethyl alcohols **1-4** in D_2O solution resulted in mono-deuterated nitrotoluenes. For example, photolysis of compound **4** in neutral D_2O solution led to the formation mono-α-

deuterated *m*-nitrotoluene (**54**) (eq. 29)[3,18].

Studies have shown that photolysis of α-mono-deuterated nitrobenzyl alcohol **55** results in azoxybenzaldehyde-α-D **56** and the normal undeuterated product **20** (eq. 30)[26].



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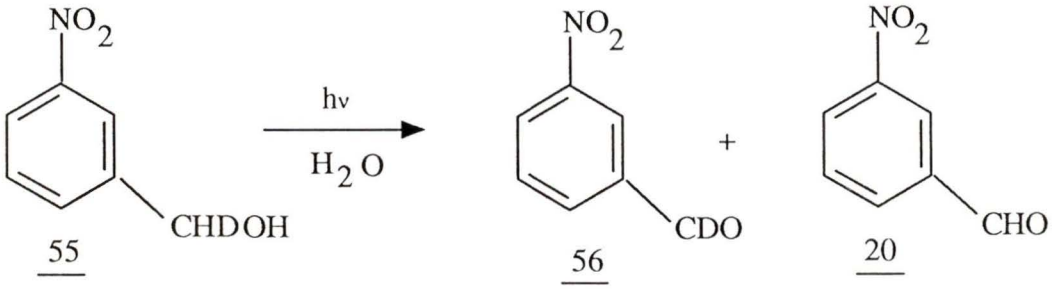


(30)

The above observations clearly show that formation of alcohols **17** and **19** on photolysis of **38** and **39** can be ruled out. For example, assuming that photolysis of **39** in H_2O solution resulted in **19**, then the same photolysis in D_2O solution would lead to the formation of mono-deuterated nitrobenzyl alcohol **55** in the same pathway as eq. 29, which will undergo further photoreaction to result in mono-deuterated aldehyde **56** (eq. 30). The fact that the aldehyde hydrogens in the products from the photoretro-aldol reaction of both **38** and **39** come from the original α-hydrogen in the

possibility of the formation of nitrobenzyl alcohols in the photoretro-aldol reaction.

2.2.5 Quantum Yields, pH and Photolysis Time Effects

Quantum yields of the photoretro-aldol reaction of **1-4**[3,20] at pH 13 and the photodecarboxylation of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-carboxylate ion (Φ = 1)[34] at pH 13 were used as secondary standards to measure the quantum yields for the formation of products in the photoretro-aldol reaction of glycols **38-42**. The photoretro-aldol reaction is pH dependent and is catalyzed by base. As shown in Figure 2 for photoretro-aldol reaction of *p*-NEG (**38**), when the pH is less than 12, quantum yields for both products are very low. However, when the pH is greater than 12, quantum yields for both products increase sharply. Similarly, quantum yields of both products for photoretro-aldol reaction of *m*-NEG (**39**) increase sharply in basic solution as indicated by Figure 3.

The ratio for the formation of nitroaldehydes and azoxybenzaldehydes is also pH dependent. Thus, **38** gave *p*-NB (**12**) as the major product and *p*-AB (**46**) as the minor product when the photolysis was carried out in pH < 12. If the photolysis time was short, the major product was still *p*-NB when the photolysis was carried out under basic conditions. However, when the photolysis was carried out in a longer period, the ratio reversed: *p*-AB (**46**) became the major product and *p*-NB (**12**) the minor. Therefore, the yield of **46** increases

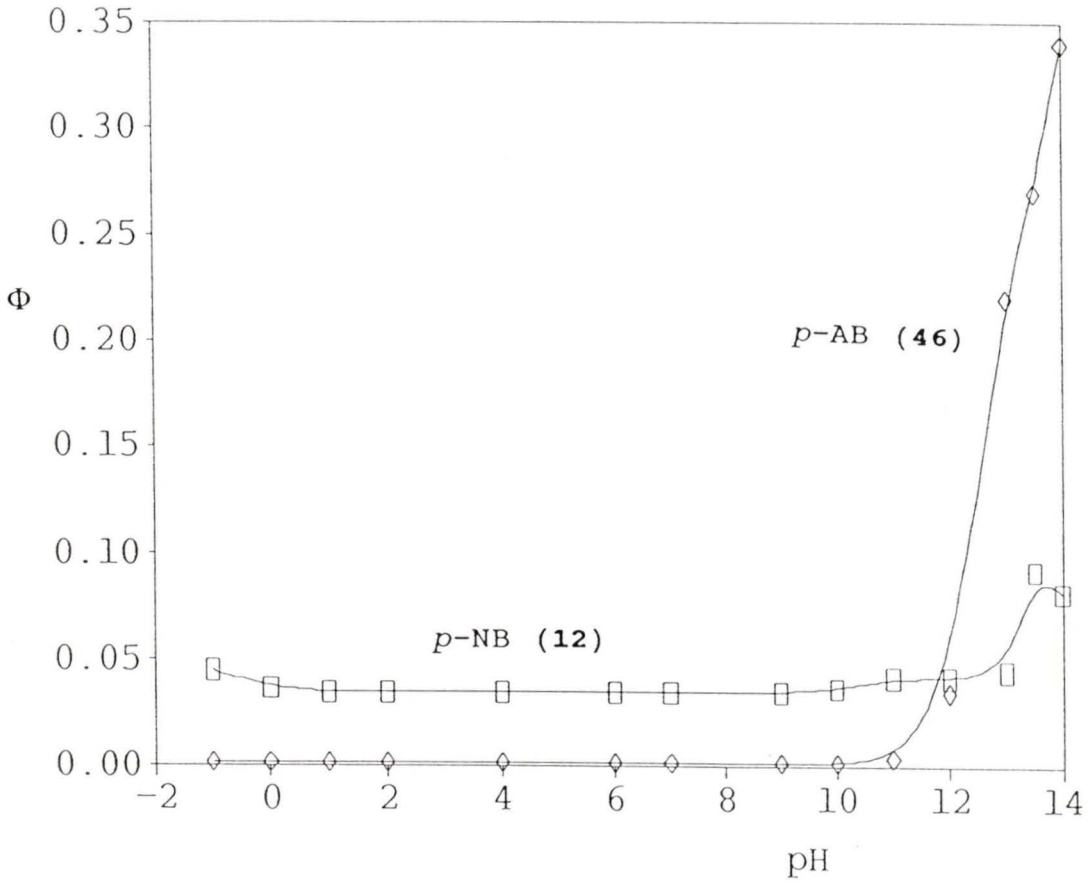


Figure 2 Plot of quantum yield (Φ) as a function of pH of the aqueous portion of the solution (25% CH_3CN) for the photoretro-aldol reaction of *p*-nitrophenyl ethylene glycol (**38**)

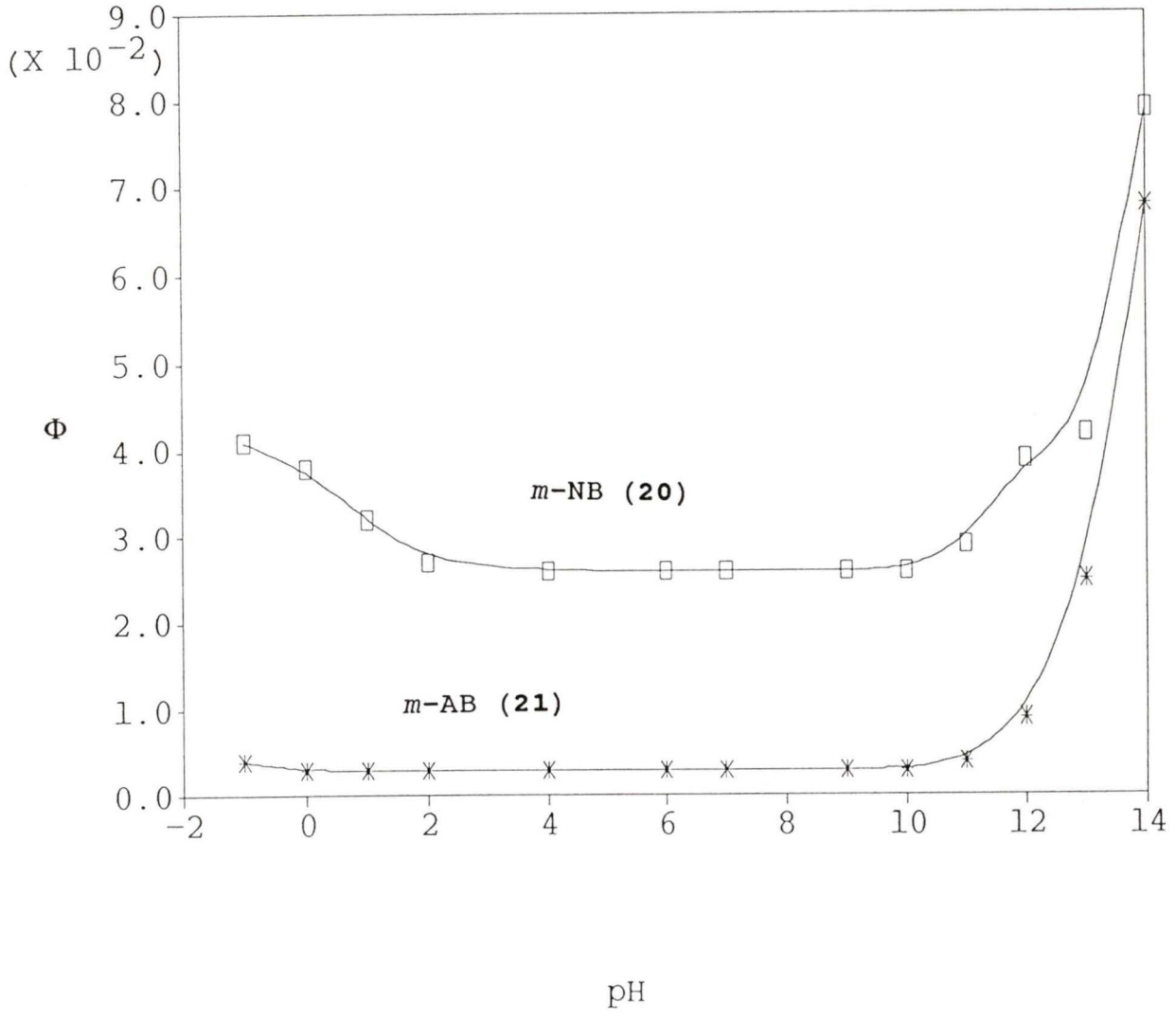


Figure 3 Plot of quantum yield (Φ) as a function of pH of the aqueous portion of the solution (25% CH_3CN) for the photoretro-aldol reaction of *m*-nitrophenyl ethylene glycol (**39**)

with photolysis time, while that of **12** decreases with photolysis time after it reaches a peak in 5-min photolysis. This effect is shown in Figure 4, which indicates that *p*-AB (**46**) is not the primary photochemical product, but is a reduced product of the primary product *p*-NB (**12**).

A similar behavior was observed for the photoretro-aldol reaction of *m*-NEG (**39**). Thus, below pH = 12, the major product was *m*-NB (**20**). Above pH = 12, if the photolysis was carried out in a short time, **20** was still the major product. With increase in photolysis time, as shown in Figure 5, yields of both products **20** and **21** increase, but the difference in yields became smaller.

The photolysis of α-(*p*-Nitrophenyl)-β-substituted ethylene glycols **40, 41** and **42** was carried out between pH 1 and 11, since in basic solution they decompose thermally. In this pH range, the quantum yield is almost independent on the pH. Their reactivity is compatible with that of **38**. In the case of glycol **40,** the major product is also *p*-NB(Φ = 0.03) and minor product *p*-AB (Φ < 0.01). Glycols **41** and **42** underwent similar photoretro-aldol reaction with compatible quantum yields, but in each case, in addition to *p*-NB and *p*-AB, *m*-methoxybenzaldehyde or benzaldehyde were also isolated, respectively. This result shows that the presence of another aromatic group in the β position, either electron-withdrawing or electron-donating, does not affect the quantum yield of photoretro-aldol reaction.

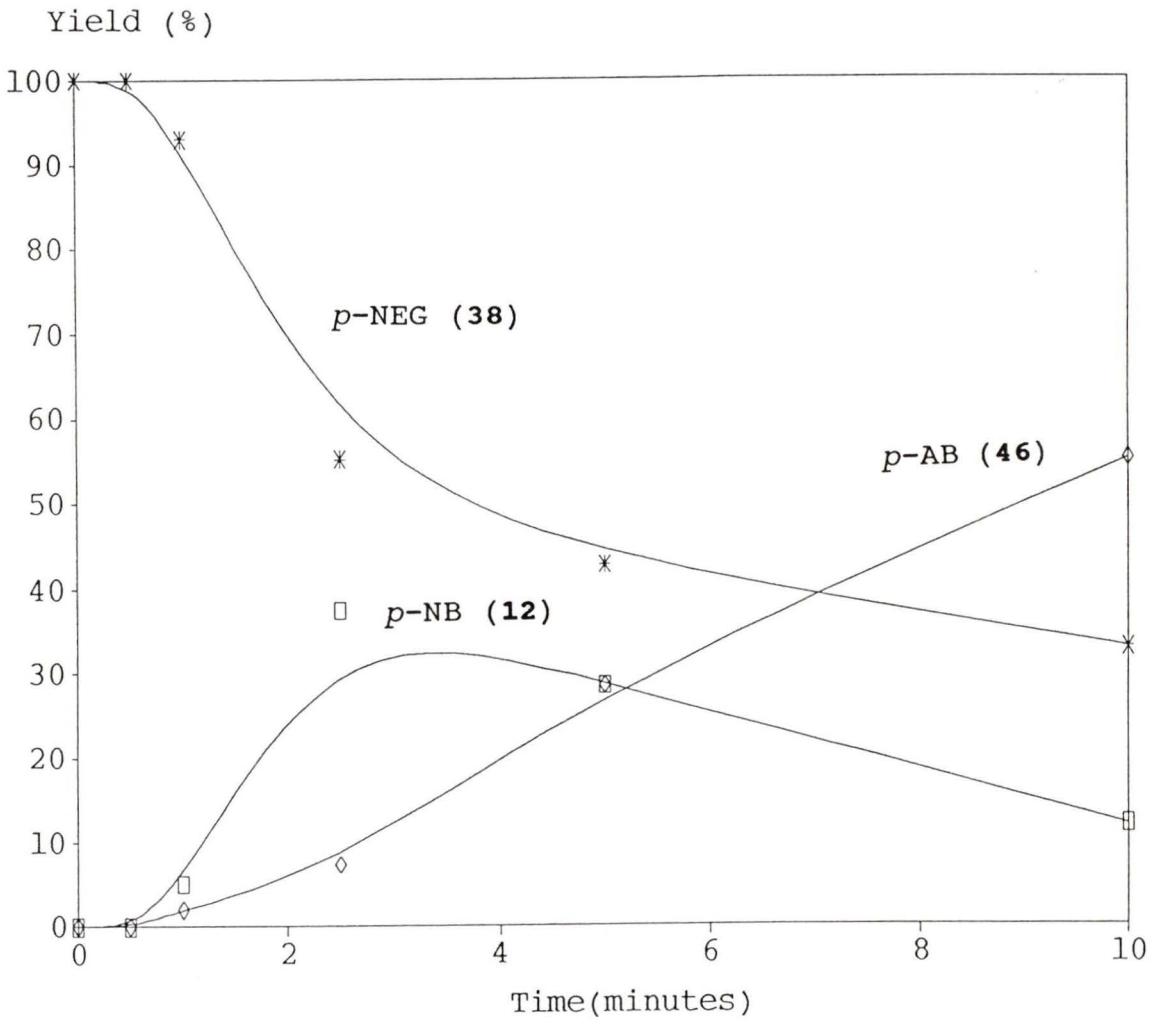


Figure 4 Plot of yield of photoproducts and loss of substrate as a function of photolysis time for the photoretro-aldol reaction of *p*-nitrophenyl ethylene glycol (**38**)

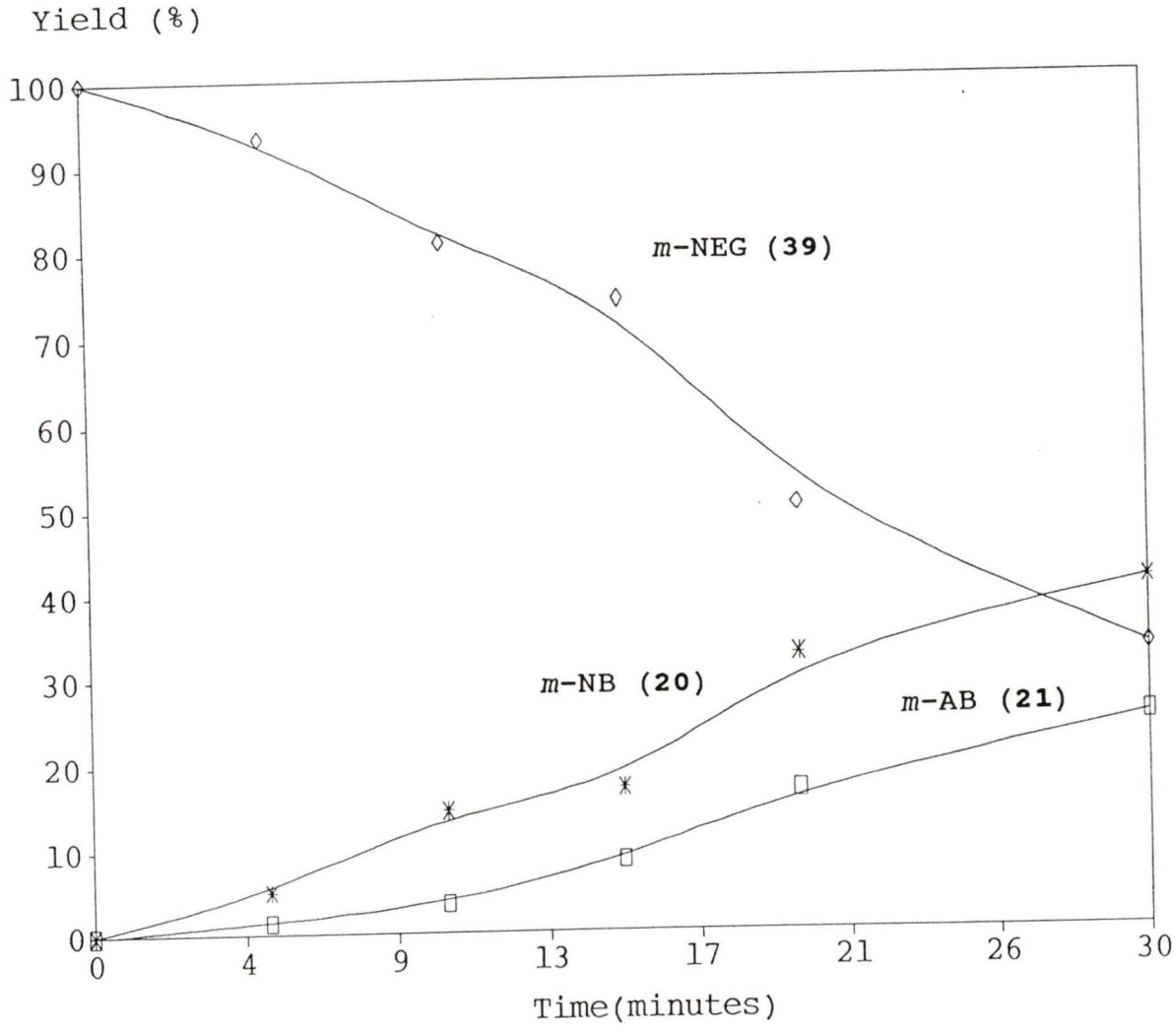


Figure 5 Plot of yield of photoproducts and loss of substrate as a function of photolysis time for the photoretro-aldol reaction of *m*-nitrophenyl ethylene glycol (**39**)

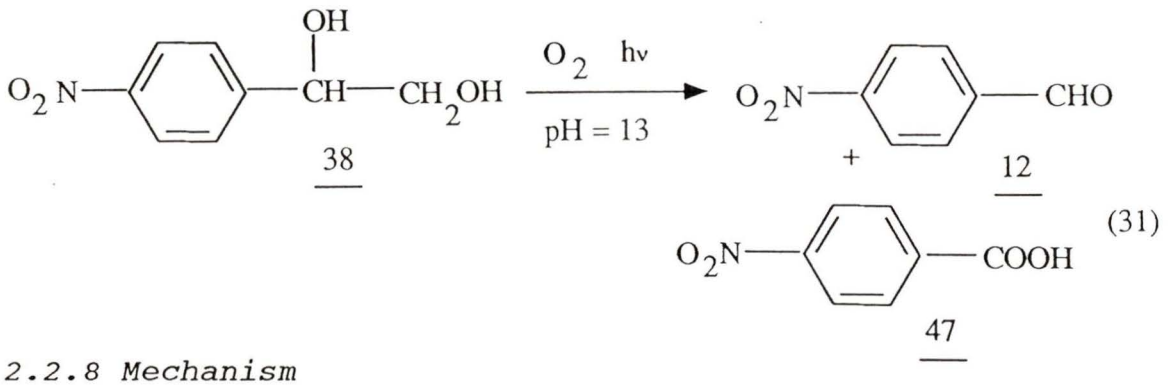
2.2.6 Effect of Externally added Electron Acceptors

It is known that nitroaromatic compounds, such as *p*-nitrobenzonitrile (**45**), are good electron acceptors[41]. Addition of *p*-nitrobenzonitrile to the *p*-NEG (**38**) system upon photolysis resulted in the sharp decrease of the yield of *p*-AB (**12**). For example, the yield of *p*-AB could be as high as 70% after one hour photolysis of *p*-NEG in pH 13.5 without the addition of the external electron-acceptor, while the yield decreased to less than 10% with the addition of an equal amount of *p*-nitrobenzonitrile, other things being equal. As a result, *p*-NB was obtained as the major product even under strongly basic conditions. The electron-acceptor was recovered intact. Similarly, addition of *p*-nitrobenzonitrile to *m*-NEG system led to the sharp decrease of the yield of *m*-AB (**21**). *m*-NB (**20**) was formed as the major product with some unreacted substrate and *p*-nitrobenonitrile recovered.

2.2.7 Photolysis of p-Nitrophenyl Ethylene Glycol under Oxygen

Oxygen is an excellent oxidizing agent for carbanions and radicals[3,42-44]. Oxidation of a carbanion by oxygen leads to a corresponding radical which will continue to react with oxygen to give a hydroperoxide and further oxidized products such as an aldehyde or an acid[3,42,43]. For example, *p*-nitrobenzyl carbanion (**7**) reacts with molecular oxygen in strongly basic solution (*t*-BuOK/*t*-BuOH) to give *p*-nitrobenzoic acid (**47**) as the final oxidation product[44]. It was therefore

expected that α-hydroxy *p*-nitrobenzyl carbanions, once generated, would react with oxygen to give oxidation products. This is what was observed. Thus, when *p*-NEG (**38**) was photolyzed in pH 13 under oxygen purge for 20 minutes, there was no *p*-AB generated. The only two products obtained, *p*-NB (**12**) (40%) and *p*-nitrobenzoic acid (**47**) (60%), are both oxidative products of the intermediate carbanion (eq. 31).



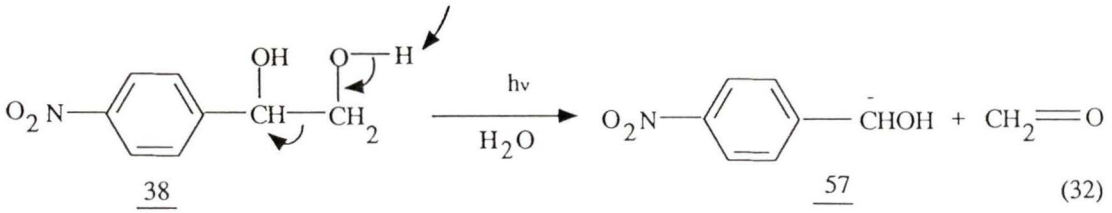
(31)

2.2.8 Mechanism

Photoretro-aldol reactions of nitrophenethyl alcohols **1-4** and a series of corresponding compounds have been well studied[3,18,20]. The primary event of these reactions is heterolytic cleavage of the benzylic C-C bond, to form a carbanion intermediate as descibed in section 1.2.

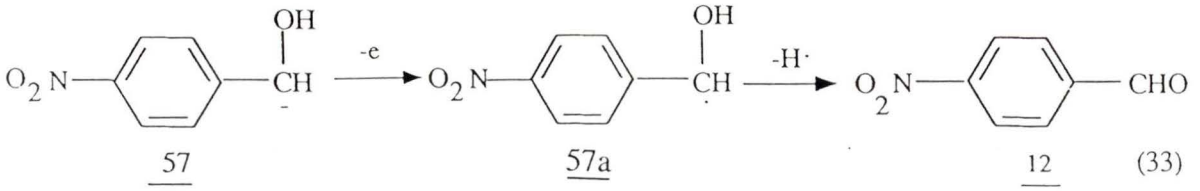
A similar mechanism can be proposed for the photoretro-aldol reactions of nitrophenyl ethylene glycols. From solvent studies, it was shown that photoretro-aldol reaction for both *p*-NEG (**38**) and *m*-NEG (**39**) involved ionic intermediates which can be stabilized in aqueous solution. From Figs. 2 and 3, it can be clearly seen that base facilitates the photoretro-aldol reaction. This is consistent

with the formation of carbanion intermediates in the reaction. As mentioned in section 2.3.3, formaldehyde is also formed in the primary step during the photoretro-aldol reaction of both *p*-NEG and *m*-NEG, together with an ionic intermediate. As an example, removal of formaldehyde from glycol **38** with the assistance from hydroxide ion or water, results in the formation of α-hydroxy nitrobenzyl carbanion **57** (eq. 32).



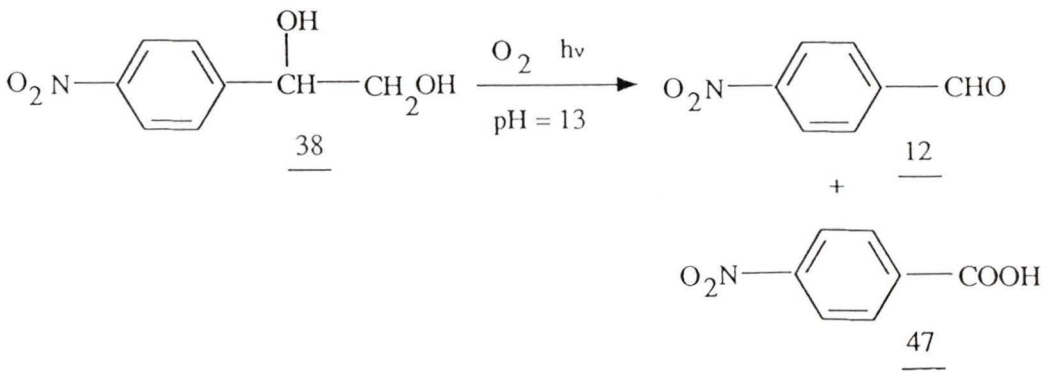
38 57 (32)

The most common reaction for a carbanion is protonation. However, unlike most carbanions, α-hydroxy nitrobenzyl carbanion **57** does not behave like a base. Products isolated from this reaction (eq. 25) indicate that carbanion **57** does not show any affinity for proton since it cannot be protonated to give the corresponding alcohol **17**, even under acidic conditions. We propose that the first step for the decay of **57** is ejection of an electron, to give the corresponding radical **57a**. The electron released from the carbanion is taken by either the parent compound, the product or an externally added electron acceptor to form radical anions, all of which are observable by ESR. The radical **57a** is unstable and gives nitrobenzaldehyde **12** as the primary product on loss of a hydrogen atom (eq. 33). Product **12** is a



57 57a 12 (33)

very good electron acceptor and can capture the electron released by the α-hydroxy nitrobenzyl carbanion (**57**), to form *p*-nitrobenzaldehyde radical anion. This radical anion can be further reduced by more electrons released from the photoretro-aldol reaction, to finally give the nitro-reduced *p*-azoxybenzaldehyde (**46**) (eq. 34). An alternative mechanistic



38 12 + 47 (34)

pathway for reaction of carbanion **57** is again initial loss of an electron (to give **57a**), followed by loss of a proton from the hydroxyl group of **57a**, which gives the radical anion of *p*-nitrobenzaldehyde (**12**) in a more direct route.

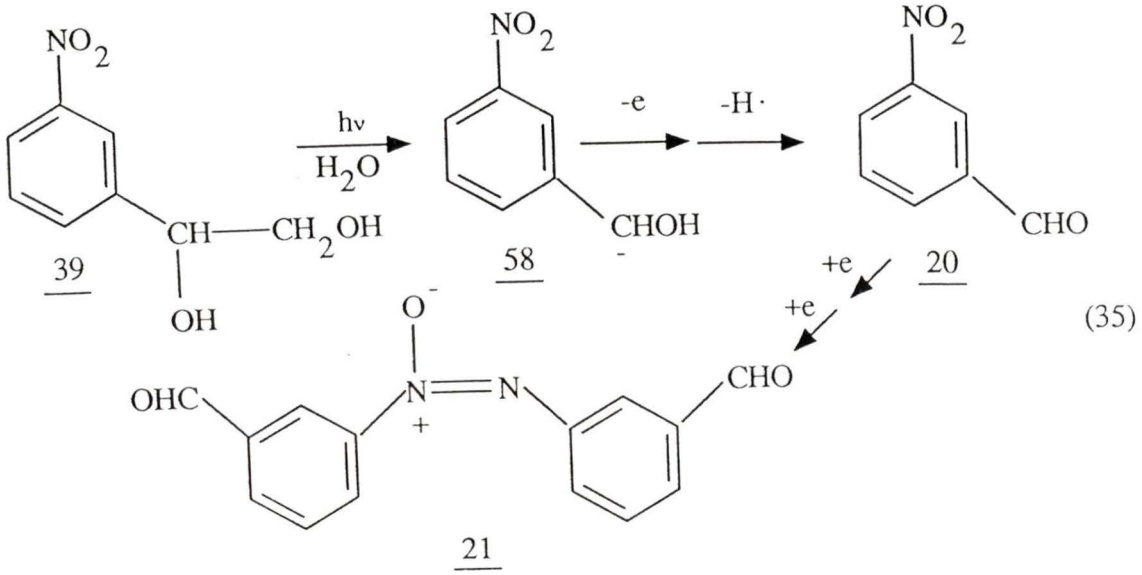
An external electron acceptor which is as good as **12**, for example, *p*-nitrobenzonitrile, readily intercepts the electron released by the α-hydroxy nitrobenzyl carbanion intermediate and effectively prevents the nitrobenzaldehyde

from accepting the electron. Therefore the reduction of the nitrobenzaldehyde **12** which leads to the formation of azoxybenzaldehyde **46** can be effectively inhibited.

Oxygen is both a good electron acceptor and a good oxidizing reagent. It not only captures the electron released from the carbanion, but also oxidizes the resulting radical to *p*-nitrobenzaldehyde (**12**) and *p*-nitrobenzoic acid (**47**). All this provides strong evidence for the photogeneration of α-hydroxy nitrobenzyl carbanions.

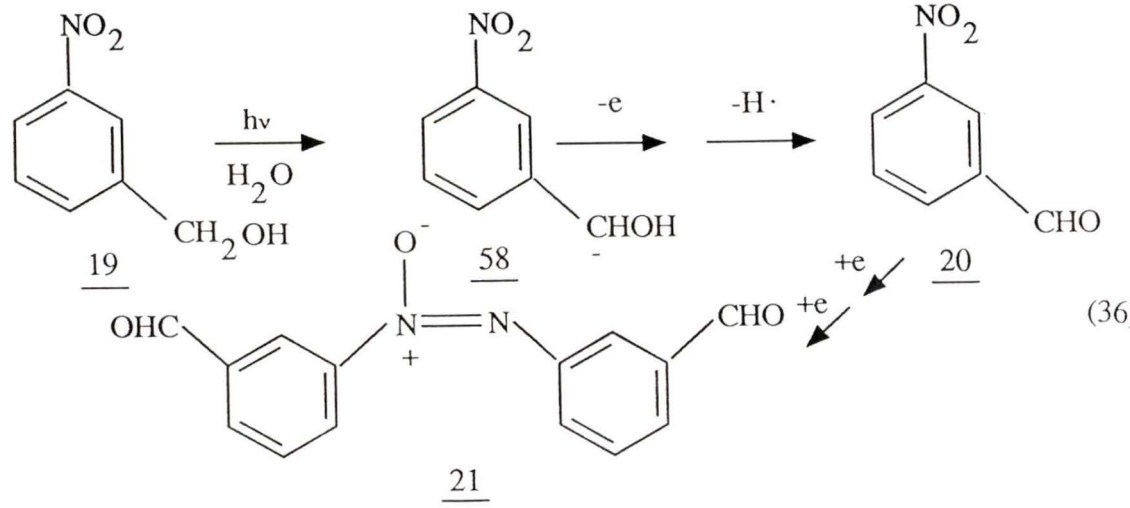
The mechanism of reaction for glycols **39-42** is almost the same as that discussed for **38**. The photolysis of **39** results in the generation of α-hydroxy *m*-nitrobenzyl carbanion (**58**) as the primary intermediate, as well as formaldehyde. As in carbanion **57**, **58** is not protonated at any pH, but rather loses an electron and a hydrogen atom to give *m*-nitrobenzaldehyde (**20**). Product **20** is a good electron acceptor and can receive the electron released from carbanion **58**, to give *m*-azoxybenzaldehyde **21** as the final product (eq. 35).

As introduced in Chapter 1, photolysis of *m*-nitrobenzyl alcohol (**19**) also resulted in the formation of *m*-nitrobenzaldehyde (**20**) and *m*-azoxybenzaldehyde (**21**) (eq. 13)[26]. These observations are very similar to those made for the photoretro-aldol reaction of **39**. Direct photolysis of **20** in aqueous solution did not lead to the formation of **21**[26], but when the pholysis of **20** was carried out in the presence of carbanions, **21** was formed as the only product in good yield,



(35)

as will be reported in Charpter 3. It is therefore reasonable to propose that the mechanism for the the photoredox reaction of **19** may be similiar to that for the photoretro-aldol reaction. That is, α-hydroxy *m*-nitrobenzyl carbanion (**58**) is also a primary intermediate for the photoredox reaction of **19** formed via C-H bond heterolysis, which undergos further reaction as described (eq. 36).



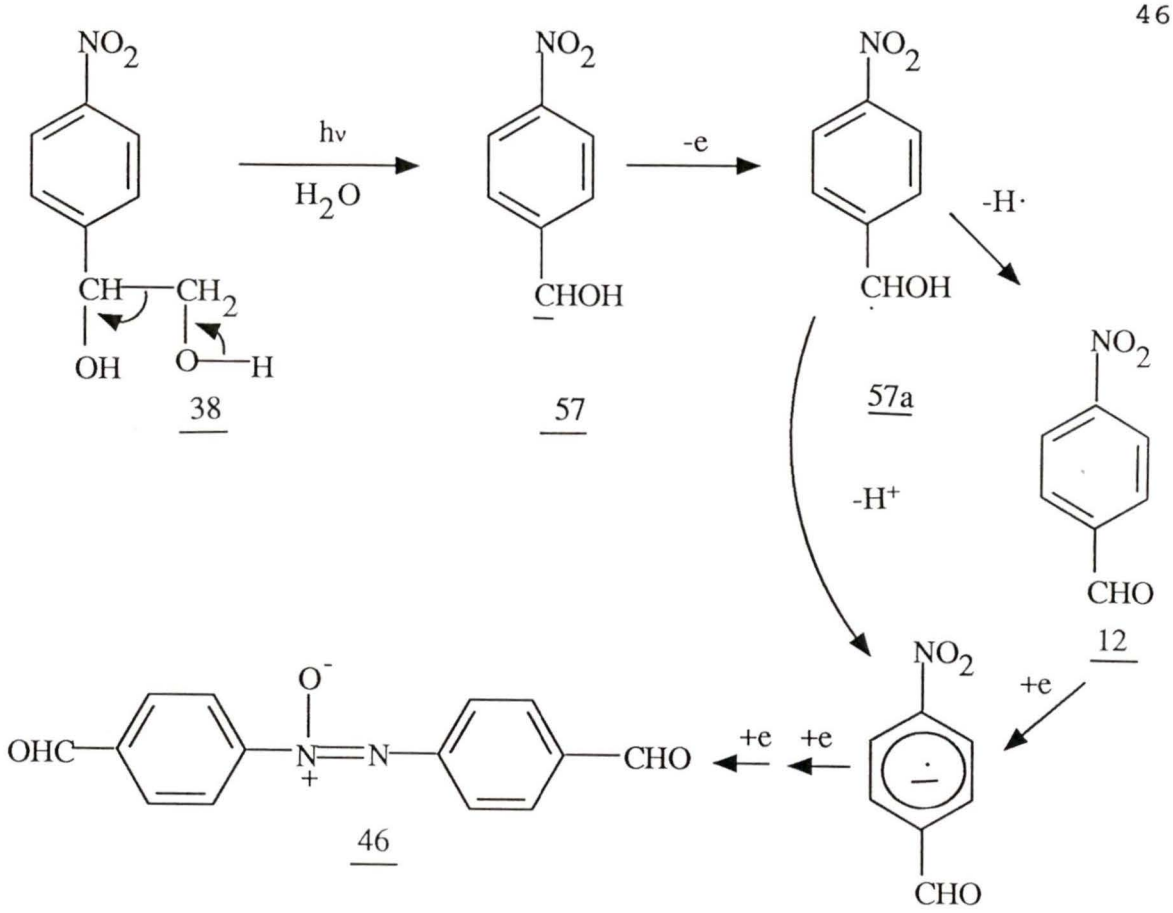
(36)

The photoredox reaction of *p*-nitrobenzyl alcohol (**17**) obviously involves a different mechanism, since it was reported that only *p*-nitrosobenzaldehyde (**18**) was formed during the photolysis under basic conditions[26]. The product was not formed via *p*-nitrobenzaldehyde (**12**) as the intermediate, since photolysis of **12** in the presence of electron sources did not result in **18**, but only **46**, (as will be discussed in Chapter 3).

As mentioned above, the reduction of aldehydes **12** and **20** can be achieved by using other carbanion sources. In Chapter 4, the reduction of nitroaromatic compounds, including both **12** and **20**, by the electron generated from other carbanion sources will be discussed in detail.

2.3 Conclusion

The photoretro-aldol reaction of *p*- and *m*-nitrophenyl ethylene glycols and their derivatives has been studied. The reaction proceeds via heterolytic benzylic C-C bond cleavage, to generate an α-hydroxy nitrobenzyl carbanion as the primary intermediate (Scheme 2). This carbanion intermediate does not undergo protonation, as expected of typical carbanions. A variety of experiments show that it readily ejects one electron, to give the corresponding radical. The radical will then quickly lose one hydrogen atom. The released electron can be trapped by either the primary photoproduct, oxygen or externally added nitroaromatic electron acceptors. Trapping



Scheme 2

of the electron by the product gives the azoxy compound as a secondary product, in addition to the initially formed nitrobenzaldehyde. Alternatively, the radical **57a** may lose a proton from the hydroxyl group, to give *p*-nitrobenzaldehyde radical ion.

2.4 Experimental

2.4.1 Materials

Dichloromethane (Van Waters and Rogers Ltd.) was purified by distillation before use. Other organic solvents employed in photolysis, extraction and chromatography were ACS grade and used without further purification. Distilled water was used for photolysis and work-up. 99.9% D_2O (MSD Isotopes) was used in solvent isotope and NMR exchange studies.

p-Nitrobenzaldehyde (*p*-NB) (**12**), *m*-nitrobenzaldehyde (*m*-NB) (**20**) and *p*-nitrobenzonitrile (**45**) were purchased from Aldrich and used as received. The synthesis of *p*-nitrophenyl ethylene glycol (*p*-NEG) (**38**), *m*-nitrophenyl ethylene glycol (*m*-NEG) (**39**), bis(*p*-nitrophenyl) ethylene glycol (**40**), 1-(*p*-nitrophenyl)-2-phenyl ethylene glycol (**41**), and 1-(*p*-nitrophenyl)-2-(*m*-methoxyphenyl) ethylene glycol (**42**) will be described below.

2.4.2 Instrumentation

Melting points were taken on a Richert melting point apparatus (uncorrected). Proton (^1H) nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R32 (90 MHz) or Bruker WM 250 (250 MHz) spectrometers. Tetramethylsilane (TMS) was used as an internal standard for the 90 MHz spectra. ^{13}C NMR spectra were recorded on a Bruker WM 250 (62.9 MHz), where the $CDCl_3$ signal (77 ppm) or acetone-d_6 signal (29.8 ppm) was used for calibration. UV spectra were taken on a Perkin-Elmer Lambda 4B spectrophotometer. IR spectra were recorded

on a Perkin-Elmer 283 instrument (NaCl discs). Mass spectra were recorded on a Perkin-Elmer Hitachi RMU-7 spectrometer with 70 ev electron impact ionization or on a Finnigan 3300 GC/MS with methane as the carrier gas for chemical ionization. Gas chromatographic analyses were carried out on a Varian 3700 instrument equipped with a Hewlet-Packard 3390A integrator and SE-55 glass capillary column. Elementary analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia. The pHs of aqueous solutions were determined by a Corning 140 pH meter.

2.4.3 p-*Nitrophenyl Ethylene Glycol (**38**)*

To 20 g (0.12 mol) of *p*-NB (**12**) dissolved in 80 ml glacial acetic acid was added 22 g of bromine (0.14 mol) dropwise. After the color of bromine had disappeared (about 2.5 h), the reaction was quenched by adding water. The α-bromo-*p*-nitroacetophenone product was precipitated as a white-yellowish solid. The product was isolated by filtration and washed with water. On drying, 24.9 g (85%) was isolated; ^{1}H NMR (90 MHz, in $CDCl_3$) δ (ppm): 4.4 (s, 2H, $-COCH_2$), 8.1-8.2 (d, J = 9 Hz, 2H, arom.), 8.3-8.4 (d, J = 9 Hz, 2H, arom.).

To a solution of 24.5 g (0.1 mol) of α-bromo-*p*-nitroacetophenone dissolved in 200 mL methanol was slowly added a solution of 2.0 g (0.21 mol) sodium borohydride dissolved in 50 mL methanol. After 1 h stirring, the reaction was quenched by adding 10% HCl, followed by extraction with

CH_2Cl_2 (200 mL) three times. The product (22.0 g, 89%), 2-bromo-1-(*p*-nitrophenyl)-ethanol, was pure enough to be used for further synthesis without purification; ^1H NMR (90 MHz, in $CDCl_3$) δ (ppm): 2.85 (broad, 1H, O**H**), 3.4-3.7 (d, 2H, -C**H**$_2$Br), 5.1 (m, 1H, -C**H**OH-), 7.6-7.7 (d, J = 9 Hz, 2H, arom.), 8.2-8.3 (d, J = 9 Hz, 2H, arom.).

To a solution of 14.4 g (0.06 mol) of 2-bromo-1-(*p*-nitrophenyl)-ethanol dissolved in 100 mL CH_3CN and 70 mL water was added 14.4 g monohydrated sodium carbonate. After 1 h reflux, the reaction was worked up by adding water and extracting with CH_2Cl_2 (200 mL) three times. The crude product was recrystallized in 95% ethanol. White yellowish *p*-nitrostyrene oxide (8.5 g, 87%) was isolated; ^1H NMR (90 MHz, in $CDCl_3$) δ (ppm): 2.70-3.4 (m, 2H, -C**H**$_2$-), 4.0 (m, 1H, C**H**), 7.45-7.55 (d, J = 9 Hz, 2H, arom.), 8.2-8.3 (d, J = 9 Hz, 2H, arom); IR (cm^{-1}) 1510 (s), 1340 (s), MS (CI) (m/z) 166 (M^+ + 1).

To a solution of 5.0 g (0.03 mol) of the epoxide dissolved in 130 mL CH_3CN was added 130 mL 10% H_2SO_4. After 4 h reflux, the reaction was quenched by adding water and extracting with CH_2Cl_2 (200 mL) three times. The crude product was recrystallized in CH_2Cl_2 to give *p*-nitrophenyl ethylene glycol (**38**) (4.2 g, 76%) was obtained as cotton-white crystals; m.p. 75-76 °C; ^1H NMR (90 MHz, in $CDCl_3$ and acetone-d_6) δ (ppm): 3.5-3.8 (broad, 2H, -C**H**$_2$-), 3.8 (broad, s, exchangeable with D_2O, 2H, O**H**), 4.9 (dd, J = 3, 8Hz, 1H, C**H**),

7.65 (d, J = 9 Hz, 2H, arom.), 8.25 (d, J = 9 Hz, 2H, arom.); IR (cm^{-1}) 3200-3400 (s), 2940 (w), 1600 (m), 1530 (s), 1350 (s); MS (CI) (m/z) 184 ($M^+ + 1$).

2.4.4 m-*Nitrophenyl Ethylene Glycol (39)*

To 20 g (0.12 mol) of *m*-NB (**20**) dissolved in 80 mL glacial acetic acid was added 22 g (0.14 mol) of bromine dropwise. After the color of bromine had disappeared (about 2.5 h), the reaction was quenched by adding water. The α-bromo-*m*-nitroacetophenone was precipitated as a white-yellowish solid. The product was isolated by filtration and washed with water. On drying, 21.0 g (71%) was isolated; ^{1}H NMR (90 MHz, in $CDCl_3$) δ (ppm): 4.45 (s, 2H, $-COCH_2Br$), 7.6-8.8 (m, 4H, arom.).

To a solution of 20.5 g (0.083 mol) of α-bromo-*m*-nitroacetophenone dissolved in 200 mL methanol was slowly added a solution of 1.7 g (0.166 mol) sodium borohydride dissolved in 50 mL methanol. After 1 h stirring, the reaction was quenched by adding 10% HCl, followed by extraction with CH_2Cl_2 (200 mL) three times. The product (20.0 g, 97%), 2-bromo-1-(*m*-nitrophenyl)-ethanol, was pure enough to be used for further synthesis without purification; ^{1}H NMR (90 MHz, in $CDCl_3$ and acetone-d_6) δ (ppm): 3.4-3.8 (m, 2H, $-CH_2OH$), 3.8 (broad, s, exchangeable with D_2O, 1H, O**H**), 5.1 (m, 1H, C**H**), 7.5-8.3 (m, 4H, arom.).

To a solution of 14.1 g (0.058 mol) of

2-bromo-1-(*m*-nitrophenyl)-ethanol dissolved in 100 mL CH_3CN and 70 mL water was added 14.0 g monohydrated sodium carbonate. After 1 h reflux, the reaction was quenched by adding water and extracting with CH_2Cl_2 (200 mL) three times. A white-yellowish product of *m*-nitrophenyl ethylene epoxide (oil, 7.5g, 78%) was isolated; ^1H NMR (90 MHz, in $CDCl_3$ and acetone-d_6) δ (ppm): 2.75-3.1 (m, 2H, -**CH**$_2$-), 3.95 (m, 1H, **CH**), 7.4-8.2 (m, 4H, arom.); IR (cm^{-1}) 1520 (s), 1350 (s); MS (CI) (m/z) 166 ($M^+ + 1$).

To a solution of 5.0 g (0.03 mol) of the epoxide dissolved in 130 mL CH_3CN was added 130 mL 10% H_2SO_4. After 4 h reflux, the reaction was quenched by adding water and extracting with CH_2Cl_2 (200 mL) three times. The crude product was recrystalized in CH_2Cl_2. *m*-nitrophenyl ethylene glycol (**39**) (4.0 g, 73%) was obtained as white crystals; m.p. 73-74 °C; ^1H NMR (90 MHz, in $CDCl_3$ and acetone-d_6) δ (ppm): 3.5-3.8 (broad, 2H, -**CH**$_2$**OH**), 3.8 (broad, s, exchangeable with D_2O, 2H, **OH**), 4.9 (dd, J = 3, 8Hz, 1H, **CH**), 7.85-8.95 (m, 4H, arom.); IR (cm^{-1}) 3100-3400 (s), 1520 (m), 1340 (s), 1040 (w); MS (CI) (m/z) 184 ($M^+ + 1$).

*2.4.5 Bis(p-nitrophenyl) Ethylene Glycol (**40**)*

p,p'-Dinitrostilbene oxide[44] was available in our laboratory, which was synthesized from *p*-nitrobenzyl bromide and *p*-nitrobenzaldehyde in basic ethanol solution. To a solution of 6.0 g (0.021 mol) of the epoxide dissolved in 130

mL CH_3CN was added 130 mL 10% H_2SO_4. After 4 h reflux, the reaction was quenched by adding water and extracting with CH_2Cl_2 (200 mL) three times. The product is insoluble in many solvents such as dichloromethane, acetone, chloroform, ethanol and carbon tetrachlororide. Therefore, it was purified by washing the product with dichloromethane and acetone. Bis(*p*-nitrophenyl) ethylene glycol (**40**) was obtained as white crystals (5.2 g, 79%); m.p. 270 °C (decomposition); ^{1}H NMR (90 MHz, in pyridine-d_6) δ (ppm): 5.35-5.45 (2s for cis and trans isomers, 2H, C**H**), 7.7-7.8 (d, J = 9 Hz, 2H, arom.), 8.15-8.25 (d, J = 9 HZ, 2H, arom.); IR (cm^{-1}) 3200-3400 (s), 1530 (m), 1350 (s); MS (CI) (m/z) 305 (M^+ + 1).

*2.4.6 1-(p-nitrophenyl)-2-phenyl Ethylene Glycol (**41**)*

1-(*p*-Nitrophenyl)-2-phenyloxirane was available in our laboratory. To a solution of 6.0 g (0.025 mol) of the epoxide dissolved in 130 mL CH_3CN was added 130 mL 10% H_2SO_4. After 4 h reflux, the reaction was quenched by adding water and extracting with CH_2Cl_2 (200 mL) three times. The product **41** was recrystalized from CH_2Cl_2 (4.5 g, 70% yield); m.p. 115-117 °C; ^{1}H NMR (90 MHz in $CDCl_3$ + acetone-d_6) δ (ppm): 3.5 (broad, 2H, O**H**), 4.6-4.90 (m, 2H, C**H**), 7.10-7.30 (m, 5H, arom.), 7.6 (d, J = 9 Hz, 2H, arom.), 8.10 (d, J = 9 Hz, 2H, arom.); IR (cm^{-1}) 3200-3700 (s), 1525 (m), 1350 (m); MS (EI) (m/z) 241 (M^+ - 18).

2.4.7 1-(p-nitrophenyl)-2-(m-methoxyphenyl) Ethylene Glycol (42)

1-(*p*-Nitrophenyl)-2-(*m*-methoxyphenyl)-oxirane was available in our laboratory. To a solution of 5.0 g (0.019 mol) of the epoxide dissolved in 130 mL CH_3CN was added 130 mL 10% H_2SO_4. After 4 h reflux, the reaction was quenched by adding water and extracting with CH_2Cl_2 (200 mL) three times. The product **42** was recrystallized from dichloromethane (3.5 g, 65% yield); m.p. 120 °C; ^1H NMR (90 MHz in $CDCl_3$ + acetone-d_6) δ (ppm): 3.5-3.6 (broad, 2H, O**H**), 3.8 (s, 3H, -OC**H**$_3$), 4.6-4.90 (m, 2H, C**H**), 7.10-7.30 (m, 4H, arom.), 8.10 (d, J = 9 Hz, 2H, arom.); IR (cm^{-1}) 3200-3700 (s), 1525 (m), 1350 (m); MS (EI) (m/z) 241 (M^+ - 18).

2.4.8 General Procedure for Photolysis

All photolyses were carried out in 200 or 100 mL quartz tubes using a Rayonet RPR 100 photochemical reactor equipped with 16 x 254 nm (or 350nm) lamps.

To a solution of 120 mg of the substrate dissolved in 50 mL CH_3CN was added 150 mL distilled water. If required, the pH of the solution was checked and adjusted using aqeous NaOH or HCl. The solution was then transferred to a quartz vessel cooled by a cold finger and photolyzed at 254 nm with continuous argon purging. The time of photolysis varied from 10 min to 1 h. After photolysis, the solution was saturated with NaCl and then extracted with 180 mL of CH_2Cl_2 (three

times). After evaporation of CH_2Cl_2, the residue was analyzed by ^1H NMR to determine the products and their yields. The products were then separated by preparative TLC (silica). For separation of nitrobenzaldehydes and azoxybenzaldehydes, CH_2Cl_2 was used as the eluting solvent. The isolated products were usually purified further by preparative TLC or by recrystallization. Known compounds could be identified by comparison of their spectra with those of authentic samples or published spectra.

2.4.9 Quantum Yield Measurement

Quantum yields of the photoretro-aldol reaction were determined by using 5*H*-dibenzo[*a*,*d*]cyclohepten-5-carboxylic acid (**34b**) (pH 10-13, $\Phi = 1.0$)[34] as the secondary actinometric reference in pH 10-14, by small scale photolysis. This can be illustrated by the determination of quantum yields for the products of photoretro-aldol reaction of glycol **39**. Thus, 122 mg (0.667×10^{-3} mol) of **39** was dissolved in 80 mL CH_3CN and 120 mL 0.1 M NaOH solution. The concentration of the solution was high enough for the absorbance (A) of the sample > 1.9 at 254 nm in the UV spectrum. The solution was then transfered to a quartz vessel cooled by a cold finger and photolyzed at 254 nm with continuous argon purging. After photolysis, the reaction mixture was worked up in the same way as in the case for the general photolysis procedures mentioned above. The residue was analyzed by ^1H NMR and the yields of products were

determined by comparing the relative integration. In another quartz vessel, 156.7 mg (0.667×10^{-3} mol) of **34b** dissolved in 80 mL CH_3CN and 120 mL 0.1 M NaOH solution was also photolyzed under identical conditions. The yield of the only product **36b** was also determined by integration of the ^1H NMR. The quantum yields of *m*-NB (**20**) and *m*-AB (**21**) were calculated by comparing the ^1H NMR integration and the photolysis time (in small scale photolysis, the yield should be proportional to the photolysis time). Quantum yields of the photoretro-aldol reaction of **39** were used as a secondary standard to determine quantum yields for the photoretro-aldol reaction of other glycols.

2.4.10 General procedure for Dark Reactions

Before photolysis, it is important to make certain that no dark reaction is taking place in the solution of interest. For this purpose, the substrate was dissolved in the same solvent except that no light was allowed to enter the system. Thus, to the solution of 120 mg of the substrate dissolved in 50 mL CH_2Cl_2 was added 150 mL distilled water. After adjusting the pH (as required), the solution was transferred to a quartz vessel covered by alminum foil and left with a continuous argon purge for several hours. The solution was then saturated with NaCl and then extracted with 180 mL of CH_2Cl_2 (three times). After evaporation of CH_2Cl_2, the residue was analyzed by ^1H NMR for any thermal reaction.

2.4.11 Photolysis of p*-Nitrophenyl Ethylene Glycol (**38**)*

To check for possible dark reactions, **38** (120 mg) was dissolved in 50 mL CH_2Cl_2 and 150 mL water with pH = 1, 7 and 13 were added. The solution was purged by argon for 4 h. There was no product isolated except the unreacted substrate.

To *p*-NEG (**38**) (120 mg) dissolved in 50 mL CH_2Cl_2 was added 150 mL water of different pH. The solutions were photolyzed for 1 h to give two products, *p*-NB (**12**) and *p*-AB (**46**). In basic solution, the photolysis time could be reduced to give the same conversion as in the neutral solution. Both products **12** and **46** were separated and purified by preparative TLC (silica; CH_2Cl_2). *p*-NB (**12**) is a known compound and was identified by comparing its spectrum with the ^1H NMR spectrum and MS spectrum of an authentic sample. *p*-AB (**46**) was further purified by recrystallization in 95% ethanol (twice). It was characterized as follows; m.p. 192 °C, ^1H NMR (250 MHz) δ (ppm): 7.8-8.7 (m, 8H, arom.), 10.1-10.2 (2s, 2H, -CHO); IR (KBr, cm^{-1}): 1690 (s), 1590 (m), 1450 (m), 1340 (m), 1200 (m); MS (EI) (m/z): 254 (M^+); Elemental Analysis, calc. for $C_{14}H_{10}N_2O_3$: C 66.14, H 3.94, N 11.02; found C 65.95, H 3.98, N 11.08.

2.4.12 Photolysis of m*-Nitrophenyl Ethylene Glycol (**39**)*

To check for possible dark reactions, **39** (120 mg) was dissolved in 50 mL CH_3CN and 150 mL water of pH = 1, 7 and 13 were added. The solution was purged by argon for 4 h. There

was no product isolated except the unreacted substrate.

To *m*-NEG (**39**) (120 mg) dissolved in 50 mL CH_3CN was added 150 mL water of different pH. The solution was photolyzed for 1 h to give two products, *m*-NB (**20**) and *m*-AB (**21**). In basic solution, the photolysis time could be reduced to give the same conversion as in neutral solution. Both products **20** and **21** were separated and purified by the TLC (silica; CH_2Cl_2). *m*-NB (**20**) is a known compound and was identified by comparing its spectra with an authentic sample. *m*-AB (**20**) was further purified by recrystallization (twice) in $CHCl_3$/ligroin (1:3). Its spectroscopic data were identical to those reported in literature[26]; m.p. 105-107 °C; ^{1}H NMR δ (ppm): 7.1-8.9 (m, 8H, arom.), 10.1-10.15 (2s, 2H, -CHO); IR (KBr, cm^{-1}): 1690 (s), 1570 (w), 1430 (m), 1260 (w), 1220 (w), 1130 (m); MS (EI) (m/z): 254 (M^+).

*2.4.13 Photolysis of Glycols **40**, **41** and **42***

Glycol **40** (120 mg) dissolved in 50 mL CH_3CN was added 150 mL water of different pH. Under thermal conditions, in acidic and neutral solution, no product was isolated except unreacted substrate. In basic solution (pH > 12.5), **40** reacted quickly to give *p*-NB (**12**) in the dark.

To glycol **40** (120 mg) dissolved in 50 mL CH_3CN was added 150 mL water of different pH < 12 (at high pH, **40** undergoes *thermal* retro-aldol reaction). The solution was photolyzed for 1 h in acidic and neutral solutions to give two products,

p-NB (**12**) and *p*-AB (**46**). Both products **12** and **46** were separated and purified by preparative TLC (silica; CH_2Cl_2). The identification of the products was similar to the photolysis of **38**.

Similarly, both glycols **41** and **42** did not have thermal reactions in acidic and neutral solution, but had thermal reactions in basic solution.

In a similar reaction pathway of glycols **38** and **40**, both glycols **41** and **42** undergo photoretro-aldol reaction in acidic and neutral solution to give **12** and **46**, as well as benzaldehyde for **41** and *m*-methoxybenzaldehyde for **42**. The purification and identification of the products are the same as in the photolysis of **38** and **40**.

2.4.14 Photolysis under Oxygen

The procedure of photolysis under oxygen is almost the same as the general procedure described above, except that oxygen, instead of argon, was purged before and throughout the photolysis.

After 20 min photolysis in pH 13 under oxygen purge, *p*-NEG (**38**) (120 mg) gave two products, *p*-nitrobenzoic acid (**47**), which is soluble in basic aqueous solution, and *p*-NB (**12**), which is insoluble. The products were separated and purified by extraction. They were identified by comparing their NMR and MS spectra with those of authentic compounds. Yields were determined by the integration of ^1H NMR spectra.

After 1 h photolysis in pH 7 under oxygen purge, *p*-NEG (**38**) was mostly recovered. No other product except a trace amount of *p*-nitrobenzoic acid (**47**) was recovered.

2.4.15 Photolysis in Deuterium Oxide

The procedure of photolysis in D_2O is slightly different from the general procedure of photolysis in water. First, of course, D_2O instead of H_2O was used as the polar solvent. Second, due to economic reasons, the photolysis was carried out in a smaller volume (100 mL) using a smaller amount of substrate. Third, in the work up step, a large volume of distilled water was added to convert all ionized exchangeable deuteriums to protons. Mass spectrometry was used to identify deuterated products quantitively, and ^1H NMR was used to determine the deuterium incorporation ratio. Photolysis of both *p*-NEG (**38**) and *m*-NEG (**39**) in aqueous solution at different pH's led to no deuteration in the products.

2.4.16 Photolysis with External Electron Acceptors

A selected external electron acceptor was dissolved in CH_3CN (50 mL) along with the substrate. To this solution was added 150 mL distilled water. The pH was subsequently adjusted, as required. The procedure afterwards was exactly the same as the general procedure described above.

After 1 h photolysis of *p*-NEG (**38**) (120 mg) in pH 13.5

with an equal amount of externally added *p*-nitrobenzonitrile (**45**), *p*-NB (**12**) was obtained in a yield greater than 80%, while *p*-AB (**46**) was obtained in a yield less than 10%. *p*-Nitrobenzonitrile (**45**) was recovered unchanged.

After 1 h photolysis of *m*-NEG (**39**) (120 mg) in pH 13.5 with an equal amount of externally added *p*-nitrobenzonitrile (**45**), *m*-NB (**20**) was obtained in a yield of 60%, while *m*-AB (**21**) was obtained in a yield less than 10%. *p*-Nitrobenzonitrile (**45**) was recovered unchanged.

CHAPTER THREE

REDUCTION OF NITROAROMATIC COMPOUNDS BY CARBANIONS

3.1 Introduction

Carbanions have been used as electron sources to reduce nitroaromatic compounds[39-41], the products being radical anions via one-electron reduction of the nitro group. The radical anion or one-electron reduction product was reported to be very stable under basic conditions[48]. Its only known reaction is electron transfer to another nitroaromatic compound[48]. It is not clear how these radical anions decay finally[3,30]. Recent studies on photoretro-aldol reaction of nitrophenethyl alcohols[3,18,20,41], for example, **1** and **3**, suggest that *p*-nitrobenzyl carbanion (**7**) photogenerated in the system ejects an electron to give *p*-nitrobenzyl radical (**8**), which recombines to give dinitrobibenzyl (**6**). The electron ejected was shown by ESR to be added to the substrate and/or products to form radical anions which could not be isolated[3,41]. In Chapter 2, it was demonstrated that the electron ejected from carbanion **57** or **58** reduces *p*-nitrobenzaldehyde (**12**) or *m*-nitrobenzaldehyde (**20**) to give *p*-azoxybenzaldehyde (**46**) or *m*-azoxybenzaldehyde (**21**), respectively. It is expected that the electron ejected from other carbanion source will also reduce nitrobenzaldehydes and other nitroaromatic compounds. Because the photodecarboxylation of *p*-nitrophenylacetate ion (**24**) can be conveniently carried out, *p*-nitrobenzyl carbanion (**7**)

photogenerated by this method will be the main source of carbanions to reduce a series of selected nitroaromatic compounds.

It is also reasonable to assume that all carbanions, either photogenerated or thermally generated, will reduce nitrobenzaldehydes and other nitroaromatic compounds, as long as electron transfer from the carbanions takes place. Therefore, it may be possible to use an enolate ion *thermally generated* as the electron source to reduce nitroaromatic compounds. *p*-Nitroacetophenone (**43**) was selected to produce the enolate anion by reacting with base in aqueous solution. Since **43** is also strongly electron-withdrawing nitroaromatic compound, it is of interest to see whether the enolate anion of **43** reduces undissociated **43**. If so, the overall reaction will be a disproportionation. On the other hand, **43** is a ketone containing an α-hydrogen, which is expected to react with base to undergo the aldol condensation[49]. The mechanism of the aldol condensation also involves the formation of an enolate anion by the removal of an α-hydrogen from the substrate, followed by the addition of this anion to the carbonyl group of another substrate[49].

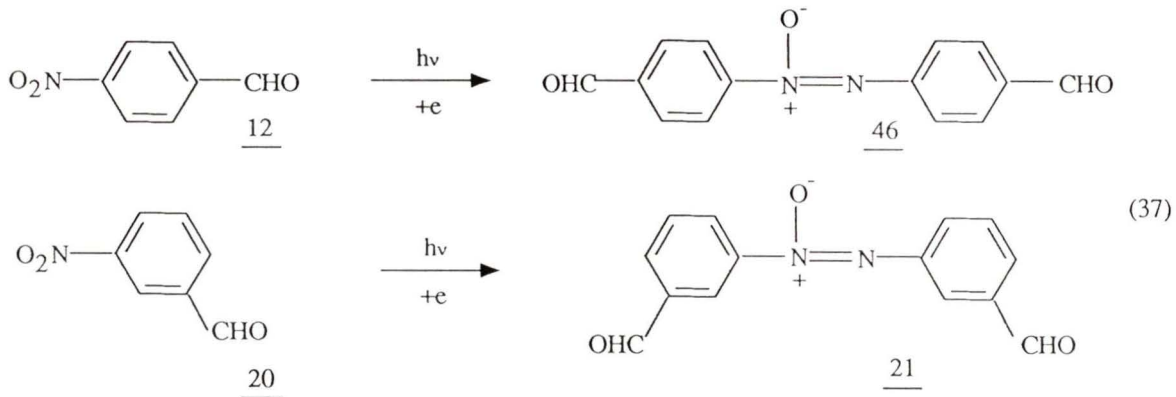
This chapter reports the reduction of a series of nitroaromatic compounds by the electron ejected from the photodecarboxylation of **24**, and an unusual electron-transfer disproportionation of *p*-nitroacetophenone (*p*-NA) (**43**) under basic conditions, to give *p*-aminoacetophenone (**59**) and

p-nitrobenzoic acid (**47**).

3.2 Results and Discussion for the Reduction of Nitroaromatic Compounds by *p*-Nitrophenylacetate Ion (24) on Photolysis

3.2.1 Product Studies

Nitroaromatic compounds **12**, **20**, **43**, **45**, **60**, and **61** were selected as substrates to be reduced by **24** in basic solution on photolysis. *p*- And *m*-nitrobenzaldehydes (**12** and **20**) were reduced to *p*- and *m*-azoxybenzaldehydes (**46** and **21**) in good yields, as shown in Table 4 (eq. 37). *p*-Nitrobenzonitrile



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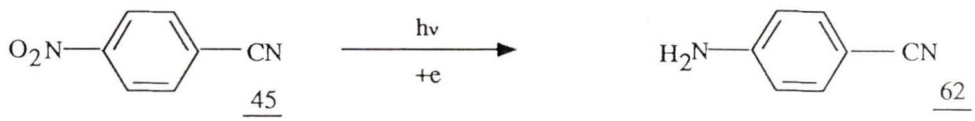
(**45**) was reduced to *p*-aminobenzonitrile (**62**) in high yield (eq. 38). *p*- And *m*-nitroacetophenones (**43** and **60**) also gave the corresponding amino products (**59** and **63**) (eq. 39), and so



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did *p*-nitrobenophenone (**61**) (eq. 40).

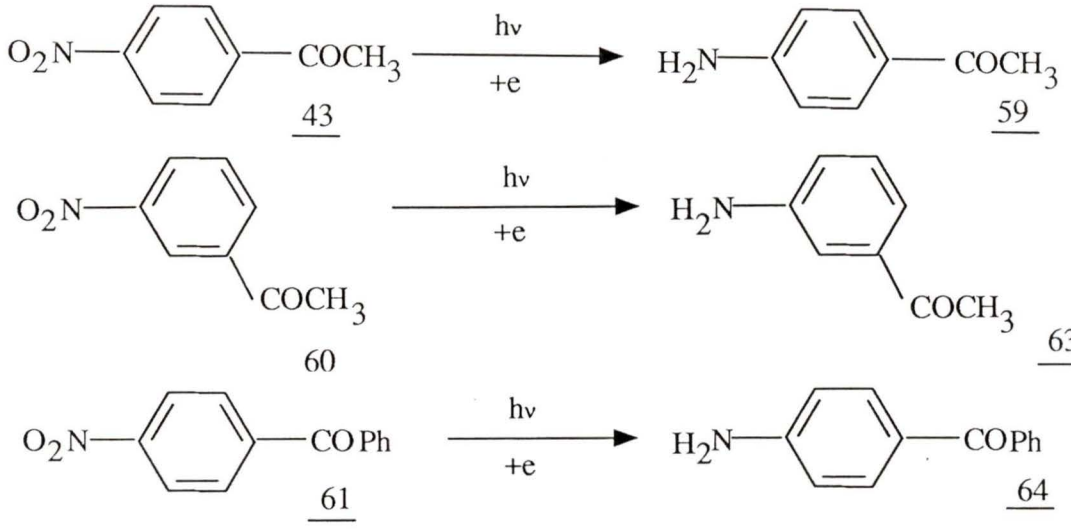


Table 4. Reduction of Some Selected Nitroaromatic Compounds by the *p*-Nitrobenzyl Carbanion Generated Photochemically*

compounds	*products*	*yields (%)*
p-nitrobenzaldehyde (**12**)	*p*-azoxybenzaldehyde (**46**)	70
m-nitrobenzaldehyde (**20**)	*m*-azoxybenzaldehyde (**21**)	55
m-nitroacetophenone (**60**)	*m*-aminoacetophenone (**63**)	95
p-nitroacetophenone (**43**)	*p*-aminoacetophenone (**59**)	60[1]
p-nitrobenzophenone (**61**)	*p*-aminobenzophenone (**64**)	30
p-nitrobenzonitrile (**45**)	*p*-aminobenzonitrile (**62**)	60

*The reduction is carried out by mixing a solution of the substrate (120 mg) and *p*-nitrophenyl acetic acid with 150 ml 1 M aq. NaOH by irradiating this solution at λ_{max}=254 nm for two hours. Errors are ±10% of quoted value. [1] It readily undergoes the disproportionation presented in the following section.

3.2.2 pH Effect

The reduction of *m*-nitroacetophenone (**60**) by **24** on photolysis was chosen to demonstrate the pH effect since this reduction has the highest yield, as shown in Table 4. The photolysis was carried out in solution of pH 7 - 14. The results sre shown in Figure 6. The yield of reduction of **60** decreased sharply with decreasing pH with almost no reaction observed below pH 9. The reason for the drop of the yield in low pH is obvious. As discussed for the photodecarboxylation of **24** in Chapter 1, when the solution becomes more acidic (lower pH), photogenerated *p*-nitrobenzyl carbanion (**7**) is more prone to be protonated, to give *p*-nitrotoluene (**5**). Therefore, the lifetime of **7** will be much shorter and electron transfer pathway is diminished, resulting in decreased yield in reduction product.

3.2.3 Mechanism

The mechanism of photodecarboxylation of **24** has been well established as discussed in Chapter 1[27-30]. The primary intermediate is the *p*-nitrobenzyl carbanion (**7**). In basic solution the major reaction pathway of **7** is electron transfer, i.e., an electron is ejected to give the corresponding radical **8** (eq. 17). As described in Chapter 2, the ejected electron from carbanions can reduce good electron acceptors, such as the nitroaromatic compounds selected above. Moderately good electron acceptors, such as aminoacetophenones, aminobenzoic

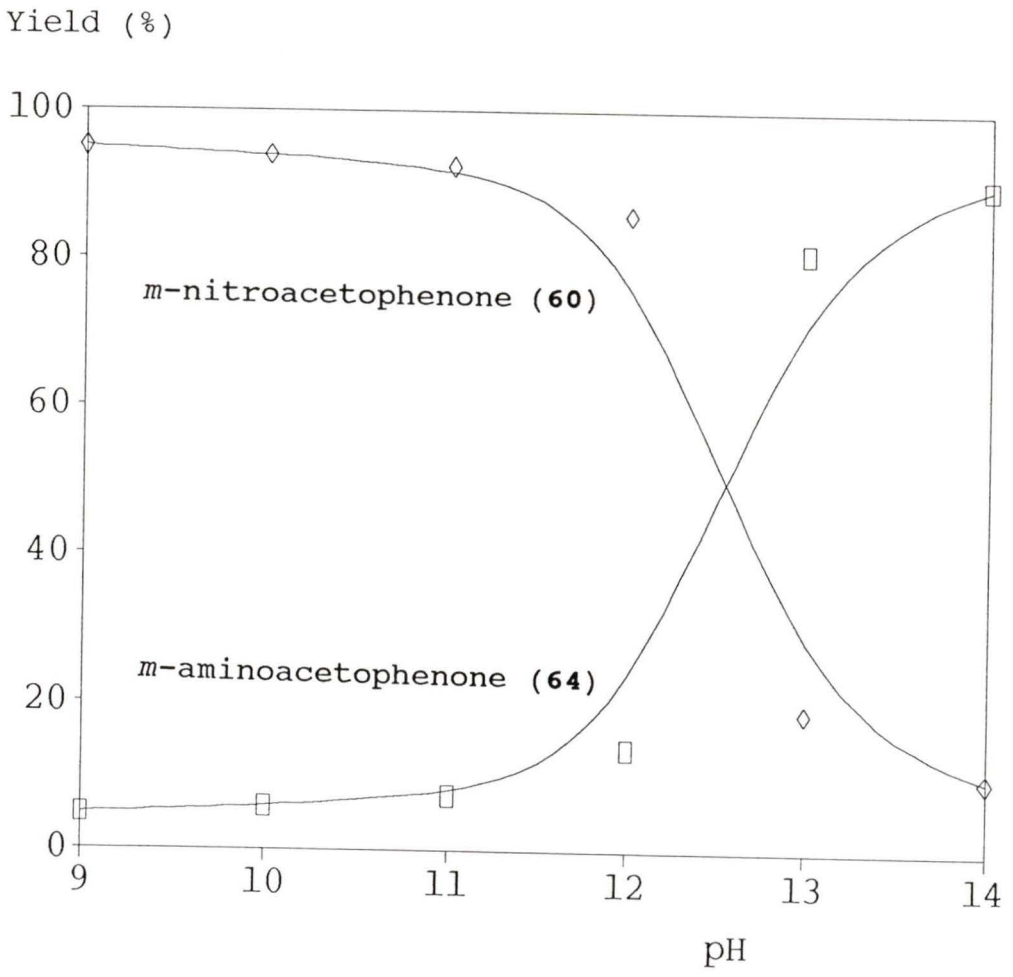
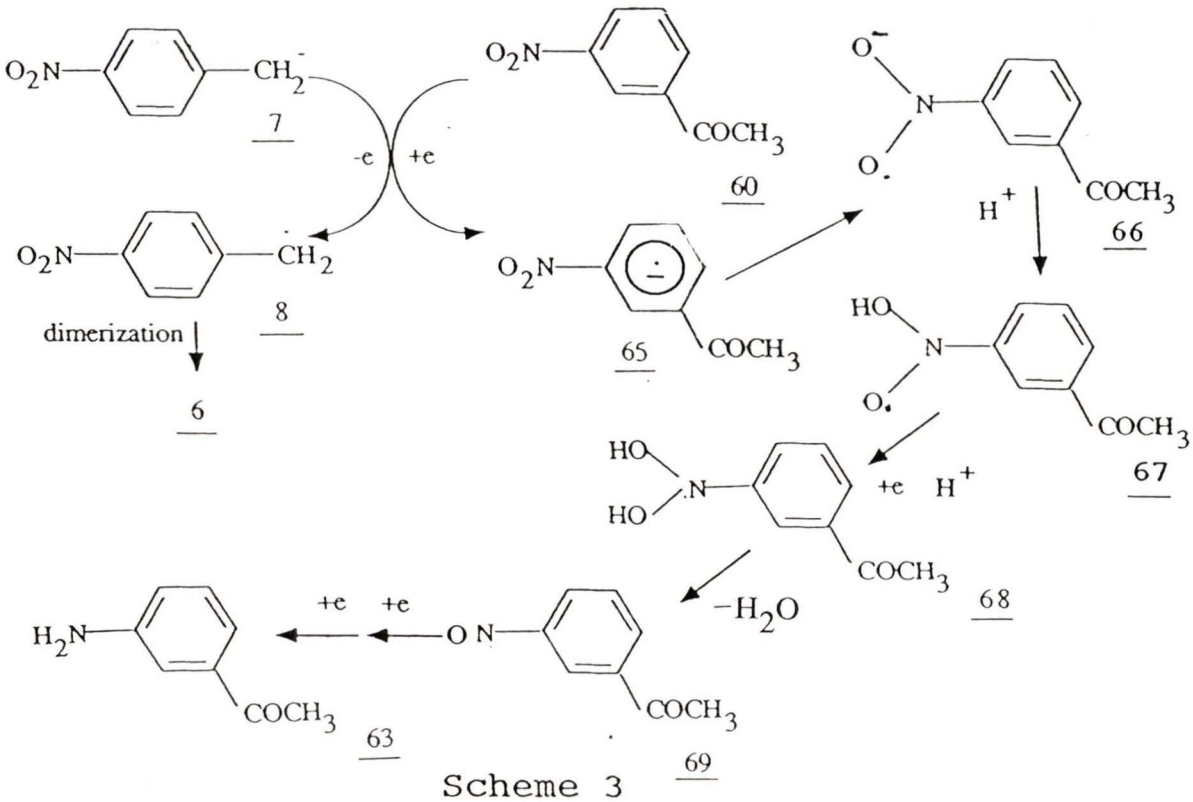


Figure 6 Plot of yield of product and loss of substrate as a function of pH of the aqueous portion of the solution (25% CH_3CN) for the reduction of *m*-nitroacetophenone (**60**) by *p*-nitrophenylacetate (**24**) after 1 h photolysis.

acids and their esters, benzoic acid, benzaldehyde, benzophenone and even nitrotoluenes were not reduced by the ejected electron. This indicates that the first step of the reduction of nitroaromatic compounds, for example *m*-nitroacetophenone (**60**), is the addition of the ejected electron to an aromatic ring to form radical anion **65** (negative charge on the ring) or one-electron reduction product **66** (negative charge at the nitro group). The subsequent steps are probably complicated. Probably, the one-electron reduction product **66** can be protonated to give **67**, which accepts one more electron to give hydrated *m*-nitrosoacetophenone (**68**). Elimination of water results in *m*-nitrosoacetophenone (**69**), which undergoes further reduction to gi[illegible]nine as final product (Scheme 3).

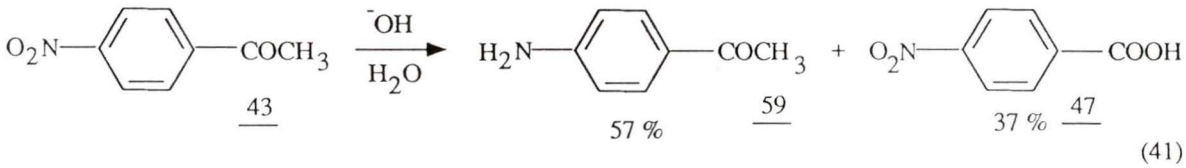


Scheme 3

3.3 Results and Discussion for the Disproportionation of *p*-Nitroacetophenone (43)

3.3.1 Product Studies

When *p*-nitroacetophenone (**43**) was added to a basic solution (NaOH) under continuous argon purge, **43** reacted to give two products. One product is soluble in acidic aqueous solution, identified as *p*-aminoacetophenone (**59**), and the other soluble in basic aqueous solution, identified as *p*-nitrobenzoic acid (**47**). The yields of **59** and **47** are 57% and 37%, respectively. The overal reaction is a disproportionation with the reduction of the nitro group in one substrate and the oxidation of methylcarbonyl in the other sunstrate (eq. 41). It was anticipated that the aldol condensation of



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43 would occur in basic solution. It was surprising that no trace of aldol condensation product was found.

When air was allowed into the system, the rate of the reaction was retarded, and when pure oxygen was used, the only product was *p*-nitrobenzoic acid (**47**).

Neither *p*-nitrobenzophenone (**61**) nor *p*-nitrobenzaldehyde (**12**) underwent the above reaction when dissolved in aqueous NaOH, showing that presence of ionizable

α-protons is required for this process. In addition, acetophenone itself failed to undergo the disproportionation, indicating the requirement of the nitro group.

3.3.2 pH Effect

The reaction of **43** with base was studied at different pH's. Below pH 11.5, no reaction was observed; all the substrate was recovered. When the pH was increased, disproportionation could be observed, and after the pH was increased to 13-14, the reaction rate leveled off, as shown in Figure 7. When freshly prepared **43** (in aqueous NaOH) was transferred to a quartz flat-cell and placed in the cavity of an ESR spectrometer (Bruker E200TT), strong ESR signals assignable to the radical anion of 4-NA were observed. In lower base strength, the signal is much weaker or not observed at all.

3.3.3 Effect of Externally added Electron Acceptor

When *p*-nitrobenzonitrile (**45**)--an excellent electron acceptor--was added the system, the yield of *p*-nitrobenzoic acid (**47**) was unchanged, but the yield of aminoacetophenone (**59**) was decreased sharply, from 58% to 30%. A new product, *p*-aminobenonitrile (**62**) was observed with a yield of 30% (eq. 42). This is because the reducing electron from the enolate ion not only reduces **43**, but also reduces the added electron acceptor **45**. The above results indicate that the

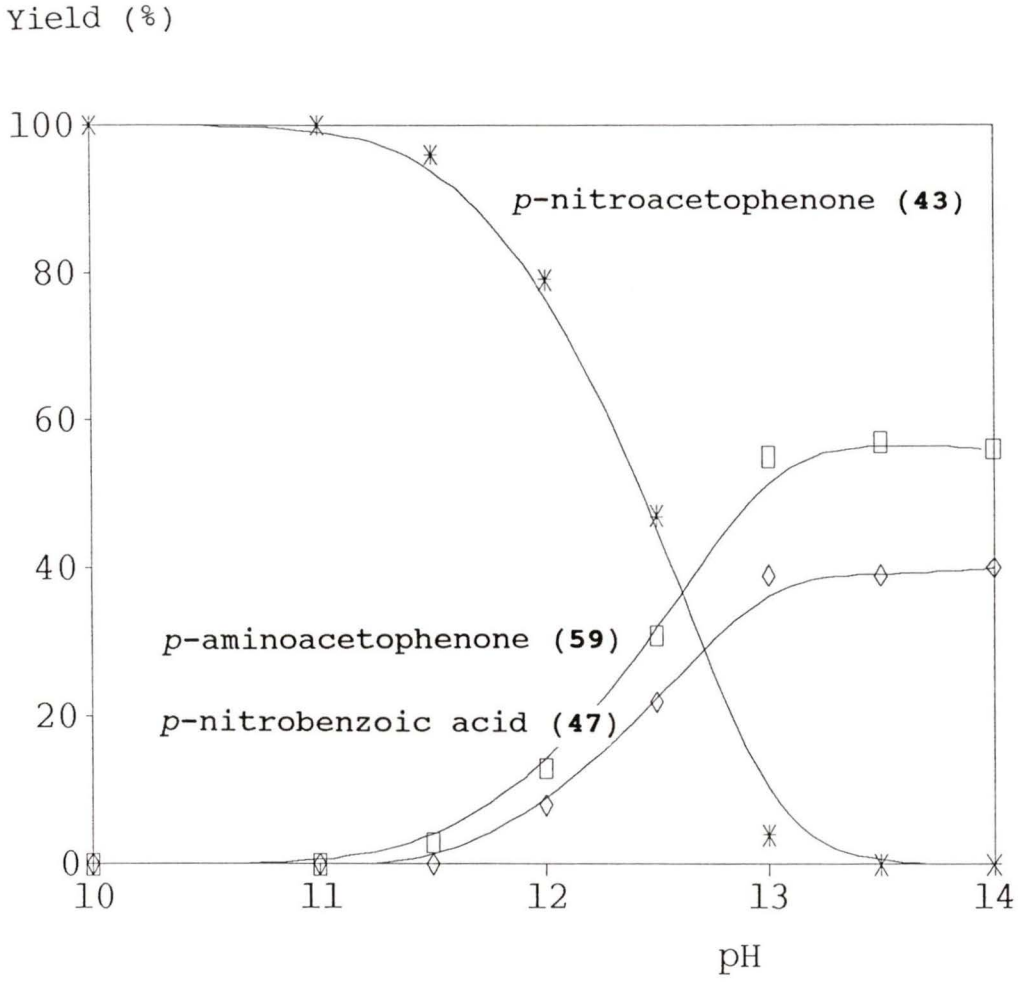
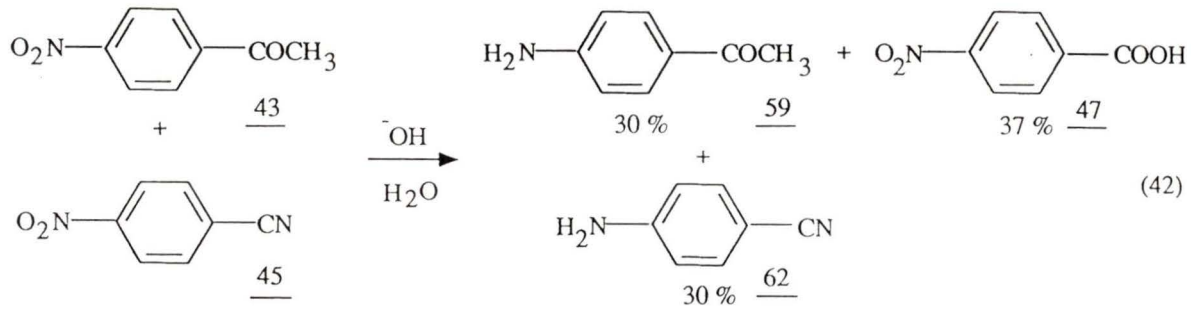


Figure 7 Plot of yield of products and loss of substrate as a function of pH of the aqueous portion of the solution (25% CH_3CN) after 3 h reaction at 22 °C.

disproportionation reaction of **43** involves electron transfer.



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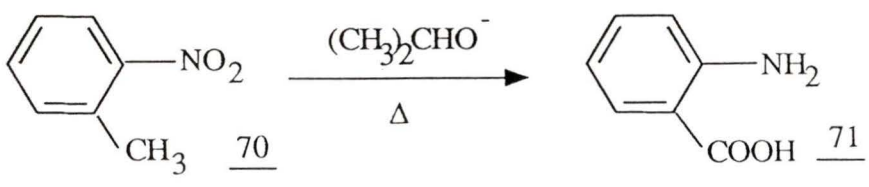
3.3.4 Mechanism

p-nitrobenzyl carbanion (**7**), once photogenerated in aqueous solution, readily ejects electrons[3,18,20]. In addition, even non-nitro substituted carbanions can also eject electrons, especially when a good electron acceptor is present in the solution[34]. Furthermore, nitroaromatic compounds in general are known to be useful oxidants of carbanions in strongly basic solution[39-41]. It is known that *o*-nitrotoluene (**70**) could be converted to *o*-anthranilic acid (**71**) via an intramolecular mechanism[52] when heated in strongly basic conditions, although the detailed mechanism of reaction is not known (eq. 43). On the other hand, **43** is known to be a good electron acceptor and its radical anion has a lifetime of



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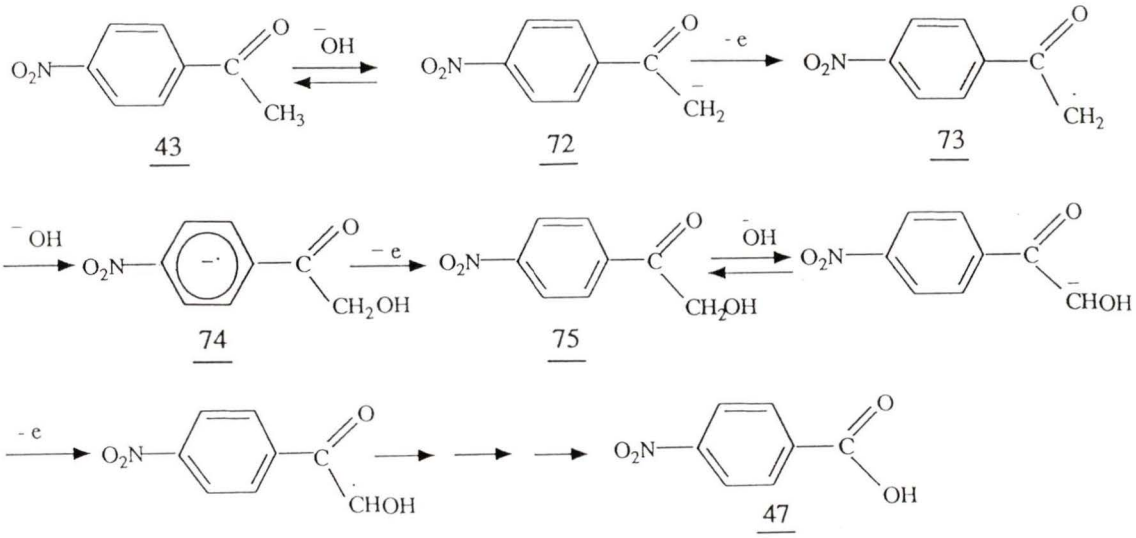
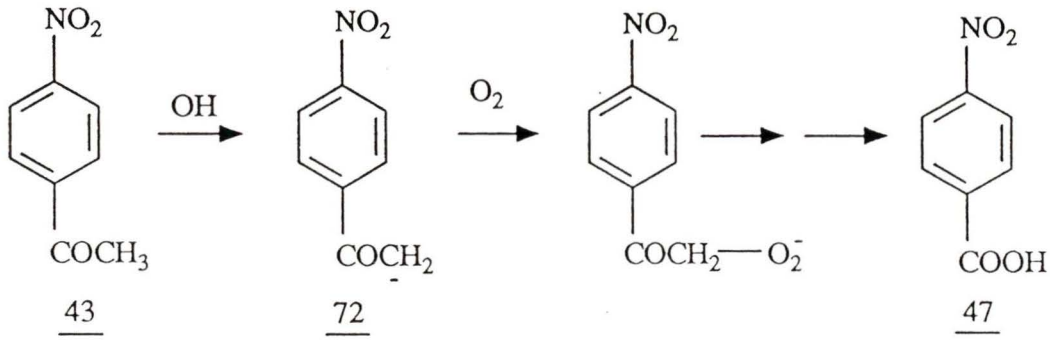
several minutes in aqueous base[41]. These observations coupled with the above results indicate that the mechanism of the reaction of *p*-nitroacetophenone (**43**) in aqueous NaOH probably involves electron transfer from the initial generated enolate anion to substrate (Scheme 4). The initial step of the redox



Scheme 4

reaction is deprotonation of an α-proton by hydroxide ion, to form the corresponding enolate ion **72**. The enolate ion will eject an electron to give radical **73**. When oxygen is allowed into the system, the reaction of enolate **72** or radical **73** with oxygen becomes the predominant pathway; in this case, oxygen, instead of the nitro group, is the oxidizing agent. The resulting hydroperoxide readily undergo further reaction to give *p*-nitrobenzoic acid (**47**) as the final product (eq. 44).



43 72 47 (44)

Without oxygen, the nitro group becomes the oxidizing moiety. In order to reduce **43** to *p*-aminoacetophenone (**59**), 6 electrons are required. This implies that sequential transfer of electrons to **43** and its subsequently derived partially reduced products from the electron source is involved. The details of the mechanism are probably complicated. A reasonable pathway is attack of the radical **73** by hydroxide ion, to give a new radical anion **74**, which transfers an electron to **43**, resulting in α-hydroxy-*p*-nitroacetophenone (**75**). Compound **75** will undergo a similar series of steps, which eventually oxidizes the carbonyl moiety to carboxyl and the methyl moiety to carbon dioxide. When an authentic sample of **75** was dissolved in aqueous NaOH, *p*-nitrobenzoic acid (**47**) was formed in 65% yield. However, no reduction product was isolated.

3.4 Conclusion

In this chapter, it has been demonstrated that carbanions in aqueous solution eject electrons which reduce nitroaromatic compounds. The carbanions can be generated either photochemically or thermally. The mechanism of the

reduction involves electron transfer at least in the initial step. *p*-Nitroacetophenone (**43**) is an electron acceptor, but its enolate ion is a special carbanion. The enolate ion ejects electrons which reduce **43** to give intermolecular disproportionation products. This disproportionation is the equivalent of the Cannizzaro reaction for aromatic aldehydes.

3.5 Experimental

3.5.1 General

Solvents, instruments and general procedures for the photolysis and dark reactions are the same as described in Chapter 2. In this experimental section, only new materials and reaction procedures will be mentioned.

3.5.2 Materials

p-Nitrophenylacetate acid (**24**), *p*-nitrobenzaldehyde (**12**), *m*-nitrobenzaldehyde (**20**), *p*-nitrobezonitrile (**45**), *p*-nitroaceto-phenone (**43**), *p*-nitrobenzophenone (**61**), *m*-nitroacetophenone (**60**) and *p*-nitrobenzoic acid (**47**) were purchased from Aldrich and used as received. α-hydroxy-*p*-nitroacetophenone (**75**) was available in our laboratory[53].

3.5.3 General Procedure for Reduction of Nitroaromatic Copounds by p*-Nitrophenylacetate ion (24) on Photolysis*

The substrate (120 mg) to be reduced, as well as *p*-nitrophenylacetate acid (**24**) (2.0 g), was dissolved in 50 mL

CH_3CN. To this solution was added 150 mL 0.5 M NaOH solution. The solution was then transferred to a 200 mL quartz vessel and irradiated at 254 nm for 2 h with continuous argon purging before and throughout the photolysis. After photolysis, the solution was filtered to remove the precipitate of *p,p'*-dinitrobibenzyl (**6**). The solution was then extracted with 50 mL CH_2Cl_2 (three times). After the evaporation of CH_2Cl_2, the residue was purified by the preparative TLC (silica) and by recrystillization. The purified products were identified by comparing their spectra (^1H NMR and MS) with those of authentic samples or published data.

3.5.4 Reduction of p-*Nitrobenzaldehyde (12) by* p-*Nitrophenylacetate ion (24) on Photolysis*

p-Nitrobenzaldehyde (**12**) (120 mg) and *p*-nitrophenylacetate acid (**24**) (2.0 g) were dissolved in 50 mL CH_3CN. To this solution was added 150 mL 0.5 M NaOH solution. The solution was then transferred to a 200 mL photo-reactor and was irradiated at 254 nm for 2 h with continuous argon purging before and throughout the photolysis. After photolysis, the solution was filtered to remove the precipitate of **6**. The solution was then extracted by 50 mL CH_2Cl_2 (three times). After the evaporation of CH_2Cl_2, the residue was purified by the preparative TLC (silica) and by recrystallization. The product was identified to be *p*-azoxybenzaldehyde (**46**); m.p. 192-193 °C (same as in Chapter

2); ^{1}H NMR (250 MHZ) δ (ppm): 7.8-8.7 (m, 8H, arom.), 10.1-10.2 (2s, 2H, -CHO); IR (KBr, cm^{-1}): 1690 (s), 1590 (m), 1450 (m), 1200 (m); MS (EI) (m/z): 254 (M^+).

3.5.5 Reduction of m-*Nitrobenzaldehyde (20) by* p-*Nitrophenylacetate ion (24) on Photolysis*

Similarly, *m*-nitrobenzaldehyde (**20**) (120 mg) and **24** (2.0 g) were dissolved in 50 mL CH_3CN. To this solution was added 150 mL 0.5 M NaOH solution. The following steps of photolysis and work-up were the same as that mentioned in last section. The product was identified to be *m*-azoxybenzaldehyde (**21**); m.p. 105-106 °C[26]; ^{1}H NMR δ (ppm): 7.1-8.9 (m, 8H, arom.), 10.1-10.15 (2s, 2H, -CHO); IR (KBr, cm^{-1}): 1690 (s), 1570 (w), 1430 (m), 1260 (w), 1220 (w), 1130 (m); MS (EI) (m/z): 254 (M^+).

3.5.6 Reduction of p-*Nitrobenzonitrile (45) by* p-*Nitrophenylacetate ion (24) on Photolysis*

p-Nitrobenzonitrile (**45**) (120 mg) and **24** (2.0 g) were dissolved in 50 mL CH_3CN. To this solution was added 150 mL 0.5 M NaOH solution. The solution was then photolyzed at 254 nm for 2 h as the previous experiment. After photolysis, the solution was filtered to remove the precipitate of *p,p'*-dinitrobibenzyl. The product was purified by liquid-liquid since it is soluble in acidic aqueous solution but not in basic aqueous solution. It was identified to be *p*-

cyanoaniline (**62**) by comparing its ^{1}H NMR and MS spectra with those published in literature.

3.5.7 Reduction of p-*Nitrobenzophenone (61) and* p-*Nitroacetophenone (43) by* p-*Nitrophenylacetate ion (24) on Photolysis*

The procedure for the reduction of **61** and **43** was similar to that mentioned in above section. After photolysis and work-up, **61** gave *p*-aminobenzophenone (**65**) and **43** gave *p*-aminoacetophenone (**59**).

3.5.8 Reduction of m-*Nitroacetophenone (60) by* p-*Nitrophenylacetate ion (24) on Photolysis*

To a solution with 130 mg of *m*-nitroacetophenone (**60**) and 2.0 g of **24** dissolved in 50 mL CH_3CN was added 150 mL 0.8 M NaOH solution. The solution was then photolyzed at 254 nm for 2 h. The product was isolated and purified by liquid-liquid extraction since It is soluble in water only when the solution is acidic. It was identified to be *m*-aminoacetophenone (**64**) by comparing its ^{1}H NMR and MS spectra with those published in literature.

The photolysis in the solutions of diferent pH was carried out under the same conditions mentioned above.

3.5.9 Disproportionation Reaction of p-*Nitroacetophenone (43)*

In a typical run, 100 mg (0.61 mol) of **43** was dissolved

in 50 mL of CH_3CN and added with stirring to 200 mL of 0.5 M NaOH (100 nmol), which was continuously purged with argon. After several minutes, the solution turned yellow and become successively darker during the reaction. After 3 h at room temperature, the solution developed a deep orange color. It was extracted twice with 100 mL portions of CH_2Cl_2, which on evaporation gave 47 mg (57%) of *p*-aminoacetophenone (**59**): m.p. 103°C; identical with an authentic sample by ^1H NMR, IR and MS). The aqueous layer was acidified with 10% HCl and extracted twice with 100 mL portions of CH_2Cl_2, which on evaporation gave 37 mg (37%) of *p*-nitrobenzoic acid (**47**): m.p. 235-237°C; identical with an authentic sample by ^1H NMR, IR and MS. The pH dependence of the reaction was determined by carrying out the reaction in different pH for 3 h and analyzing the ratio of the products and substrate by integration of ^1H NMR spectra.

When oxygen was used in place of argon, the solution never took on the dark orange color observed above during the reaction. Direct extraction of the solution with CH_2Cl_2 gave no observable product by ^1H NMR. Extraction of the acidified solution gave only **47** (75 mg; 74%).

The experiment for addition of external electron acceptor, *p*-nitrobenzonitrile (**45**), was similar to the above, except that 100 mg of **45** was added to the solution. Direct extraction gave **59** and *p*-cyanoaniline (**62**), which could be separated by the preparative TLC and identified by comparing

their ^1H NMR, IR and MS spectra with those of authentic samples, respectively.

3.5.9 Disproportionation of α-hydroxy-p-Nitroacetophenone (75)

A solution of 100 mg (0.61 mol) of **75** dissolved in 50 mL of CH_3CN was mixed with 200 mL of 0.5 M NaOH (100 nmol) with stirring and continuously purging with argon. After several minutes, the color of the solution was changed as that of **43** mentioned above. After 3 h reaction at room temperature, the solution was extracted twice with 100 mL portions of CH_2Cl_2, which on evaporation gave no observable product. The aqueous layer was acidified with 10% HCl and extracted twice with 100 mL portions of CH_2Cl_2, which on evaporation gave 60 mg (65%) of **47**.

3.5.10 ESR Studies of Disproportionation of 43

In a typical run, 0.02 g of **43** (0.01 M) was dissolved in 3 mL CH_3CN (30%). The solution and 7 mL water (pH 13) were then purged with argon for 10 min, respectively, before they were combined. The combined solution (10 mL) was taken in an ESR flat-cell immediately and the spectrum was then recorded.

CHAPTER FOUR

PHOTODECARBOXYLATION OF α-HYDROXYARYLACETIC ACIDS AND THEIR DERIVATIVES IN AQUEOUS SOLUTION

4.1 Introduction

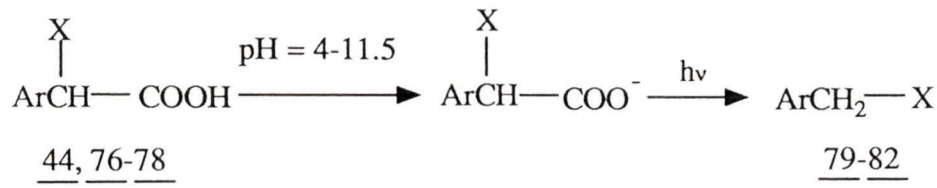
α-Arylacetic acids are of special interest in mechanistic studies of photodecarboxylation because of the simplicity of their structure and the ability of the aryl group to stabilize the incipient ionic or radical intermediate. The photodecarboxylation of α-arylacetic acids has therefore been well documented[27-34]. However, the quantum efficiencies of the known reactions are generally low (Φ < 0.02) except a few special cases, e.g. *p*-nitrophenylacetic acid (**24**) (Φ = 0.6)[27]. We now report the efficient photodecarboxylation of α-hydroxylarylacetate ions and their derivatives.

Thus, mandelate (MN) (**44**), α-methoxyphenylacetate (MPA) (**76**), *p*-methoxymandelate (*p*-MMN) (**77**) and α-hydroxy-α-(2-naphthyl)acetate (HNA) (**78**) ions have been found to undergo highly efficient photodecarboxylation (Φ = 0.2-0.5) in pH 4-11.5, to furnish benzyl alcohol (BT) (**79**), α-methoxytoluene (MT) (**80**), *p*-methoxybenzaldehyde (*p*-MB) (**81**) and 2-naphthalenemethanol (NAOL) (**82**), respectively (eq. 45). While under strongly basic conditions, the photodecarboxylation gave a dimeric product of the radical formed by the ejection of an electron from the suggested carbanion intermediate.

4.2 Results and Discussion

4.2.1 Product Studies and pH Effect

The photolysis of MN (**44**), MPA (**76**) *m*-MMN (**77**) and HNA (**78**) in aqueous solution (pH = 4-11.5), yielded only one product via elimination of CO_2. These reactions can be generalized in eq. 45. The quantum efficiencies for the



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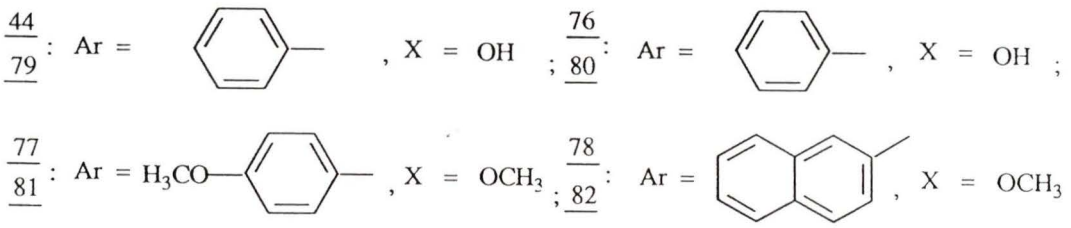


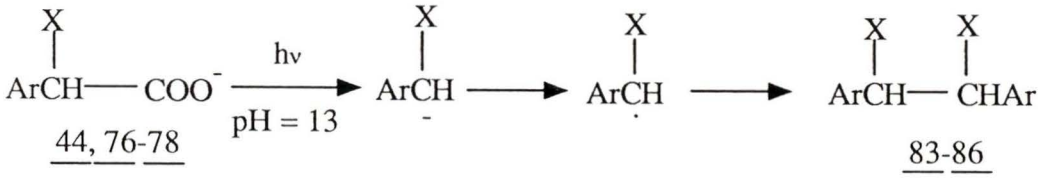
Table 5. Products and Quantum Yields of Photodecarboxylation of MN (44), MPA (76), *p*-MMN (77) and HNA (78)*

Substrates	MN (**44**)	MPA (**76**)	*p*-MMN (**77**)	HNA (**78**)
Products	BA (**79**)	MT (**80**)	*p*-MB (**80**)	NMOL (**82**)
Φ	0.41	0.28	0.28	0.40

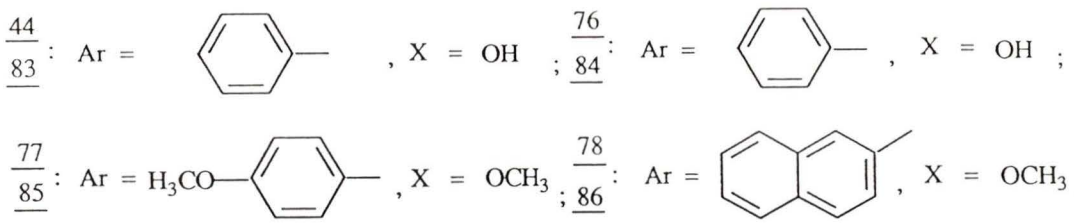
*Photolysis was carried out in aqueous solution (pH = 4-11.5).

Errors are ±15% of quoted value.

products are high, as shown in Table 5. In pH < 3.5, no reaction was observed. Between pH 4 and 11.5, quantum yields for reaction are constant as shown in Figure 8 for the photodecarboxylation of HNA (**78**). However, when the pH was raised to 13, the quantum yields of formation **78-82** decreased sharply, and dropped to zero at pH 13. Instead, new products ArCHX-CHXAr (**83-86**) were formed, which are the dimers of α-hydroxyarylmethyl radicals (eq. 46). The isolated products



44, 76-78 83-86 (46)



83-86 are mixtures of *meso*- and *d,l*-forms, which can be identified by ^{1}H NMR and GC spectra. Shown in Figure 9 are the GC traces of hydrobenzoin (PhCHOHCHOHPh) isolated from the photolysis of MN (**44**) and authentic hydrobenzoins.

The failure of the photodecarboxylation in acidic solution suggests that the reactive form of the photodecarboxylation is the carboxylate ion.

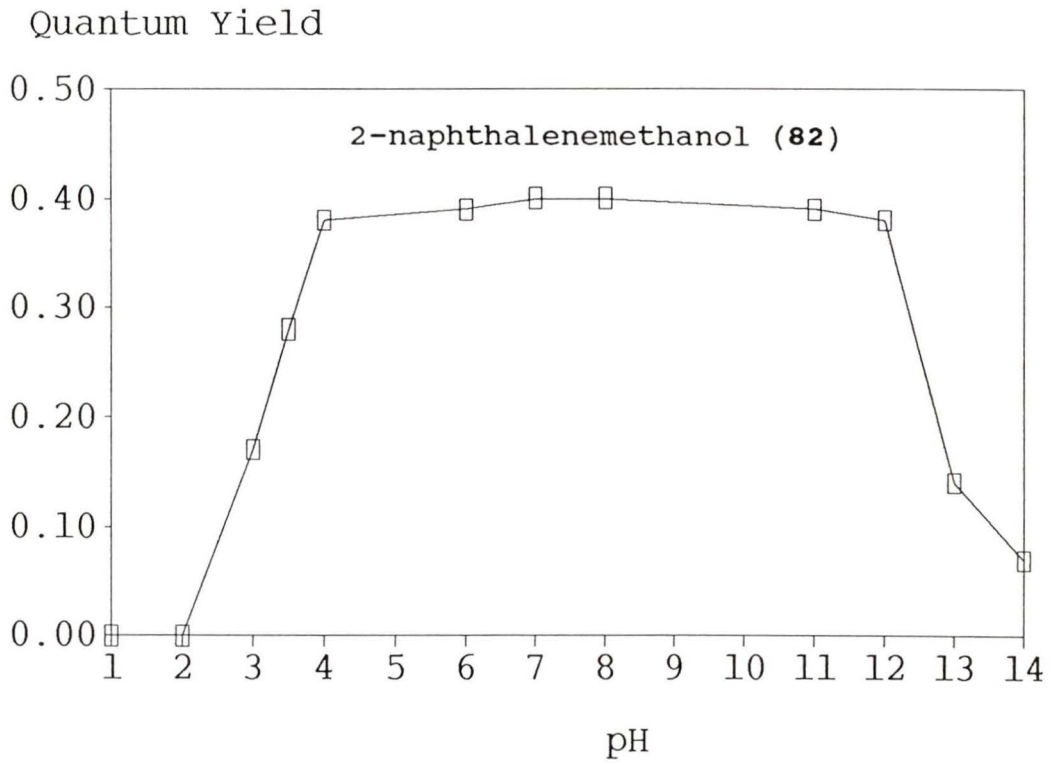


Figure 8 Plot of quantum yield (Φ) as a function of pH of the aqueous portion of the solution (15% CH_3CN) for the photodecarboxylation of HNA (**78**).

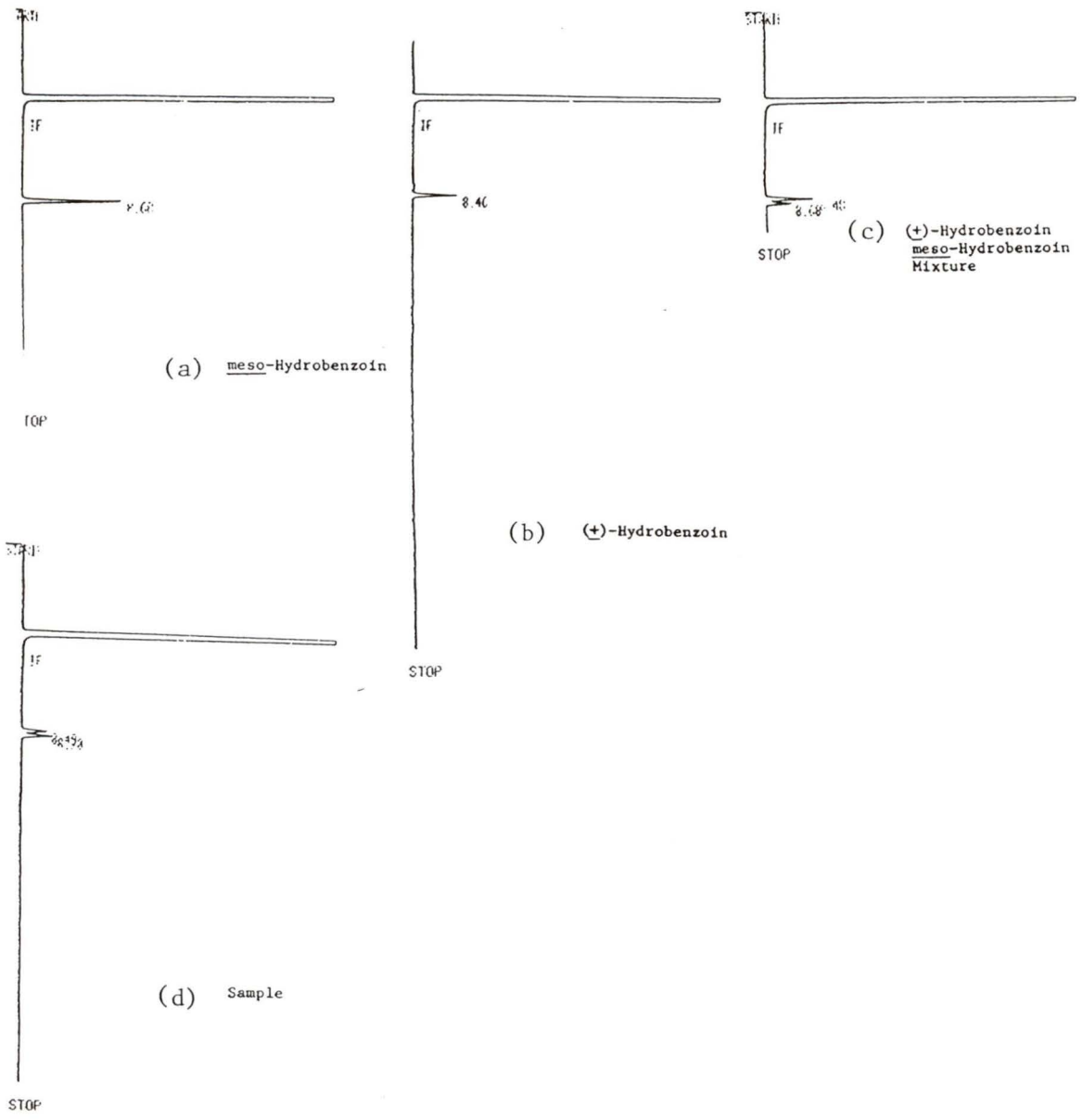


Figure 9 GC Spectra of hydrobenzoin: (a) authentic *meso*-isomer; (b) authentic *d,l*-isomer; (c) 50:50 mixture of authentic *meso*- and *d,l*-isomers; (d) product isolated from 0.5 h photolysis of MN (**44**) at pH 13.

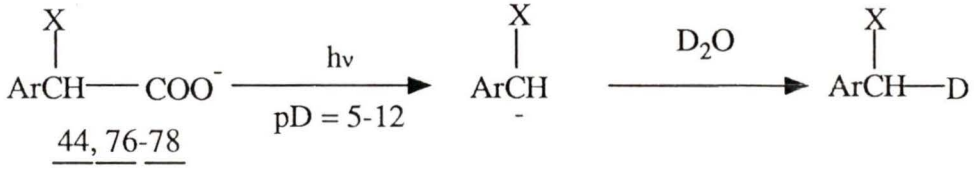
The methyl ester of mandelic acid (**44a**) did not react *at all* upon photolysis for 2 h under the same conditions, again indicating the requirement of the carboxylate ion.

4.2.2 Solvent and Isotopic Effects

The solvent effect is an important criterion for the distinction between radical and ionic pathways[33,34]. In general, radical reactions are independent of the polarity of solvent, while ionic reactions are greatly affected. To establish the relationship of the photodecarboxylation with the polarity of the solvent, the photolysis of **44**, **76-78** was carried out in pure methanol or CH_3CN. No photodecarboxylation was observed in these solvents and all the substrate was recovered.

When **44** or **76-78** was dissolved in basic D_2O solution (pD = 13), the substrate was not deuterated even after reflux overnight, indicating that the α-proton to the carbonyl carbon cannot be deprotonated. This fact enables us to study the solvent isotope effect of the photodecarboxylation and to establish the mechanism.

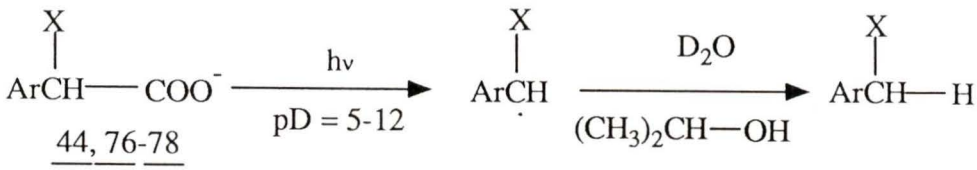
An ionic mechanism for the photodecarboxylation of **44** and **76-78** involves primary α-hydroxyarylmethyl carbanions, which abstract a proton from solvent to furnish the final products **79-82**. When the photolysis was carried out in D_2O solution, a deuterium instead of a proton will be abstracted to furnish α-monodeuterated products (eq. 47). This was



44, 76-78 (47)

observed when we photolyzed **44** and **78** in D_2O solution (pD = 5-12).

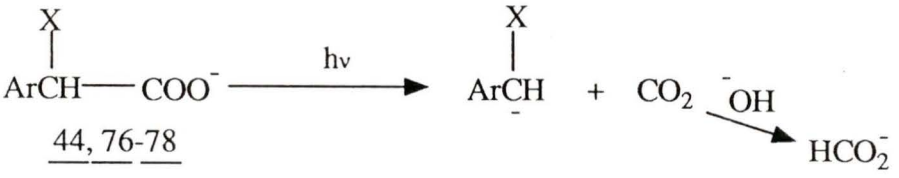
On the other hand, a radical mechanism involves primary radical intermediates **83**, which cannot abstract a hydrogen from water, and must dimerize. However, when a good hydrogen doner (e.q., $(CH_3)_2CHOH$) and D_2O are both present in the solution, the resulting product will be *without* deuterium incorporation if it is a radical mechanism (eq. 48), while, in



44, 76-78 (48)

contrast, the resulting product will be found to have one-deuterium incorporation if it is an ionic mechanism (eq. 47). Thus, when both **44** and **78** were photolyzed in 8% 2-propanol (a good hydrogen donor) D_2O solution, the products were found to have one-deuterium incorporation just as in the case when the photolysis was carried out in D_2O solution without 2-propanol. These observations together with the above results indicate that the mechanism of the photodecarboxylation of **44, 76-78** involves carbanions **87-90** as primary intermediates.

After photolysis of **44** or **78** in neutral solution, the pH of the solution increased 2.5-3 units. In contrast, under basic conditions, other things being equal, the pH of the solution decreased slightly (ca. 0.3 units) These observations are consistent with the ionic mechanism. Thus, under neutral and acidic conditions, as shown in eq. 49, CO_2



44, 76-78 (49)

generated in this system is released to the solution. Since the primary carbanion intermediate is a much stronger base than the carboxylate ion, the final pH should increase. However, in basic solution, CO_2 reacts with base so that the actual pH decreases.

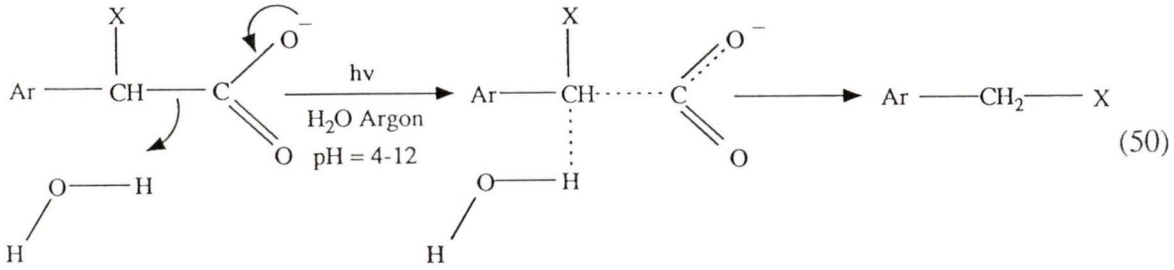
In D_2O solution (pD 5-11), the quantum yield of the photodecarboxylation was found to be reduced significantly (Φ_H/Φ_D 1.3), as shown in Table 6. We therefore propose that

Table 6. Solvent Isotope Effect for the Photodecarboxylation of MN (44), MPA (76), *p*-MMN (77) and HNA (78)*

Substrates	MN (44)	MPA (76)	*p*-MMN (77)	HNA (78)
Φ_H/Φ_D	1.21	1.22	1.19	1.45

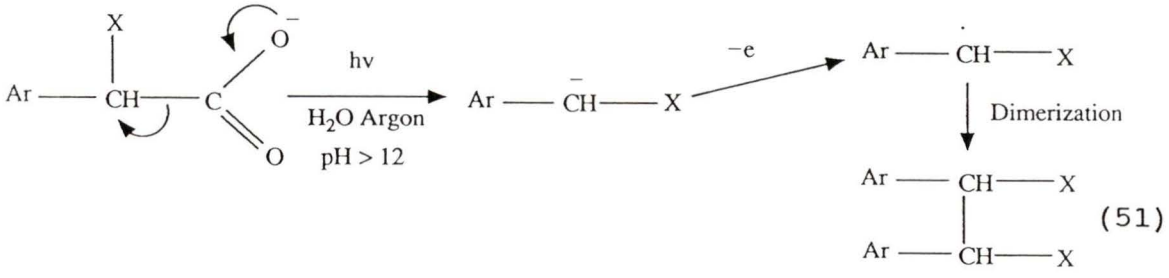
*Photolysis was carried out in H_2O or D_2O with pH = pD and argon purging. Yields were obtained by GC analysis (Errors: ±5% of quoted value).

the carbanion intermediates photogenerated under pH 4-11.5 are probably short-lived and the cleavage of C-C bond may be concerted with the protonation from solvent protons (eq. 50).



(50)

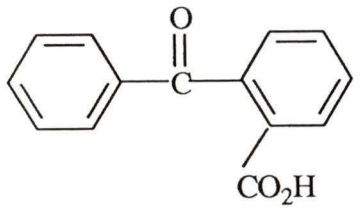
However, under strongly basic conditions, the carbanion intermediates are relatively long-lived. As α-hydroxy-*p*-nitrobenzyl carbanion does, carbanions **87-90** all readily eject an electron to give the corresponding radicals, which dimerize to give **79-82**, respectively (eq. 51).



(51)

4.2.3 Multiplicity of the Photodecarboxylation and Properties of the Primary intermediate

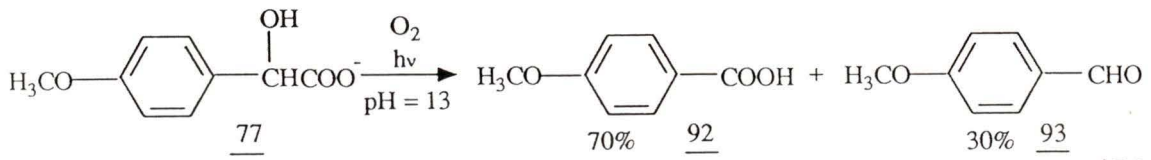
2-Benzoylbenzoic acid (BBA) (**91**) is a useful triplet sensitizer[3,20,34]. Its triple energy (ca. 68 kcal/mol) is higher than that of HNA (**91**) (ca. 60 kcal/mol)[54,55]. When **91** was used to sensitize the photolysis of NHA under the typical



2-Benzoylbenzoic acid (**91**)

conditions, except in a wavelength of 350 nm, no product was isolated. This experiment indicates that the multiplicity of the reactive excited state is the singlet.

It was well established that benzyl carbanions can eject electrons to give radicals and radical products in basic solution, which can be readily oxidized by oxygen. When the photolysis of **44**, **76-78** was carried out under oxygen purging, the result of the photolysis was also pH-dependent. Thus, when the photolysis was carried out with oxygen purging under pH 4-11.5, the product was the same as isolated under argon purge, so is the quantum yield. However, when the photolysis was carried out with oxygen purging under the basic conditions (pH > 12), products **83-86** disappeared. Instead, the corresponding aldehydes and acid were formed. For example, photolysis of *p*-MMN (**77**) led to the formation of *p*-methoxybenzoic acid (**92**) (70%) and *p*-methoxybenzaldehyde (**93**) (30%) (eq. 52).



(52)

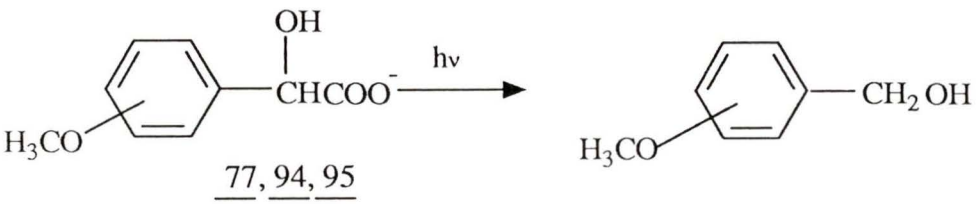
4.2.4 Effect of an α-Substituent on the Efficiency of Photodecarboxylation

As described in the previous sections, the photodecarboxylation reaction of α-hydroxyarylacetate ions and their derivatives are highly efficient. In contrast, the quantum yields of the photodecarboxylation of simple α-arylacetate ions, such as 1- and 2-naphthylacetate, phenylacetate and methoxyphenylacetate ions, were found to be very low ($\Phi < 0.01$). The effect of an α-hydroxyl or methoxyl on the photodecarboxylation is therefore significant. It is a general trend that more substitution, especially an α-electronegative substituent such as a hydroxyl, leads to the reduction of adjacent C-C bond strength[56] so that the benzylic C-C bond in an α-hydroxy or methoxyarylacetate ion is so weak that the energy absorbed from the light is sufficient to break this C-C bond. This has been substantiated by the photodecarboxylation reactions found for a set of α-substituted arylacetate ions. Thus, the arylacetate ions with an α-electronegative group such as an amino, fluoro or chloro were found to be also photo-active (α = 0.08-0.20). However,

if the α-substituent is not a negative group, the quantum yield will be low. Such is the case for α-methyl, α-cyclopentyl and α-cyclohexyl phenylacetate ions ($\Phi < 0.02$), as well as the phenylacetate ions mentioned above.

4.2.5. Relative Reactivity of o,m,p-Methoxymandelates

As mentioned above, *p*-MMN (**77**) undergoes photodecarboxylation compatible with MN (**44**) and HNA (**78**). However, *m*-methoxymandelate (*m*-MMN) (**94**) did not react *at all* upon photolysis under same conditions in pH 4-11.5. *o*-Methoxymandelate (*o*-MMN) (**95**) was photolabile, but its quantum yield is less than 0.01 (Table 7, eq. 53). This



77, 94, 95 (23)

Table 7. Quantum Yields of Photodecarboxylation of Methoxymandelates(MMN)*

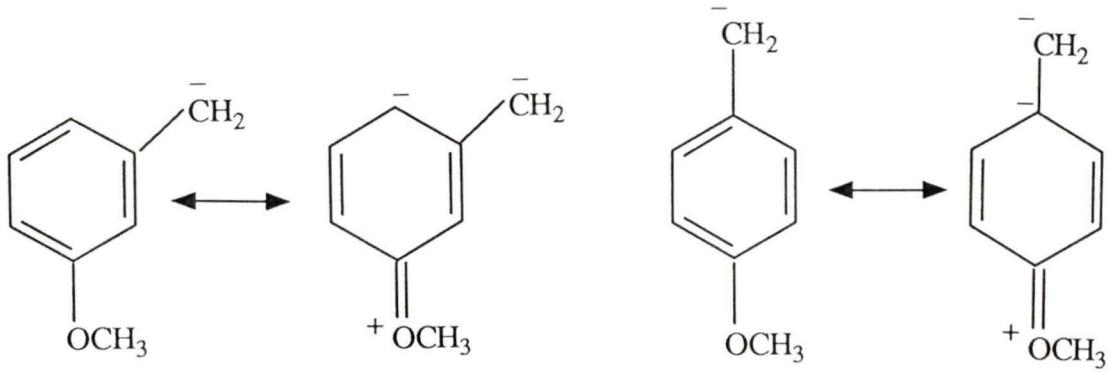
Substrates	*p*-MMN (**77**)	*m*-MMN (**94**)	*o*-MMN (**95**)
Φ	0.28	0.00	0.01

*Photolysis was carried out in aqueous solution (pH = 4-11.5) and yields were obtained by GC analysis (Errors: ±5% of quoted value).

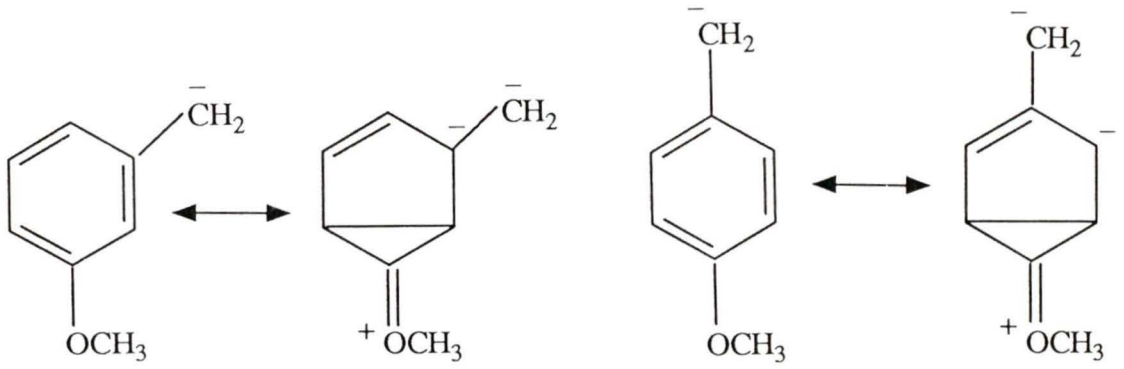
observation, indicating that the photochemical generation of benzyl carbanion is inhibited by *m*-methoxyl substitution, provides a first example in which the carbanion is destabilized by a *m*-methoxy substitute. This is in contrast to the expectation based on the knowledge of ground state chemistry. The reverse of the ground-state behavior in excited state was long observed and interpreted by the *meta effect*[36]. Shown in Figure 10 (a) is the ground state of methoxybenzyl moieties. According to the *meta effect*, in the excited state, the structure of methoxybenzyl moieties is depicted by Figure 10 (b), in which the negative charge of the methoxy group is delocalized to its *meta*, rather than *para* position. That is why *p*-MMN (**77**) is much more reactive than *m*-MMN (**94**) toward photolysis in aqueous solution.

4.3 Conclusion

α-Hydroxyarylacetate ions and their derivatives undergo efficient photodecarboxylation in aqueous solution. The mechanism is an ionic one and involves primary carbanion intermediates. In pH < 12, the photodecarboxylation may be concerted or the carbanion intermediates are relatively short-lived. In higher pH, the carbanion intermediates are relatively long-lived. The reverse of ground-state behavior in the excited state is observed for the photodecarboxylation of methoxymandelate ions, in which the reaction of the *p*-isomer is much more efficient than the *m*-isomer.



(a) ground state



(b) first-excited state.

Figure 10 Resonance structure of *p*- and *m*-methoxybenzyl carbanions: (a) ground state; (b) first-excited state.

4.4 Experimental

4.4.1 General

Solvents, instruments and general procedures for the photolysis and dark reactions are the same as described in Chapters 2 and 3. In this section, only the new materials and different reaction procedures will be mentioned.

4.4.2 Materials

Mandelic acid (**44**), α-methoxyphenylacetic acid (**76**), *p*-methoxymandelic acid (**77**), *m*-methoxymandelic acid (**94**), *o*-methoxymandelic acid (**95**), phenylacetic acid, *p*-methoxyphenylacetic acid, *m*-methoxyphenylacetic acid, 1-naphthylacetic acid, 2-naphthylacetic acid, 2-benzoylbenzoic acid (BBA) (**91**) and 2-naphthylaldehyde were purchased from Aldrich and used as received. α-Hydroxy-α-(2-naphthalene) acetic acid (**78**) was synthesized from 2-naphthylaldehyde in a one-pot reaction via the pathway described below[57].

4.4.3 Synthesis of α-Hydroxy-α-(2-naphthalene)acetic Acid (78)

In a 500 mL flask were placed 0.5 mol of LiCl, 1.0 mol of KOH and 200 g of ice. To this mixture were added 200 mL of 1,4-dioxane, 0.25 mol of 2-naphthylaldehyde and 0.25 mol of $CHBr_3$. The mixture was put in a ice bath and was stirred for 24 h. To ensure pH > 12, 0.125 mol of KOH was added to this system before stirring. Then the mixture was allowed to stir at 32 °C for another 24 h. The solution was then transferred

to an 800 mL beaker and diluted to 600 mL with water. The solution was extracted three times with 50 mL portions of ether. The aqueous layer was then acidified to pH 1 and extracted four times with 50 mL portions of ether. The combined ether was dried over $MgSO_4$, filtered and evaporated to obtain the crude acid (solid). The crude acid was purified by washing it with hot ligroin and $CHCl_3$; m.p. 156 °C (literature 158 °C)[58]; ^1H NMR and MS spectra being the same as those reported in literature.

4.4.4 General Procedure for Photolysis

The solution of 120 mg of substrate dissolved in 200 mL water with predetermined pH was transferred to a 200 mL photo-reactor and was irradiated at 254 nm for the required period with continuous argon purging before and throughout the photolysis. After photolysis, the solution was basified and extracted by 80 mL portions of CH_2Cl_2 (three times). After the evaporation of CH_2Cl_2, the residue was purified by preparative TLC (silica) and the product(s) were identified by their ^1H NMR, GC, IR and MS spectra in comparison with those of an authentic sample or those reported in literature. The aqueous solution was acidified to approximately pH 1 and extracted by four 50 mL portions of CH_2Cl_2. The substrate was recovered. If not, evaporation of water was required before the extraction. The product and the substrate were then combined to determine the yield of the product by the

integration of ^{1}H NMR.

*4.4.5 Photolysis of Mandelic Acid (**44**)*

The solution of 120 mg of **44** dissolved in 200 mL water was irradiated at 254 nm for 5-30 min with continuous argon purging before and throughout the photolysis. In pH 4-11.5, only one product was isolated, which was identified as benzyl alcohol (**79**); ^{1}H NMR (90 MHz) δ: 2.0 (s, 1H, O**H**), 4.6 (s, 2H, C**H**$_2$), 7.3 (s, 5H, arom.); MS (EI) (m/z): 108 (M^+). Above pH 11.5, a new product was also isolated and its yield increased with the increase of pH, until pH 13 (0.1 M NaOH solution), the new product became the only isolated product, which was identified as the mixture of *d,l*-and *meso* forms of hydrobenzoin (**83**) by their ^{1}H NMR, GC, IR and MS spectra in comparison with those of an authentic sample; ^{1}H NMR (90 MHz) δ: 4.3 (s, 2H, O**H**), 4.65-4.75 (2s, 2H, C**H**), 7.15-7.35 (m, 10H, arom.); MS (EI) (m/z): (196) ($M^+ - H_2O$).

*4.4.6 Photolysis of α-Methoxyphenylacetic Acid (**76**)*

The procedure of photolysis **76** is the same as that described in the previous section. Also, in pH 4-11.5, only one product was isolated, which was identified as benzyl methyl ether (**80**); ^{1}H NMR (90 MHz) δ: 3.35 (s, 3H, -OC**H**$_3$), 4.4 (s, 2H, C**H**$_2$), 7.3 (s, 5H, arom.); MS (EI) (m/z): 122 (M^+). Above pH 11.5, a new product was also isolated and it was the only isolated one above pH 13, which was identified as the

mixture of *d,l*-and *meso* forms of dimethyl hydrobenzoin ether (**84**) by their ^{1}H NMR, GC, IR and MS spectra in comparison with those reported in literature; ^{1}H NMR (90 MHz) δ: 3.15-3.25 (2s, 6H, -OC**H**$_3$), 4.3 (s, 2H, C**H**), 7.3 (s, 10H, arom.); MS (EI) (m/z): 210 (M^+ - CH_3OH).

4.4.7 Photolysis of α-Hydroxy-α-(2-naphthalene) acetic Acid (78)

The procedure of photolysis **78** is the same as that described for **44**. In pH 4-11.5, only one product was isolated, which was identified as 2-naphthalanemethanol (**82**); ^{1}H NMR (90 MHz) δ: 4.8 (s, 2H, C**H**$_2$), 7.2-8.0 (m, 7H, arom.); MS (CI) (m/z): 159 (M^+ + 1). Above pH 11.5, a new product was also obtained. The product was identified as the mixture of *d,l* and *meso* forms of hydronaphtoin (**86**) by their ^{1}H NMR, GC, IR and MS spectra in comparison with those reported in literature[58]; m.p. 218 °C; ^{1}H NMR (90 MHz) (pyridine-d_6) δ: 3.0 (s, 2H, O**H**), 4.8 (s, 2H, -C**H**), 7.3-7.9 (m, 14H, arom.); IR (KBr): 3400 (s), 3040 (s), 2980 (m), 1590 (m), 1500 (s), 1060 (s); MS (EI) (m/e): 296 (M^+ - H_2O).

4.4.8 Photolysis of p-Methoxymandelic Acid (77), m-Methoxymandelic Acid (94) and o-Methoxymandelic Acid (95)

The procedure for photolysis of **77** is the same as that described for **44**. In pH 4-11.5, photolysis of **77** gave only one product, which was identified as *p*-methoxybenzyl alcohol

(**81**); ^{1}H NMR (90 MHz) δ: 2.0 (s, 1H, O**H**), 3.8 (s, 3H, -OC**H**$_3$), 4.55 (s, 2H, C**H**$_2$), 6.8-6.9 (d, J = 9 Hz, 2H, arom.), 7.2-7.3 (d, J = 9 Hz, 2H, arom.); MS (CI) (m/z) 139 (M^+ + 1). Above pH 11.5, a new product was also isolated and it became the only product isolated above pH 13, which was identified as the mixture of *d,l* and *meso* forms of di-(*p*-methoxy)-hydrobenzoin (**85**) by their ^{1}H NMR, GC, IR and MS spectra in comparison with those reported in literature; ^{1}H NMR (90 MHz) δ: 2.7 (s, 2H, O**H**), 3.7 (2s, 6H, -OC**H**$_3$), 4.5-4.7 (2s, 2H, C**H**), 6.68-6.78 (d, J = 9 Hz, 2H, arom.), 6.7-6.8 (d, J = 9 Hz, 2H, arom.), 7.0-7.1 (d, J = 9 Hz, 2H, arom.), 7.1-7.2 (d, J = 9 Hz, 2H, arom.); IR (KBr): 3340 (s), 2900 (s), 2815 (m), 1600 (m), 1500 (m), 1480 (m), 1280 (s), 1160 (m), 1040 (s); MS (EI) (m/z): 270 ($M^+ - H_2O$).

The procedure for photolysis of **94** and **95** is the same as that described for **77**. In the pH range studied (1-14), the *m*-isomer **94** did not give any observed product in GC upon photolysis for 2 h. All the substrate was recovered. The *o*-isomer **95** gave a trace amount of *o*-methoxybenzyl alcohol (**96**) upon photolysis, which was identified by comparing its GC, ^{1}H NMR, IR and MS spectra with those pulished in the literature for the same compound.

4.4.9 Photolysis of α-Aminophenylacetic Acid (97), α-Fluorophenylacetic Acid (98) and α-Chlorophenylacetic Acid (99)

Photolysis of acetic acids **97-99** was studied under the same conditions as described above. The identification procedure was also similar to that mentioned above. In pH 4-11.5, **97** gave benzyl amine (**100**); ^{1}H NMR (90 MHz) δ: 3.8 (s, 2H, NH_2), 4.85 (s, 2H, CH_2), 7.3 (s, 5H, arom.); MS (EI) (m/z): 105 (M^+); the same as those for an authentic sample. Similarly, **98** gave benzyl fluoride (**101**) and **99** benzyl chloride (**102**). Above pH 12, **97** gave a mixture of *d,l* and *meso* forms of 1,2-diphenylethylene diamine (**103**), which has the same spectra as reported in literature.

*4.4.10 Methoxyphenylacetic Acid, Naphthylacetic Acids, α-Methylphenylacetic Acid, α-Cyclopentylphenylacetic Acid, α-Cyclohexylacetic Acid and methyl ester of mandelic acid (**44a**)*

Photolysis of these compounds was carried out individually in pH 4-13 under the same conditions as above, except that the photolysis time (2-4 h) was much longer for these compounds. No product was isolated and all the substrate was recovered in every case.

*4.4.11 Photolysis of MN (**44**), MPA (**76**), p-MMN (**77**) and HNA (**78**) in D_2O*

The substrate (80 mg) was dissolved in 2 mL CH_3CN and 18 mL D_2O in a 20 mL quartz tube. The solution was purged by a stream of argon and was then photolyzed for 1-5 min at 254 nm. The product mixture was diluted by H_2O and extracted with

50 mL portions of CH_2Cl_2 three time. The compound isolated was analyzed by ^1H NMR, GC and GC-MS.

MN (**44**) gave α-D-benzyl alcohol; ^1H NMR (90 MHz) δ: 4.6 (broad, 1H, C**H**), 7.3 (s, 5H, arom.); MS (EI) (m/z): 109 (M^+).

MPA (**76**) gave α-D-benzyl methyl ether; ^1H NMR (90 MHz) δ: 3.35 (s, 3H, -OC**H**$_3$), 4.4 (broad, 1H, C**H**), 7.3 (s, 5H, arom.); MS (EI) (m/z): 123 (M^+).

p-MMN (**77**) gave α-D-*p*-methoxybenzyl alcohol; ^1H NMR (90 MHz) δ: 3.8 (s, 3H, -OC**H**$_3$), 4.55 (broad, 1H, C**H**), 6.8-6.9 (d, J = 9 Hz, 2H, arom.), 7.2-7.3 (d, J = 9 Hz, 2H, arom.); MS (EI) (m/z): 139 (M^+).

HNA (**78**) gave 2-α-D-naphthalenemethanol; ^1H NMR (90 MHz) δ: 4.8 (broad, 1H, C**H**), 7.2-8.0 (m, 7H, arom.); MS (EI) (m/z): 159 (M^+).

The yields of the photolysis were determined by GC. The solvent isotope effects were calculated by taking the ratio of the conversion of photolysis in H_2O versus D_2O under the same conditions (pH is approximately equal to pD).

4.4.12 Triplet Sensitization

Triplet sensitization of reaction was carried out for HNA (**78**) using sodium benzophenone-2-carboxylate (**91**) as the triplet sensitizer. Thus, 120 mg of **78** and 1 g of **91** were dissolved in 30 mL CH_3CN and 170 mL NaOH solution to make pH 12.5. The solution was transferred to a 200 mL quartz tube (under the conditions, **91** absorbed > 95% of the light), and

was then photolyzed at 350 nm for 30 min. The reaction mixture was worked up as the standard method mentioned above. No product was isolated.

*4.4.13 Photolysis of MN (**44**), p-MMN (**77**) and HNA (**78**) under O_2*

The substrate (120 mg) to be studied was dissolved in 20 mL CH_3CN and 180 mL H_2O in a 200 mL quartz tube. The solution was purged by a stream of oxygen and was then photolyzed for 30 min at 254 nm. The product mixture was basified and extracted with 50 mL portions of CH_2Cl_2 three times. Evaporation of the solvent gave non-acidic products. The aqueous solution was acidified to pH 1 and was then extracted with three more portions of CH_2Cl_2. Evaporation of the extract resulted in the acidic products. In pH 4-11.5, the results for all the substrates are the same as those reported in previous sections for the same photolysis carried out with argon purging. In pH 13, all the substrates gave new products. *p*-MMN (**77**) gave *p*-methoxybenzaldehyde (**92**); ^{1}H NMR (90 MHz) δ: 3.85 (s, 3H, -OC**H**$_3$), 6.95-7.05 (d, J = 9 Hz, 2H, arom.), 7.8-7.9 (d, J = 9 Hz, 2H, arom.), 9.9 (s, 1H, -C**H**O); MS (EI) (m/z): 136 (M^+) and *p*-methoxybenzoic acid (**93**); ^{1}H NMR (90 MHz) δ: 3.85 (s, 3H, -OC**H**$_3$), 6.95-7.05 (d, J = 9 Hz, 2H, arom.), 7.9-8.0 (d, J = 9 Hz, 2H, arom.), 9.3 (broad, 1H, -COO**H**), MS (EI) (m/z): 152 (M^+). These spectra are identical with those reported for the same compounds in literature[59].

Similarly, MN (**44**) gave benzaldehyde and benzoic acid, HNA (**78**) gave 2-naphthylaldehyde and 2-naphthoic acid.

References

1. Buncel, E.; Durst, T., "Comprehensive Carbanion Chemistry", Elsevier, New York, **1980.**
2. Turro, N.J., "Modern Molecular Photochemistry", Chapter 13, Benjamin/Cummings, Menlo Park, **1978.**
3. Wan, P.; Muralidharan, S., *J. Am. Chem. Soc.*, **1988**, *110*, 4336.
4. Streitwieser, Jr., A., "Solvolytic Displacement Reactions, New York, **1962.**
5. Wan, P.; Yates, K., *J. Org. Chem.*, **1983**, *48*, 136.
6. March, J., "Advanced Organic Chemistry", 3rd ed., Wiley, New York, **1985**, p.160.
7. Reutov, O.A.; Beletskaya, I.P.; Butin, K.P.,"CH Acids",Pergamon, New York, **1978.**
8. Streitwieser, Jr., A.; Taylor, D.R., *J. Chem. Soc. D*, **1970**, 1284.
9. Streitwieser, Jr., A., Guibe, F., *J. Am. Chem. Soc.*, **1978**, *100*, 4532.
10. Streitwieser, Jr., A.; Ciuffarin, E.; Hammons, J.H., *J. Am. Chem. Soc.*, **1967**, *89*, 63.
11. Pearson, R.G.; Dillon, R.L., *J. Am. Chem. Soc.*, **1953**, *75*, 2439.
12. Guthrie, J.P.; Cossar, J.; Klym, A., *J. Am. Chem. Soc.*, **1984**, *106*, 1351.

13. Streitwieser, Jr., A.; Hollyhead, W.B.; Dudjaatmaka, A.H.; Owens, P.H.; Kruger, T.L.; Rubenstein, P.A.; MacQuarrie, R.A.; Brokaw, M.L.; Chu, W.K.C.; Niemeyer, H.M., *J. Am. Chem. Soc.*, **1971**, *93*, 5088.

14. Reeve, W.; Erikson, C.M.; Aluotto, P.F., *Can. J. Chem.*, **1979**, *57*, 2747.

15. Streitwieser, Jr. A.; Nebenzahl, L.L., *J. Am. Chem. Soc.*, **1976**, *98*, 2188.

16. Harned, H.S.; Robinson, R.A., *Trans. Faraday Soc.*, **1940**, *36*, 973.

17. Filler, R.; Wang, C.-S., *Chem. Commun.*, **1968**, 287.

18. Wan, P.; Muralidharan, S., *Can. J. Chem.*, **1986**, *64*, 1949.

19. Margerum, J.D.; Brault, R., *J. Am. Chem. Soc.*, **1966**, *88*, 4733.

20. Mualidharan, S., Ph.D. Thesis, University of Victoria, **1989**.

21. a) Russell, G.A.; Janzen, E.J., *J. Am. Chem. Soc.*, **1967**, *89*, 300. b) Reference 18.

22. Chow, Y.L.; "The Chemistry of the Amino, Nitro and Nitroso Compounds and Their Derivatives", Patai, S., ed.; Wiley, New York, **1982**, Chapter 6.

23. Ciamician, G.; Silber, P., *Chem. Ber.*, **1901**, *34*, 2040.

24. Wubbels, G.G.; Hautala, R.R.; Letsinger, R.T., *Tetrahedron Lett.*, **1970**, 1689.

25. Wubbels, G.G.; Kalhorn, T.F.; Johnson, D.E.; Campbell, D., *J. Org. Chem.*, **1982**, *47*, 4664.

26. Wan, P.; Yates, K.; *Can. J. Chem.*, **1986**, *64*, 2076.

27. Margerum, J.; Petrusis, C.T., *J. Am. Chem. Soc.*, **1969**, *91*, 2467.

28. Buncel, E; Venkatachalam, T; Menon, B, *J. Org. Chem.*, **1984**, *49*, 413.

29. a) Craig, B.B.; Weiss; R.G.; Atherton, S.J., *J. Phys. Chem.*, **1987**, *91*, 5906. b) Maclelland, R.A.; Steenken, S., *Can. J. Chem.*, **1987**, *65*, 353.

30. Craig, B.B.; Pace, M.D., *J. Chem. Soc., Chem. Commun.*, **1987**, 1144.

31. Stermitz, F.; Huang, W.; *J. Am. Chem. Soc.*, **1971**, *93*, 3427.

32. a) Meiggs, T; Miller, S., *J. Am. Chem. Soc.*, **1972**, *94*, 1989. b) Meiggs, T; Grossweiner, L.; Miller, S., *J. Am. Chem. Soc.*, **1972**, *94*, 7981. c) Givens, R.s.; Matuszewski, B.; Neywick, C., *J. Am. Chem. Soc.*, **1974**, *96*, 5547. d) Jaeger, D., *J. Am. Chem. Soc.*, **1974**, *96*, 6216. e) Davidson, R.; Harrison, K.; Steiner, P., *J. Chem. Soc., C.*, **1971**, 3484.

33. Epling, G.A.; Lopes, A., *J. Am. Chem. Soc.*, **1977**, *99*, 2700.

34. McAuley, I.; Krogh, E.; Wan, P., *J. Am. Chem. Soc.*, **1988**, *110*, 600.

35. a) Tolbert, L.M., *Org. Photochem.* **1983**, *6*, 177. b) Fox, M.A., *Chem. Rev.*, **1979**, *79*, 253.

36. (a) Zimmerman, H.E., "Advances in Photochemistry", Vol.

1, Noyes, A., *et al.*, Eds., Interscience, New York, **1963**, p. 183. (b) Zimmerman, H.E.; Sandel, V.R., *J. Am. Chem. Soc.*, **1963**, *85*, 915. (c) Zimmerman, H.E.; Somasekhera, S., *J. Am. Chem. Soc.*,

37. Tolbert, L.M., *Acc. Chem. Res.*, **1986**, *19*, 268.
38. Morrison, H.A., "The Chemistry of Nitro and Nitroso Groups", Feuer, H., Ed.; Wiley, Ney York, **1969.**
39. Russell, G.A.; Janzen, E.G.; Strom, E.T., *J. Am. Chem. Soc.*, **1964**, *86*, 1807.
40. a) Guthrie, R.D.; Cho, N.S., *J. Am. Chem. Soc.*, 1979, *101*, 4698. b) Guthrie, R.D.; Hartmann, C.; Neil, R.; Nutter, D.E., *J. Org. Chem.*, **1987**, *52*, 736. c) Han, C.H.; Brauman, J.I., *J. Am. Chem. Soc.*, **1988**, *110*, 4048.
41. Muralidharan, S.; Wan, P., *J. Chem. Soc., Chem. Commun.*, **1987**, *110*, 4336.
42. Dopp, D., *Top. Curr. Chem.*, **1975**, *55*, 49.
43. Frolov, A.N.; Kuznetsova, N.A.; El'tsov, A.V., *Russ. Chem. Rev. Engl. Trans.*, **1976**, *45*, 1024.
44. Rafizadeh, K.; Yates, K., *Org. Prep. Proceed. Int.*, **1985**, *17*, 140.
45. Stowell, J.C., "Carbanions in Organic Synthesis", Wiley, New York, **1979.**
46. Jones, J.R., "The Ionisation of Carbon Acids", Academic Press, London, **1973.**
47. Russell, G.A.; Moye, A.J.; Janzen, E.G.; Mak, S.; Talaty, E.R., *J. Org. Chem.*, **1976**, *32*, 137.

48. Meot-Ner, M.; Neta, P., *J. Phys. Chem.*, **1986**, *90*, 4648.

49. Reference 6, pp 829-834.

50. Ashby and co-workers have proposed a single electron transfer mechanism for both the Cannizzaro and aldol condensation reactions: Ashby, E.C.; Coleman, D.; Gamasa, M., *J. Org. Chem.*, **1987**, *52*, 4079.

51. Reference 6, pp 1117-1119.

52. Lock, G., *Ber.*, **1940**, *73*, 1377.

53. Wan, P.; Xu, X., *J. Org. Chem.*, **1989**, *54*, 4473.

54. Murov, S.L., "Handbook of Photochemistry", Marcel Decker, New York, **1973**.

55. Yip, R.W.; Sharma, D.K.; Giasson, R.; Gravel, D., *J. Chem. Phys.*, **1984**, *88*, 5770.

56. Carey, F.A.; Sundberg, R.J., "Advanced Organic Chemistry-Part A: Structure and Mechanism", 2nd ed., Plenum Press, New York, **1983**,

57. Edward, L.; Compere, Jr., *J. Org. Chem.*, **1968**, *33*, 2565.

58. Chenevert, R.; Ampleman, G., *Synthesis*, **1987**, 739.

59. *Aldrich Catalog Handbook of Fine Chemicals*, 1988-1989 ed., Milwaukee, **1988**.

VITA

Surname: Xu Given Name: Xigen

Place of Birth: Jiangxi, CHINA Date of Birth: May 30, 1963

Educational Institutions Attended:

University of Victoria	1987-1990
Shanghai Institute of Organic Chemistry	
Academia Sinica	1982-1985
Jiangxi University	1978-1982

Degrees Awarded:

M.Sc.	Shanghai Institute of Organic Chemistry	
	Academia Sinica	1985
B.Sc.	Jiangxi University	1982

Honours and Awards:

University of Victoria Dean Scholarship 1987-1988

Publications:

Journal Papers:

1) Wan, P.; Xu, X., Enhanced Photodecarboxylation Efficiency of α-Hydroxy-substituted Arylacetic Acids in Aqueous Solution., *Tetrahedron Lett.*, **1990**, 2809.

2) Wan, P.; Xu, X., Disproportionation of 4-Nitroacetophenone to 4-Aminoacetophenone and 4-Nitrobenzoic Acid., *J. Org. Chem.*, **1989**, *54*, 4473.

Conference Papers:

1) Xu, X.; Wan, P., Photogenerated *p*-Nitrobenzyl Carbanions as Reducing Agents in Aqueous Solution: Presented at Canadian Chemical Conference and Exhibition, Victoria, **June 1989.**

2) Xu, X.; Muralidharan, S.; Wan, P., Photoretro-aldol Type Reaction of Nitrophenyl Ethylene Glycols: The Chemistry of Photogenerated α-Hydroxynitrobenzyl Carbanions: Presented at Canadian Chemical Conference and Exhibition, Victoria, **June 1989.**

3) Krogh, E.; Xu, X.; Wan, P., Structure-reactivity Studies of Photodecarboxylation of α-Arylacetic Acid in Aqueous Solution: Presented at Canadian Chemical Conference and Exhibition, Victoria, **June 1989.**

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