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CONCERNING THE MECHANISM OF DISPLACEMENT OF NITRO GROUPS FROM ACTIVATED AROMATIC SYSTEMS

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Abstract: The photostimulated reactions of p-nitrobenzophenone and p-nitrobenzonitrile with a variety of nucleophiles have been investigated. Displacement of the nitro group is observed in all cases. The rates of the reactions were measured by FT-IR. The rates were slowed by substances such as sulfur, air, Galvinoxyl and p-benzoquinone. In several cases rates of loss of starting material were monitored by quenching the reaction mixtures and isolating product and starting material. These reactions also showed inhibition of their rates in the presence of inhibitors. These results indicate that the reactions are chain processes. It is concluded that the substrates are converted into their corresponding radical anions which then react with the nucleophiles in a bimolecular displacement reaction. The alternate mechanism, which involves dissociation of the radical anions, is precluded because they are known not to dissociate.

The reactions of many aryl compounds with various nucleophiles have been observed to follow

$$\mathrm{ArX} + \mathrm{Nu}^- \rightarrow \mathrm{ArNu} + \mathrm{X}^- \qquad (1)$$

the overall sequence of equation (1). Three mechanisms have been suggested for these transformations. One of these the $S_{RN}1$ mechanism is outlined in Scheme I. This mechanism suggests that an electron is added to the aryl compound, 1, to give a radical anion , 2, which dissociates to an aryl radical, 3. The aryl radical is thought to combine with the nucleophile to give the radical anion. 4. Transfer of an electron from 4 to 1 yields the product, 5, and 2 and thus the chain is continued.[1]

$$\underset{\underline{1}}{\text{ArX}} + \text{e} \rightarrow \underset{\underline{2}}{\text{ArX}^{\dot{-}}} \tag{2}$$

$$\text{ArX}^{\dot{-}} \rightarrow \underset{\underline{3}}{\text{Ar}\cdot} + \text{X}^{-} \tag{3}$$

$$\text{Ar}\cdot + \text{Nu}^{-} \rightarrow \underset{\underline{4}}{\text{ArNu}^{\dot{-}}} \tag{4}$$

$$\text{ArNu}^{\dot{-}} + \text{ArX} \rightarrow \underset{\underline{5}}{\text{ArNu}} + \text{ArX}^{\dot{-}} \tag{5}$$

Scheme I

Another mechanism follows an addition elimination sequence as outlined in Scheme II.[2]

$$\text{ArX} + \text{Nu}^{-} \rightarrow \underset{\underline{6}}{\text{ArXNu}^{-}} \tag{6}$$

$$\text{ArXNu}^{-} \rightarrow \text{ArNu} + \text{X}^{-} \tag{7}$$

Scheme II

The third mechanism that has been postulated is outlined in Scheme III. This mechanism suggests that the radical anion, 2, is formed by electron transfer and it then reacts with the nucleophile to give the radical anion, 4. Transfer of an electron from 4 to 1 gives the product and continues the chain. Recently it has been argued that the available data and new experimental results support the mechanism of Scheme III in many instances.[3] In particular it was argued that there is no real evidence for the mechanism of Scheme I.

$$\text{ArX}^{\dot{-}} + \text{Nu}^{-} \rightarrow \underset{\underline{4}}{\text{ArNu}^{\dot{-}}} + \text{X}^{-} \tag{8}$$

$$\text{ArNu}^{\dot{-}} + \text{ArX} \rightarrow \underset{\underline{5}}{\text{ArNu}} + \text{ArX}^{\dot{-}} \tag{9}$$

Scheme III

The mechanisms of Schemes I and III both involve radical anions in chain reactions. They are different in that the mechanism of Scheme I also involves aryl radicals whereas that of Scheme III does not. The mechanism of Scheme II does not involve radical anions or radicals and it is not a chain reaction.

The Pross-Shaik[4] theory concerning single electron transfer as the underlying theme of organic reactions suggests that Scheme II involves initial electron transfer from an electron source, Nu^-, for

$$\begin{tikzcd} Nu^- + ArX \arrow[r] & {[Nu^{\cdot}ArX^{\cdot}]^-} \arrow[r] \arrow[dr] & \underset{\underline{6}}{ArXNu^-} & (10) \\ & & Nu^{\cdot} + \underset{\underline{2}}{ArX^{\cdot-}} & (11) \end{tikzcd}$$

example, to ArX followed by bond formation (10). Alternatively bond formation does not occur and $ArX^{\cdot-}$ is generated (11). It is evident then that Schemes II and III represent a continium. The factors that will determine which path shall be followed are not as yet delineated.

The mechanisms of Schemes I and III can be distinguished from that of Scheme II by observation of the chain character of these mechanisms as contrasted to the nonchain character of Scheme II. Traditionally the effects of inhibitors and initiators have been employed to distinguish chain reactions from nonchain reactions. Catalysis by light has been employed as a mechanistic diagnostic tool as well.

Evidence for the mechanism of Scheme III has been provided by Chambers and Adams[5]. They showed that p-dinitrobenzene radical anion generated electrochemically reacted with the water in the solvent dimethylformamide to give p-nitrophenol. Shein has suggested that substitution reactions of p-dinitrobenzene[6], p-nitrochlorobenzene[7] and 2,4-dinitrochlorobenzene[8] involve reactions of nucleophiles with the radical anions derived from the nitro compounds. Abe and Ikegami[9] have shown that the displacement of nitrite ion from o- and p-dinitrobenzenes involves attack by the hydroxide ion on the respective radical anions.

In a recent report[10] it was shown that nitro groups of p-nitrobenzonitrile and 4-nitrophthalonitrile are displaced by the lithium salts of 2-R-5-nitro-1,3-dioxanes. It was also shown that the radical anions from these substances were present in the reaction mixtures. It was found that oxygen slows the reactions which suggests that they are chain reactions.

It has also been shown[3] that the p-halonitrobenzenes react with sodium benzenesulfinate with displacement of halide ion. The rates of the reactions are enhanced by light and slowed by Galvinoxyl. The radical anions from the p-halonitrobenzenes do not dissociate and thus it was concluded that the substitution reaction involves displacement by the nucleophile on the radical anions.

Kornblum et al.[11] reported that 4-nitrobenzophenone, ethyl and methyl p-nitrobenzoates, p-nitrobenzonitrile, o- and p-dinitrobenzenes and 4-nitrophenyl phenyl sulfone react with a variety of nucleophiles with displacement of nitrite ion. The rates of the reactions show an interesting solvent dependence with the order being HMPA > DMSO > DMF.

Knudson and Snyder[12] found that a moderately activated nitro group in a substituted nitrobenzene is displaced by reaction with the anion of an aldoxime in DMSO solution.

More recently Sammes et al.[13] have studied the displacement of nitro groups from p-nitrobenzaldehyde, methyl p-nitrobenzoate, trifluoromethyl p-nitrobenzene p-nitrobenzonitrile and p-dinitrobenzene by phenoxide ions. They showed that the reaction of p-dinitrobenzene with 2,6-dibromo-4-methylphenoxide ion was completly inhibited by adding one equivalent of 1,1-diphenylpicrylhydrazyl. They concluded that the reactions were radical in character. They did not elaborate on this conclusion.

Zhao and Huang[14] have allowed anions of various heterocyclic ketene aminals to react with 1-fluoro, 1-chloro, 1-bromo and 1-iodo-2,4-dinitrobenzenes. The reaction rates followed the order F > Cl > Br > I. The reactions were stopped or inhibited by ferric chloride. The epr spectrum of the radical anion of 1-bromo-2,4-dinitrobenzene was recorded during the reaction. They concluded that a chain process was involved in the overall transformations.

One of the major tests for the chain character of these reactions has been studies of the effects of inhibitors on their rates. The effect of light and initiators have also been used to establish that these are chain reactions. Rossi and de Rossi[1] have reviewed the role of inhibitors and the effect of light and initiators on these aromatic substitution reactions. Some reactants react just as fast in "dark" reactions as they do under illumination. These have been called "spontaneous reactions". Other reactants require photostimulation or initiation by an electron source.

Various inhibitors have been employed to establish the chain nature of the overall substitution reactions. Typically substances such as dinitrobenzenes, dioxygen, di-t-butyl nitroxide, tetraphenylhydrazine and sulfur have been used. In general addition of these materials has led to retardation of the reaction rates rather then pure inhibition. Bunnett and Trabor[15] found that dioxygen did not inhibit the reaction of iodobenzene with diethylphosphite anion whereas p-dinitrobenzene led to significant retardation. In another series of experiments, Scamehorn and Bunnett[16] found that iodo and bromobenzene reacted with potassium enolate ion in DMSO at 25° in the dark to form the expected substitution product. These reactions were inhibited by p-dinitrobenzene, benzophenone and di-t-butlynitroxide. On the other hand, dioxygen, nitrobenzene and ferric nitrate acted as accelerants.

Swartz and Bunnett[17] studied the reactions of iodo and bromotoluenes with potassium diphenylphosphide ion in ammonia and DMSO. The reactions occur in the dark. They were subject to stimulation by light and inhibition by various electron acceptors. These studies indicate that when these substitutions follow a chain mechanism, retardation in the rates of the reactions should be observed for at least some inhibitors. It is important to be aware that problems with some inhibitors may arise i. e. retardation may not be observed.

It seemed of interest to further investigate the mechanism of the nitro group displacement reaction. p-Nitrobenzophenone, 7, and p-nitrobenzonitrile, 8, were chosen as substrates. The reason for these choices was that both of the radical anions of these substrates have been characterized and they have been shown not to dissociate.[18,19] The reaction of p-nitrobenzonitrile with the anion of benzaldoxime has also been studied. The reaction of p-dinitrobenzene with the potassium salt of 2-nitropropane has also been studied. The radical anion of p-dinitrobenzene does not dissociate[5]. The fact that none of these radical anions dissociate removes the mechanism of Scheme I from consideration.

There is a further observation that eliminates the mechanism of Scheme I. In a related series Kornblum et al.[11] noted that when p-nitrophenyl phenyl sulfone was allowed to react with the lithium salt of 2-nitropropane the product of nitrite ion displacement was formed in 76% yield. When the same substrate was allowed to react with the sodium salt of methylmercaptan two products were formed. The product from the loss of nitrite ion was formed in 61% yield and the product formed by loss of benzenesulfinate ion was formed in 17% yield. Clearly if the same intermediate radical anion dissociates as in equation (3) then there should be no effect on the nature of products as a function of the nucleophile. The mechanism of Scheme I requires that two dissociations must occur, loss of nitrite ion and benzenesulfinate ion. This mechanism requires that two products be formed irrespective of the nature of the nucleophile. The mechanisms of Scheme II and III allow the nucleophile to play a role in determining the products of the reactions and thus they are in consonance with the variation in products as a function of changes in the nucleophile.

RESULTS AND DISCUSSION

Two different kinds of experiments have been conducted to test whether the displacement of nitrite ion is a chain process. The reaction of p-nitrobenzonitrile with the lithium salt of 2-nitropropane was conducted at room temperature under illumination for 6 h. The product was shown by ^{1}H NMR to be p-cyano-α-nitrocumene. The same reaction was conducted in the dark and with the addition of 50 mole percent sulfur. The product in this case consisted of 46% of the starting material and 54% of p-cyano-α-nitrocumene. These results show that sulfur inhibits the reaction.

p-Dinitrobenzene was allowed to react with the potassium salt of 2-nitropropane under irradiation for 5 h. The product was shown to be only α,p-dinitrocumene. No starting material remained. The same reaction was conducted in the dark and in the presence of 50 mole percent Galvinoxyl. The product was shown by ^{1}H NMR spectroscopy to be a mixture of starting material, 72 %, and α,p-dinitrocumene, 28 %. Clearly Galvinoxyl is inhibiting the reaction.

The reaction of the sodium salt of benzaldoxime and p-nitrobenzonitrile in DMSO was conducted under irradiation for 19 h. The product was shown by ^{1}H NMR spectroscopy to consist of starting material, 19 %, and p-cyanophenol, 81 %. A duplicate experiment was conducted in the dark and in the presence of 20 mole percent sulfur. The product was shown by ^{1}H NMR spectroscopy to consist of starting material, 50 %, and p-cyanophenol, 50 %. Once again some inhibition has been found.

The other reactions that have been investigated are those of p-nitrobenzophenone, 7, and p-nitrobenzonitrile, 8, with the lithium salt of 2-nitropropane, 9, sodium ethoxide, 10, sodium phenoxide, 11, sodium thiophenoxide, 12, and sodium p-chlorothiophenoxide, 13, in HMPA as the solvent. Not all possible combinations have been included. The progress of each reaction was monitored by following the disapperance of the nitro group absorption by FT-IR. The concentrations were determined from known plots of the nitro groups absorption against concentration. Various substances were used as potential inhibitors. They were air, gently bubbled through the reaction mixture, Galvinoxyl at 10 mole percent, sulfur, at 20 and 50 mole percent, and p-benzoquinone at 20 and 50 mole percent. All of the inhibitors and reactants were soluble in HMPA. The results of the experiments are presented graphically in the Experimental section.

The reactions of 7 were studied more extensively than those of 8. Most of the reactions showed very little catalysis by light. This is not totally unexpected, both 7 and 8 are good electron acceptors and thus initiation is quite facile. The reactions of ethoxide, phenoxide and the thiophenoxides showed very rapid initial rates followed by virtual cessation of reaction. In some cases it was necessary to halve the concentration of nucleophile to observe retardation.

The effects of Galvinoxyl, 10 mole percent, sulfur, 20 mole percent and benzoquinone, 20 and 50 mole percent, on the rates of reaction of 7 with 9 were retardation in all cases. Air seemed to be the most effective inhibitor with sulfur being the least effective.

The rate of the reaction of 7 with ethoxide ion, 0.2 mole to 0.1 mole, in the presence of 20 mole percent of sulfur was slower relative to the light and dark reactions.

The reaction of 7 with sodium phenoxide, 11, mole ratio 2:1, showed significant retardation by sulfur, 20 mole percent, while the light and dark reactions proceeded at virtually the same rate.

When the two same reactants, mole ratio 1:1, were allowed to react in the presence of Galvinoxyl, 10 mole percent, some retardation was found. When air was bubbled through a mole ratio 2:1 reaction mixture of these same reactants virtual cessation of the reaction was found.

The reaction of 7 with sodium thiophenoxide, 12, 2:1, was retarded by 20 mole percent sulfur.

The rate of the reaction of 7 with sodium p-chlorothiophenoxide, 13, in the mole ratio 1:1 was only slightly affected by 20 mole percent of sulfur. When the reactants were allowed to react in the ratio 2:1 and in the presence of 50 mole percent sulfur definite retardation was observed.

The reaction of 8 with the lithium salt of 2-nitropropane, 9, was significantly retarded by 20 mole percent of sulfur. Both the light and dark reactions proceeded at the same rate. Ethoxide ion reacted with the cyano group and thus it was not included. The reaction of 8 with sodium phenoxide, 11, mole ratio 2:1, was slowed by sulfur, 20 mole percent. A very similar result was obtained from the reaction of 8 with sodium thiophenoxide, 12, mole ratio, 2:1 and in the presence of 20 mole percent sulfur.

All of these results are in agreement with reactions that involve chains. It is important to note that the general features observed in this study mimic those found by Bunnett and his co-workers[15-17] when they studied the effect of additives on "spontaneous reactions". These reactions are characterized as showing a rapid burst of product formation followed by a significant slowing of the reaction rate and by a much slower build up of product. A search of the preparative literature concerning these reactions reveals that it is common to use significant excesses of the nucleophiles to obtain good yields of the substitution products, It appears that as the concentration of the nucleophile drops other reactions of the radical anions may become more important.

The basic mechanistic conclusion that results from these studies is that the reactions involve chains which is of course accepted by all previous workers[1]. The important addition is that these reactions occur with substrates whose radical anions are stable towards dissociation. The mechanism of Scheme III is supported by these results. The remaining question is, is there a need for invoking the mechanism of Scheme I for any substrate? This issue has been discussed in detail earlier[3] and there is no need to repeat the arguments here

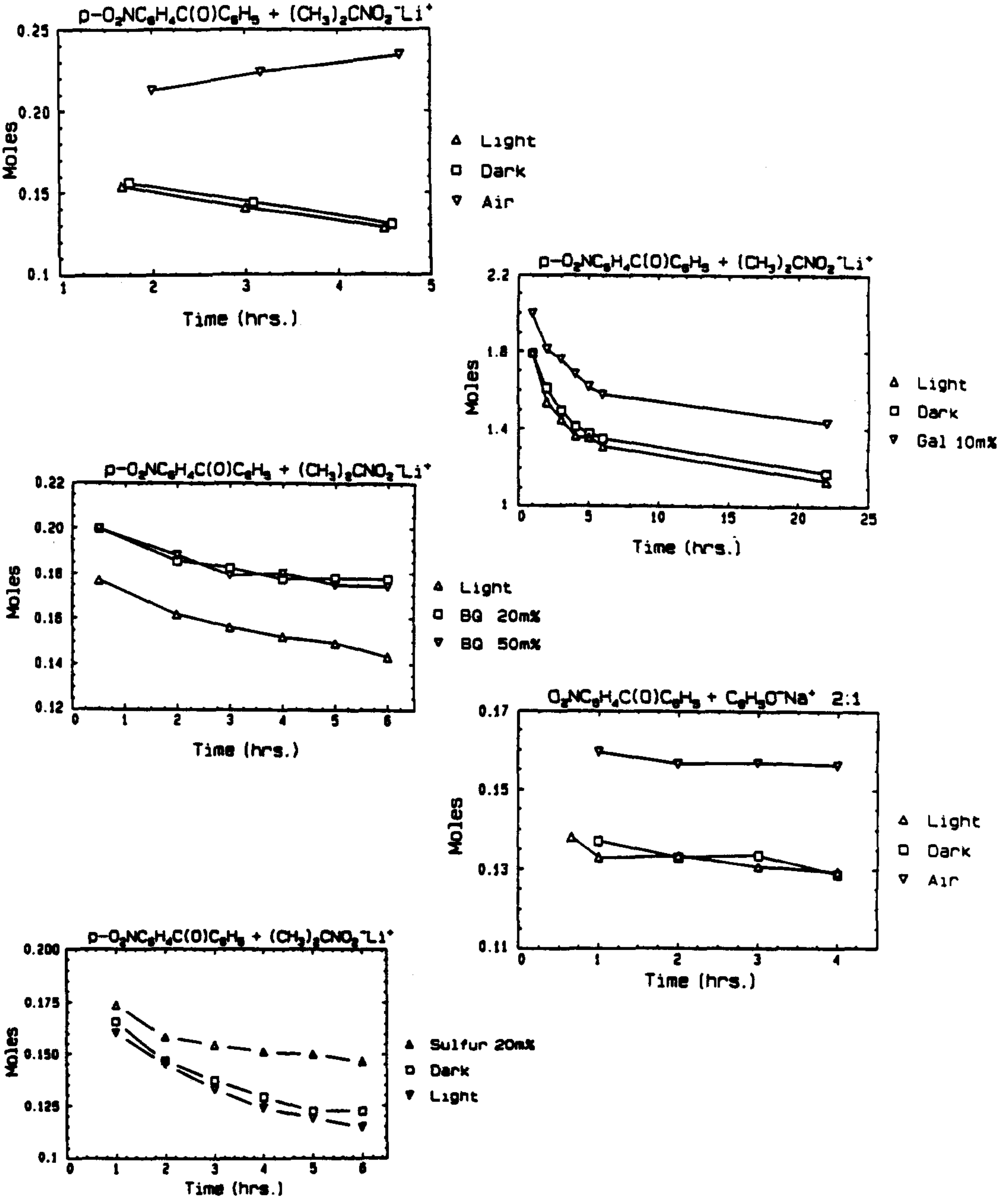
EXPERIMENTAL

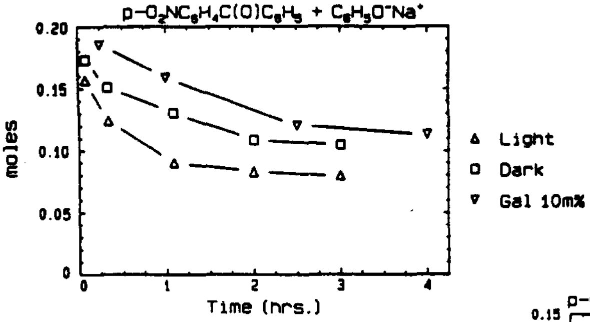
All of the reactions except as noted were conducted in HMPA and under a positive pressure of nitrogen. In the illuminated experiments two 40 watt fluorescent lamps were used. The flasks were positioned ca. 6 inches from the lamps, in the dark reactions the flasks were wrapped with aluminum foil and they were kept in the dark. The courses of the reactions were followed by TLC.

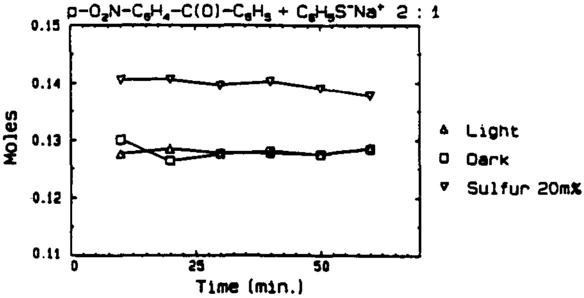
The qualitative rate measurements were obtained by removing aliquotes from the reaction mixtures and measuring the intensity of the nitro group absorption of the starting material. A Mattson-Cygnus 100 FT-IR spectrometer was used to obtain the IR spectra. A sodium chloride cell with a path length of 0.1 mm was used. Compound 7 has its nitro group absorption at 1524 cm^{-1} and compound 8 at 1529 cm^{-1}. Standard calibration curves of intensity of absorption as a function of concentration were established. The experiments were conducted under three different conditions, under illumination, in the dark and in the dark in the presence of inhibitor.

Proton NMR spectra were recorded on a VXR-200 NMR spectrometer. All ^1H chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard. Coupling

QUALITATIVE KINETIC DATA




p-O2NC6H4C(O)C6H5 + C6H5O⁻Na⁺
moles
0.20
0.15
0.10
0.05
0
0
1
2
3
4
Time (hrs.)
△ Light
□ Dark
▽ Gal 10m%


p-O2N-C6H4-C(O)-C6H5 + C6H5S⁻Na⁺ 2 : 1
Moles
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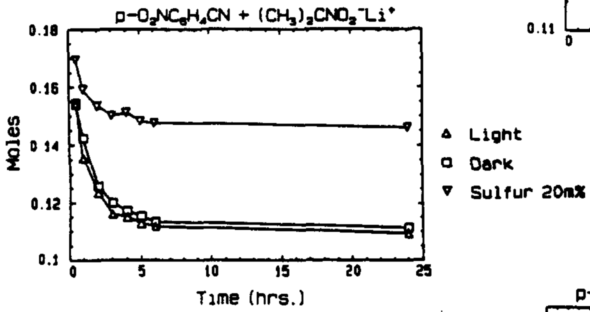
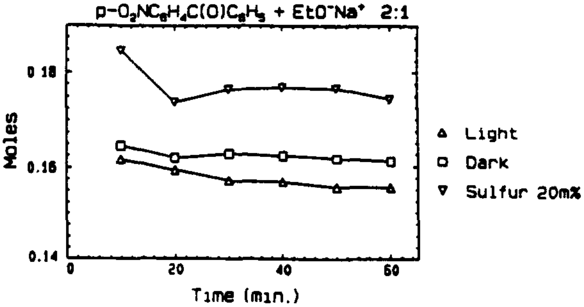
0.14
0.13
0.12
0.11
0
25
50
Time (min.)
△ Light
□ Dark
▽ Sulfur 20m%


p-O2NC6H4CN + (CH3)2CNO2⁻Li⁺
Moles
0.18
0.16
0.14
0.12
0.1
0
5
10
15
20
25
Time (hrs.)
△ Light
□ Dark
▽ Sulfur 20m%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Moles
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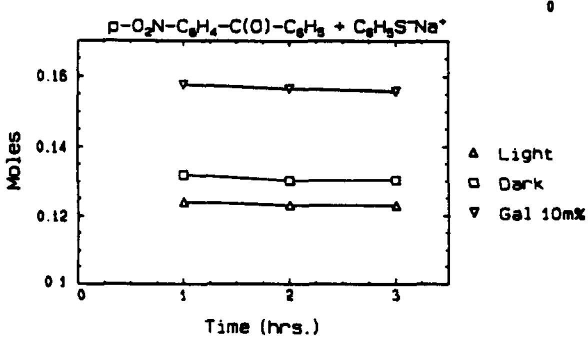
0.16
0.14
0
20
40
60
Time (min.)
△ Light
□ Dark
▽ Sulfur 20m%


p-O2N-C6H4-C(O)-C6H5 + C6H5S⁻Na⁺
Moles
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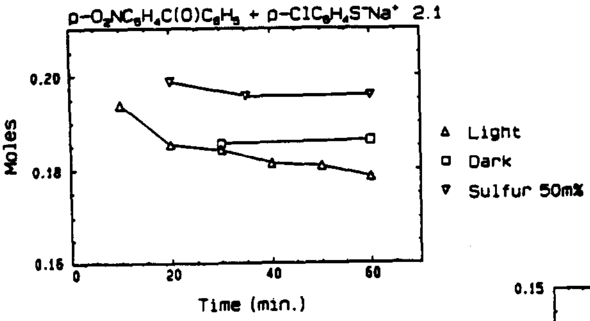
0.14
0.12
0.1
0
1
2
3
Time (hrs.)
△ Light
□ Dark
▽ Gal 10m%


p-O$_2$NC$_6$H$_4$C(O)C$_6$H$_5$ + p-ClC$_6$H$_4$S$^-$Na$^+$ 2.1
Moles
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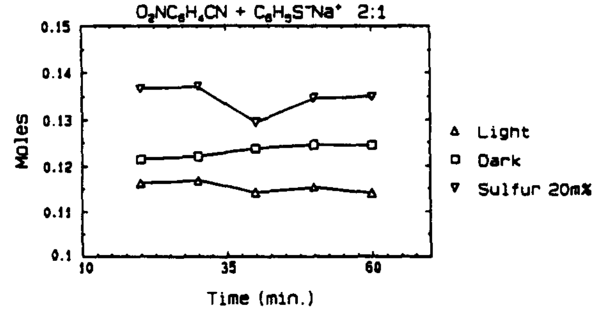
0.16
0
20
40
60
Time (min.)
△ Light
□ Dark
▽ Sulfur 50m%


O$_2$NC$_6$H$_4$CN + C$_6$H$_5$S$^-$Na$^+$ 2:1
Moles
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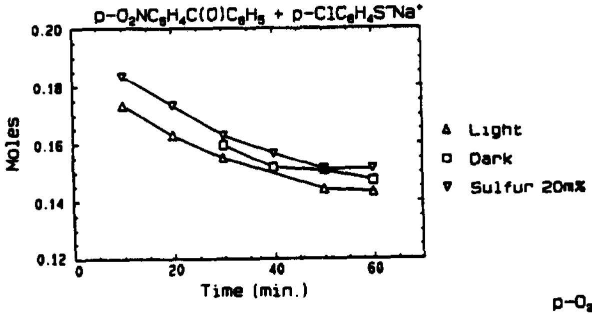
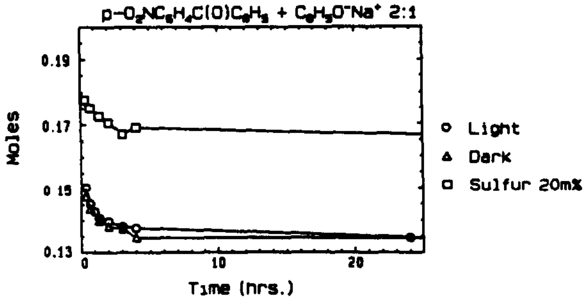
0.13
0.12
0.11
0.1
10
35
60
Time (min.)
△ Light
□ Dark
▽ Sulfur 20m%


p-O$_2$NC$_6$H$_4$C(O)C$_6$H$_5$ + p-ClC$_6$H$_4$S$^-$Na$^+$
Moles
0.20
0.18
0.16
0.14
0.12
0
20
40
60
Time (min.)
△ Light
□ Dark
▽ Sulfur 20m%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Moles
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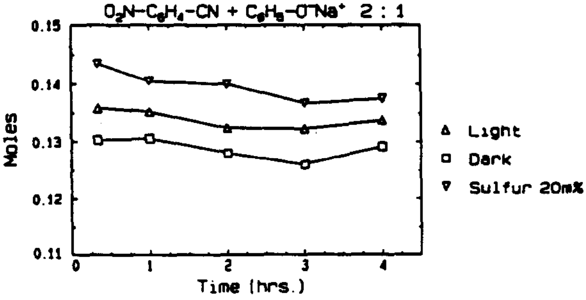
0.15
0.13
0
10
20
Time (hrs.)
○ Light
△ Dark
□ Sulfur 20m%


O$_2$N-C$_6$H$_4$-CN + C$_6$H$_5$-O$^-$Na$^+$ 2 : 1
Moles
0.15
0.14
0.13
0.12
0.11
0
1
2
3
4
Time (hrs.)
△ Light
□ Dark
▽ Sulfur 20m%

constants are reported in Herz. The multiplicity of a signal is indicated using the following abbreviations: singlet, s; broad singlet, br.s.; doublet, d; triplet, t; quartet, q; multiplet, m. Carbon NMR spectra were obtained on a Varian VXR-200 NMR spectrometer. Chemical shift values are reported in parts per million relative to tetramethylsilane. The spectra were obtained with full proton decoupling. Analysis by the Robertson Laboratory, Madison NJ.

Preparation of 9. The procedure of Kornblum, Boyd and Ono[20] was followed. The product was obtained as a free flowing white solid in 91% yield.

Preparation of 13. The procedure of Kornblum, Boyd and Ono[20] was followed. The sodium salt of p-chlorothiophenol was obtained as a white powder in 96% yield.

Preparation of 12. A procedure similar to that of the preparation of 13 was followed. The product was formed in 98% yield.

Preparation of 4-Benzoyl-α-nitrocumene[11]. To a solution of 4-nitrobenzophenone, 0.227 g (0.001 mol) in 5 ml of HMPA was added 9, 0.475 g (0.005 mol). The reaction mixture was stirred for 24.5 h at room temperature. It was then poured into 100 ml of ice water. The resulting mixture was extracted 3 times with 50 ml portions of ethyl acetate. The combined extracts were washed with water, dried over magnesium sulfate, and then concentrated under vacuum. The resulting yellow oil was chromatographed on silica gel to give 0.98 g, 36% of a white solid, m.p. 72-74° (lit.[11] 69.5-70.5°). The ^{1}H NMR spectrum in $CDCl_3$ had absorptions at δ 2.1(s, 6H) and δ 7.5-7.9 (m, 9H). The IR spectrum in HMPA had a strong nitro group absorption at 1543 cm^{-1} and carbonyl absorption at 1661 cm^{-1}.

Preparation of 4-Ethoxybenzophenone. 4-Nitrobenzophenone, 0.454 g (0.002 mol) and sodium ethoxide, 0.274 g (0.004 mol) dissolved in 10 ml of HMPA were allowed to react for 59.5 h. The reaction mixture was poured into 200 ml of ice water. The resulting solution was extracted with three 70 ml portions of methylene chloride. The combined organic extracts were evaporated. The residue was dissolved in 100 ml of diethyl ether. The ether solution was washed with 20 ml of cold concentrated hydrochloric acid, 50 ml of a saturated solution of sodium bicarbonate and water. The ether solution was dried over magnesium sulfate and concentrated to give 0.130 g (29%). The product was recrystalized to give the desired compound, m.p.45-47° (lit.[21]47°). The ^{1}H NMR spectrum in $CDCl_3$had resonances at δ 1.50 (t, J=7, 3 H) δ 4.10 (q, J=7, 2H) and a multiplet δ 7.50-7.80 (9 H).

Preparation of 4-Phenoxybenzophenone. 4-Nitrobenzophenone, 0.227 g (0.001 mol) and sodium phenoxide, commercial material, 0.581 g (0.005 mol) were allowed to react in 9 ml of HMPA for 24 h. After isolation 0.252 g (92%) of a white solid was obtained, m.p. 71-72° (lit.[11] 69-70°). The ^{1}H NMR spectrum was a complex multiplet at δ 7.2-7.8.

Preparation of 4-Thiophenoxybenzophenone. 4-Nitrobenzophenone, 0.454 g (0.002mol) and sodium thiophenoxide 1.32 g (0.01 mol) were allowed to react in 10 ml of HMPA for 6 h. The crude product, 57% yield, was recrystallized from hexane, m.p. 68-70° (lit.[22] 71-72°). The ^{1}H NMR spectrum was a complex multiplet δ 7.2-7.8.

Preparation of 4-(4-chloro)-thiophenoxybenzophenone. 4-Nitrobenzophenone, 0.454 g (0.002 mol) and sodium salt of 4-chlorothiophenoxide, 1.67 g (0.01 mol) were allowed to react in 10 ml of HMPA for 18 h. The crude product was recrystallized from ether-hexane, 1:1, to give 0.436 g (71%) of a flaky-pearly solid, m.p. 128-130°. The ^{1}H NMR spectrum was a complex multiplet δ 7.4-7.8. Anal. Calcd for $C_{19}H_{13}ClOS$, C, 70.26; H, 4.03 Found C, 70.45; H, 3.89.

Preparation of 4-Cyano-α-nitrocumene. 4-Nitrobenzonitrile, 0.296 g (0.002 mol) and the lithium salt of 2-nitropropane, 0.38 g (0,004 mol) dissolved in 10 ml of HMPA were allowed to react for 25 h. to give 0.142 g (37%) of product m.p. 57-59° (lit.[20] 59.5-60.5°). The ^{1}H NMR spectrum had resonances at δ 2.0 (s 6H) and δ 7.55 and δ 7.8 (total 4 H).

Preparation of 4-Phenoxybenzonitrile. 4-Nitrobenzonitrile, 0.296 g (0.002 mol) and sodium phenoxide 1.16 g (0.01 mol) in 10 ml of HMPA were allowed to react for 24 h. The yield of product was 0.239 g (61%) m.p. 37-39° (lit.[23] 43-45°). The ^{1}H NMR spectrum showed only aromatic hydrogens. The ^{13}C NMR spectrum, $CDCl_3$ solvent, had the expected nine resonances. Two resonances at δ 161.64 and 154.77 are identified as aromatic carbons bonded to oxygen. The carbon of the nitrile group is found at δ 118.86 and the aromatic carbon bearing the nitrile group is found at δ 105.78. The other resonances were found at δ 134.12, 130.24, 125.16, 120.41 and 117.89.

Preparation of 4-Thiophenoxybenzonitrile. 4-Nitrobenzonitrile, 0.296 g (0.002 mol) and sodium thiophenoxide, 1.322 g (0.01 mol) dissolved in 10 ml of HMPA were allowed to react for 6 h. The yield of a light yellow liquid was 0.235 g (56%). The ^{1}H NMR spectrum showed only aromatic hydrogens. The ^{13}C NMR spectrum in D-6-acetone had nine resonances as expected. The resonance at δ 109.48 is assigned to the carbon bearing the cyano group. The resonance at δ 118.98 is assigned to the cyano group carbon. Two resonances at δ 145.00 and 131.43 are assigned to carbons bonded to sulfur. The remaining resonances are found at δ 128.08, 130.14, 130.75, 133.25 and 135.00.

Preparation of 4-(4-Chlorothiophenoxy)benzonitrile. 4-Nitrobenzonitrile, 0.296 g (0.002 mol) and the sodium salt of 4-chlorothiophenoxide, 1.66g (0.01 mol) were allowed to react in 10 ml of HMPA for 19 h. The yield of product was 0.437 g (89%) m.p. 85-87° (lit.[24] 88°). The ^{1}H NMR spectrum showed only aromatic protons.

Reaction of p-Dinitrobenzene with the Potassium Salt of 2-Nitropropane in the Presence and Absence of 50 mole % Galvinoxyl. Potassium t-butoxide, 0.247 g (0.0022 mol) was dissolved in 10 ml of HMPA. To this solution was added, with stirring, 2-nitropropane, 0.2 g (0.0022 mol) and p-dinitrobenzene, 0.836 g (0.002 mol). The reaction mixture was irradiated for 5 h. It was then poured into water and the solid that formed was separated by filtration and air dried to constant weight to give 0.342 g (81%) of a yellow powder. The ^{1}H NMR spectrum of this material was identical to that of an authentic sample of α,p-dinitrocumene.

A duplicate experiment was carried out in the dark and in the presence of 50 mole % of Galvinoxyl. A dark yellow powder, 0.262 g was recovered. The ratio of p-dinitrobenzene to α,p-dinitrocumene was 72:28 as determined by ^{1}H NMR integration.

Preparation of p-Cyanophenol. A modified procedure of Knudson and Snyder[12] was followed. Sodium hydride, 0.096 g (0.004 mol) was allowed to react with 2 ml of DMSO. To this mixture was added benzaldoxime, 0.484 g (0.0004 mol) in 2 ml of DMSO. The resulting mixture was stirred for 1 h to give a thick paste, To this paste was added p-nitrobenzonitrile, 0.296 g (0.002 mol). The reaction mixture turned to a clear brown liquid. After 24 h. the reaction mixture was poured into ice water and acidified to pH 3 with concentrated hydrochloric acid. The resulting aqueous solution was extracted with diethyl ether The ether solution was extracted with 5% sodium hydroxide solution which was then acidified. The acidified aqueous solution was extracted with ether. The ether extract was dried over magnesium sulfate and concentrated to give 0.114 g (48%) of a yellow solid, m.p. 108-110° (lit.[12] 111-112°). The ^{1}H NMR spectrum showed resonances for aromatic protons only.

Reactions of p-Nitrobenzonitrile with the Sodium Salt of Benzaldoxime. p-Nitrobenzonitrile, 0.296 g (0.002 mol), sodium hydride 0.123 g (0.0051 mol) and benzaldoxime, 0.484 g (0.004 mol) were allowed to react in 10 ml of DMSO under illumination for 19 h. After quenching the reaction mixture, the product, a yellow solid, 0.282 g, was shown by ^{1}H NMR spectroscopy to be a mixture of starting material, 19 % and p-cyanophenol, 81 %.

The experiment was repeated in the dark and in the presence of sulfur, 20 mole percent. A yellow oil, 0.300 g, was obtained. The ^{1}H NMR spectrum indicated starting material, 50 % and p-cyanophenol 50 %.

Reaction of p-Nitrobenzonitrile with the Lithium Salt of 2-Nitropropane. p-Nitrobenzonitrile, 0.444 g (0.003 mol) and the lithium salt of 2-nitropropane, 0.570 g (0.006 mol) in 10 ml of HMPA were irradiated for 6 h. The reaction mixture was poured onto ice and the product, 0.270 g, was isolated by filtration. The ^{1}H NMR spectrum showed it to be pure p-cyano-α-nitrocumene.

The reaction was repeated in the dark and in the presence of 50 mole percent of sulfur. The product, 0.290 g, was shown to be 46 % of starting material and 54 % of p-cyano-α-nitrocumene by ^{1}H NMR spectroscopy

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