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# Acid-Promoted Nucleophilic Aromatic Substitution in Deoxygenation of Nitro and Nitroso Compounds<sup>1</sup>

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The products of deoxygenation of aryl nitro and nitroso compounds with triethyl phosphite in aprotic media can usually be rationalized in terms of aryl nitrene intermediates.<sup>2-5</sup> We found and reported<sup>1</sup> that the presence of acetic acid led to the formation of products which appeared to arise from nucleophilic atomatic substitution processes. Subsequent studies of deoxygenation reactions in alcohols have further elucidated the nature of nucleophilic aromatic substitution processes which accompany deoxygenation of nitrosobenzene.<sup>6</sup> These reactions have been formulated in terms of an intermediate zwitterion A. Recent studies



of other aspects of deoxygenation reactions have also been interpreted in terms of such a nitrenoid intermediate.<sup>7-9</sup>

Yield data were reported<sup>10</sup> in the earlier communication for deoxygenation of nitrobenzene (1a), o-nitrotoluene (1b), p-nitrotoluene (1c), 2,4-dimethylnitrobenzene (1d), nitrosobenzene (2a), o-nitrosotoluene (2b), and p-nitrosotoluene (2c) in solutions containing about 5% by volume acetic acid. We report here the experimental details of the original study and spectral data. Although apparently general in scope, the reaction is characterized by low yields and, because of the difficulties in rapid separation of products, is not conducive to detailed mechanistic study.

The photochemical deoxygenation of nitrobenzene in excess pure triethyl phosphite gives only a trace of triethyl N-phenylphosphorimidate.<sup>2</sup> The deoxygenation of nitrosobenzene in excess triethyl phosphite similarly gives no characterizable aromatic product.<sup>4</sup> Polymeric material, presumably derived from phenylnitrene, is formed in both reactions. The presence of acetic acid (5% by volume) in the reaction medium led to the formation of diethyl oaminophenylphosphonate (4), diethyl p-aminophenylphosphonate (5), aniline (6), and *o*-hydroxyacetanilide (3). The latter two compounds were identified by spectral comparison with authentic samples. The structures assigned to 4 and 5 were based on the following data. The composition was deduced from elemental analysis. The solubility of the compounds in aqueous acid and the infrared spectra indicated the presence of primary amine groups in each molecule. The proton nmr, and in particular the P-H coupling pattern,<sup>11</sup> permitted the assignment of the substituent group positions. The nmr signal positions and multiplicity are given in the Experimental Section. The structural assignment of 5 was confirmed by synthesis from *p*-nitrophenylphosphonic acid by esterification and reduction.<sup>12</sup> In 4 a broad singlet assigned to the NH<sub>2</sub> group is present at  $\delta$  5.45. A similar signal is observed for the NH<sub>2</sub> group in each of the *o*-aminophenylphosphonates examined in this study and this signal was used to supplement aromatic C-H signals in structural assignments. Hydrogen bonding to the phosphoryl oxygen is probably responsible for the deshielding.

The rapid exothermic reactions of nitroso aromatics with triethyl phosphite<sup>3,4</sup> usually closely parallel the photochemical deoxygenation of nitro aromatics under similar conditions and it has been suggested that the photochemical deoxygenation proceeds through nitroso intermediates.<sup>2</sup> This general similarity was also true for the present TEP-acetic acid reaction system. Deoxygenation of nitrosobenzene gave 4 (3%), 5 (6%), and 3 (11%) as well as diethyl N-phenylphosphoramidate (7, 3%).

Analogous types of products were obtained for the substituted systems 1b-d and 2b-c. The individual reaction products are identified in the Experimental Section and the spectral data which served for structural assignment are also given there. These data permitted straightforward structural assignment, with the exception of 14 and 15, the two isomeric diethyl aminoarylphosphonates from 1d. One of these was identified as the ortho substitution product, diethyl 2-amino-3,5-dimethylphenylphosphonate (14), on the basis of the nmr spectrum. The amino signal is at  $\delta$ 5.2 in the region indicative of an ortho disposition of the amino and diethoxyphosphono substituents. The aromatic signals consist of a singlet at  $\delta$  6.88 partially overlapping a doublet,  $J_{\rm P-H} \simeq 14$  Hz, centered at  $\delta$  7.0. Neither of the methyl groups shows the fine coupling which characterizes methyl groups ortho to a diethyl phosphono group. The second phosphonate must be diethyl 4-amino-2,5-dimethylphenylphosphonate (15). The two aromatic protons do not reveal any mutual splitting. Each shows what must be a PH coupling: a signal at  $\delta$  6.90 ( $J_{\text{H-P}}$  = 6 Hz) and at  $\delta$ 7.23 ( $J_{\rm H-P}$  = 15 Hz). One of the methyl groups reveals a small (~1 Hz) splitting. The amino signal is at  $\delta$  3.7. The magnitude of the P-H splitting of the aromatic proton signals places the diethyl phosphono substituent ortho to one hydrogen and meta to the other. The upfield aromatic signal reveals the meta P-H coupling favoring the assigned structure over the other possible isomer, diethyl 5amino-2,4-dimethylphenylphosphonate. Formation of 15 would involve methyl migration in the aromatization step following nucleophilic attack by triethyl phosphite at the 4 position, rather than introduction of the phosphono group at the meta position as indicated originally.<sup>1</sup>

Nitrosobenzene and o- and p-nitrosotoluene were also deoxygenated in a reaction solution consisting of a 1:1 mixture of TEP-acetic anhydride and which also contained benzene and small amounts of acetic acid. Nucleophilic aromatic substitution was again observed but the principal products were o-acetoxyacetanilides. Thus nitrosobenzene gave 2-acetoxyacetanilide (16, 6%). p-Nitrosotoluene gave 2-acetoxy-4-methylacetanilide (17, 46%) and o-nitrosotoluene gave 2-acetoxy-6-methylacetanilide (18, 16%). These products were identified by hydrolysis to known hydroxyacetanilides as described in the Experimental Section. The possible involvement of an O,N-diacetylphenylhydroxylamine intermediate was investigated, but O,N-diacetyl-4-methylphenylhydroxylamine was shown to be stable to the conditions of the deoxygenation reaction, thus excluding it from further consideration as an intermediate.

The salient result of the present investigation is the formation of diethyl aminophenylphosphonates and o-hydroxyacetanilides from nitro and nitroso aromatics in the presence of acetic acid. The structures of these products clearly indicate the incursion of aromatic nucleophilic substitution processes when acetic acid is present. Diethyl aminophenylphosphonates have not been reported in previous studies of deoxygenation reactions of nitro or nitroso aromatics<sup>2-5</sup> and we have reexamined the deoxygenation of nitrosobenzene and found that diethyl aminophenylphosphonates are not formed in the absence of acetic acid. Unfortunately, the complexity of the reaction mixture and the attendant difficulty in obtaining precise product yields or mass balance detract from the significance of detailed mechanistic discussion. Although a nitrene might be formed and subsequently protonated, it is perhaps more likely, in view of the results in alcoholic solution,<sup>6</sup> that the deoxygenation intermediate A is diverted by protonation prior to nitrene formation. This comparison is clouded, however, by the possible involvement of strong solvent effects.

#### Experimental Section<sup>13</sup>

General Procedure for Photochemical Deoxygenation. A solution containing 0.100 mol of the nitro aromatic in triethyl phosphite (190 ml) containing acetic acid (10 ml) was irradiated for 15 hr using a 200-W Type S Hanovia lamp in a water-cooled immersion well under a nitrogen atmosphere. A Pyrex filter was used. Under these conditions the reaction solution temperature remained below 30°. The reaction mixture was then diluted with ether and washed thoroughly with sodium bicarbonate solution. The ether was dried and evaporated and subjected to vacuum distillation below 100° to remove triethyl phosphite, triethyl phosphate, and unreacted nitro aromatic. The composition of the triethyl phosphate-nitro aromatic fraction was estimated by nmr to determine the amount of unreacted nitro compound. The residue was dissolved in ether and partitioned into neutral and acidsoluble fractions by extraction with dilute hydrochloric acid. These mixtures were chromatographed on silicic acid using benzene-ether. Yields quoted are calculated on the basis of the amount of nitro aromatic which reacted.

General Procedure for Deoxygenation of Nitroso Compounds. A solution of the nitroso compound (5.0 g) in 50 ml of benzene was added slowly to a solution of triethyl phosphite (95 ml) and acetic acid (5 ml) maintained at 0°. A nitrogen atmosphere was maintained. Unreacted triethyl phosphite and acetic acid were removed by distillation at 25° (0.1 mm). Triethyl phosphate was distilled at 40-50° (0.1 mm) with gentle heating. The residue was separated into neutral and acid-soluble fractions by extraction with dilute hydrochloric acid and chromatographed as described for the products of the photochemical reaction.

Nitrobenzene (1a). Recovered 1a accounted for 21% of the starting material. Aniline (4%) was eluted first followed by diethyl o-aminophenylphosphonate<sup>14</sup> (4, 8%) as an oil purified by distillation: nmr (CCl<sub>4</sub>)  $\delta$  7.0-7.5 (m, 2), 6.4-6.8 (m, 2), 5.45 (broad s, 2), 4.03 (quintet, 4), 1.30 (t, 6). The other major product was diethyl p-aminophenylphosphonate (5, 8%): mp 126-127° (lit.<sup>12</sup> mp 115-119°) after recrystallization from benzene-hexane; nmr (CCl<sub>4</sub>)  $\delta$  7.60 (d of d,  $J_{\rm H-H}$  = 8,  $J_{\rm H-P}$  = 13 Hz, 2), 6.70 (d of d,  $J_{\rm H-H}$  = 8,  $J_{\rm H-P}$  = 4 Hz, 2), 4.08 (quintet overlapping broad signal, 6) 1.30 (t, 6).

From the neutral fraction there was obtained crystalline 2-hydroxyacetanilide (3, 6%), identified by spectral comparison with an authentic sample.

Nitrosobenzene (2a). Chromatography of the basic products gave 4 (3%) eluted with 3:1 benzene-ether and 5 (6%), eluted with 1:1 benzene-ether. Chromatography of the neutral fraction on silicic acid gave 2-hydroxyacetanilide (3, 11%) and diethyl N-phenylphosphoramidate (7, 3%). All products were identified by

spectral comparison (infrared and/or nmr) with samples from the photochemical deoxygenation or authentic samples.

Synthesis of 5. Reaction of 4-nitrophenylphosphonic<sup>15</sup> acid with ethanol in the presence of cyclohexylcarbodiimide<sup>16</sup> gave diethyl 4-nitrophenylphosphonate<sup>12</sup> having expected spectral features. Reduction in ethanol with Pd/C catalyst gave  $5,1^2$  having infrared and nmr spectra identical with those of the product from the deoxygenation reactions.

**p-Nitrotoluene (1b).** Recovery of unreacted 1b was 26%. The basic product gave p-toluidine (10%) and diethyl 2-amino-5-methylphenylphosphonate (8, 11%), which was purified by distillation: nmr (CCl<sub>4</sub>)  $\delta$  6.9–7.3 (m, 2), 6.60 (d of d,  $J_{H-H} = 8$ ,  $J_{P-H} = 6$  Hz, 1), 5.38 (s, 2) 4.03 (quintet, 4), 2.19 (s, 3), 1.28 (t, 6). The neutral fraction gave 2-hydroxy-4-methylacetanilide (9, 27%) and diethyl N-(p-tolyl)phosphoramidate (10, 2%), both of which were identified by spectral comparison with authentic samples. The authentic sample of 9 was prepared from 3-methyl-6-nitrophenol by the procedure of Proskouriakoff and Titherington.<sup>17</sup>

**p-Nitrosotoluene (2b).** Benzene-ether (3:1) eluted a trace of p-toluidine. The major basic product 8 (9%) was eluted by 1:1 ether-benzene and identified by comparison with 8 from the photochemical deoxygenation of p-nitrotoluene. A third fraction contained what appeared to be a second aminophenylphosphonate, but conclusive identification of this compound was not accomplished. The neutral product was chromatographed on silicic acid. Benzene-ether (4:1) eluted 9 (23%) and 10 (3%), both of which were identified by spectral comparison with the samples from the photochemical deoxygenation.

o-Nitrotoluene (1c). Unreacted 1c accounted for 33% of the starting material. Chromatography of the acid-soluble material gave o-toluidine (2%) followed by diethyl 2-amino-3-methylphen-ylphosphonate (11, 2%) purified by bulb-to-bulb distillation: nmr (CCl<sub>4</sub>)  $\delta$  7.0-7.4 (overlapping doublet and doublet of doublets, 7.05 d,  $J_{\rm H-H}$  = 8 Hz, 7.0-7.4, d of d,  $J_{\rm H-H}$  = 8,  $J_{\rm P-H}$  = 14 Hz, 2), 6.5 (six-line m,  $J_{\rm H-H}$  = 8,  $J_{\rm H-H}$  = 8,  $J_{\rm P-H}$  = 4 Hz, 1), 5.37 (br s, 2), 4.0 (quintet, 4), 2.10 (s, 3), 1.28 (t, 6). There was also eluted diethyl 4-amino-3-methylphenylphosphonate (12, 10%): mp 81-83° after recrystallization from ether-hexane; nmr (CCl<sub>4</sub>)  $\delta$  7.1-7.7 (d at 7.50,  $J_{\rm P-H}$  = 13 Hz, overlapping m, 2), 6.72 (d of d,  $J_{\rm H-H} \simeq$  8,  $J_{\rm H-P}$  = 4 Hz, 1), 4.45 (s, 2), 4.08 (quintet, 4), 2.12 (s, 3), 1.30 (t, 6).

From the neutral fraction diethyl N-o-tolylphosphoramidate (7%) was isolated and identified by spectral comparison with authentic material.

o-Nitrosotoluene (2c). Chromatographic separation of the basic product gave o-toluidine (1%), diethyl 2-amino-3-methylphenylphosphonate (2%), and diethyl 4-amino-3-methylphenylphosphonate (9%). The only product isolated from the neutral fraction was diethyl N-(2-methylphenyl)phosphoramidate (12%). In each case identification was made by spectral comparison with the products from the photochemical reaction.

2,4-Dimethylnitrobenzene (1d). The recovery of 1d was 13%. The neutral fraction gave 2,4-dimethyl-6-hydroxyacetanilide (16, 14%) as crystalline solid, mp 184-185° (lit.<sup>18</sup> mp 186-187°). Chromatography of the remaining neutral fraction gave diethyl N-(2,4-dimethylphenyl)phosphoramidate (17, 9%). Separation of the basic fraction by chromatography gave 14 (6%) as an oil purified by bulb-to-bulb distillation: nmr (CCl<sub>4</sub>)  $\delta$  6.8-7.0 (d,  $J_{\rm H-P} \simeq 14$  Hz, overlapping singlet at 6.88, 2), 5.2 (br s, 2), 4.0 (quintet, 4), 2.19 (s, 3), 2.09 (s, 3), and 1.30 (t, 6). A second aminophosphonate fraction gave 15: mp 98-99° from benzene-hexane; nmr  $\delta$  7.23 (d,  $J_{\rm H-P} = 15$  Hz), 6.90 (d,  $J_{\rm H-P} \simeq 2$  Hz, 3), 2.13 (s, 3), 1.29 (t, 6).

Deoxygenation of Nitrosobenzene in the Presence of Acetic Anhydride. A solution containing 0.5 mmol of 2a in benzene (50 ml) was slowly added at 0° to 300 ml of 1:1 TEP-acetic anhydride. Attempts to completely remove acetic acid from commercial acetic anhydride were not successful and the acetic anhydride used contained 1-2% acetic acid on the basis of nmr. When the addition was complete, the benzene was removed using a rotary evaporator and TEP and acetic anhydride were removed at  $\sim 0.1$  mm. The residue was chromatographed on silicic acid. Benzene-ether eluted 2-acetoxyacetanilide (18, 6%), mp 123-124° (lit.<sup>19</sup> mp 124.5-125°).

Ether eluted a substance which was probably diethyl 2-acetamidophenylphosphonate (19, 3%): mp 139-140° after recrystallization from benzene; nmr  $\delta$  7.6-8.0 (m, 4), 4.12 (quintet, 4), 2.22 (s, 3), 1.34 (t, 6).

Identification of 18 was confirmed by brief hydrolysis with 10% NaOH in 1:1 methanol-water to 2-hydroxacetanilide (3). Tlc

comparison with authentic 4-acetoxyacetanilide indicated that no detectable amount of this compound was formed in the reaction.

Deoxygenation of p-Nitrosotoluene in the Presence of Acetic Anhydride. The reaction was carried out as described for nitrosobenzene. 2-Acetoxy-4-methylacetanilide (20, 46%) crystallized from the crude product, mp 154-155° (lit.<sup>20</sup> mp 153-154°), and was identified by spectral data and hydrolysis to 2-hydroxy-4methylacetanilide which was identical with an authentic sample.17 A small amount (2%) of 4-methylacetanilide was isolated from the mother liquors.

Deoxygenation of o-Nitrosotoluene in the Presence of Acetic Anhydride. The reaction was carried out as for nitrosobenzene. Trituration of the crude product with hot hexane gave 2-acetoxy-6-methylacetanilide (21, 16%), mp 142-143° (lit.<sup>21</sup> mp 141-143°),22 after recrystallization from ether-hexane. The identification was accomplished by partial hydrolysis to 2-hydroxy-6methylacetanilide, mp 161-162° (lit.17 mp 160-161°), and complete hydrolysis by 2-hr reflux with 15% aqueous sodium hydroxide to 2-hydroxy-6-methylaniline, mp 149–150.5° (lit.<sup>24</sup> mp 150°).

O,N-Diacetyl-4-methylphenylhydroxylamine (22). 4-Methylphenylhydroxylamine<sup>25</sup> (2.0 g, 16 mmol) was dissolved in ether (20 ml) containing pyridine (2 ml) and treated with a solution of acetyl chloride (2.6 g, 32 mmol) in ether (10 ml) at 0°. The solution was washed with water, dried over sodium sulfate, and evaporated to give the product as an oil purified by distillation at diffusion pump vacuum: ir (neat) 1800, 1690 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$ 7.2-7.6 (m, 4), 2.40 (s, 3), 2.20 (s, 3), 2.05 (s, 3).

Stability of O, N-Diacetyl-4-methylphenylhydroxylamine under Deoxygenation Conditions. A solution of 22 (0.30 g, 1.45 mmol), TEP (15 ml), acetic anhydride (15 ml), and benzene (6 ml) was stirred at 0° under nitrogen for 2 hr. The benzene was removed at reduced pressure and TEP and acetic anhydride were removed at 0.1 mm. Chromatography of the residue gave 97% recovery of 22.

Registry No. 1a, 98-95-3; 1b, 99-99-0; 1c, 88-72-2; 1d, 89-87-2; 2a, 586-96-9; 2b, 623-11-0; 2c, 611-23-4; 4, 31238-50-3; 5, 42822-57-1; 8, 42822-58-2; 11, 42822-59-3; 12, 42822-60-6; 14, 42822-61-7; 15, 42822-62-8; 16, 42822-63-9; 19, 42822-64-0; 22, 27451-20-3; 4-methylphenylhydroxylamine, 623-10-9.

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## A General Synthesis of 1,3-Dithiol-2-ones

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Although specific preparations of 1,3-dithiol-2-one<sup>1</sup> (vinvlene dithiocarbonate) and of several substituted analogs<sup>2</sup> have been described, a general synthesis of compounds in this series has never been reported.<sup>3</sup>

In the course of another investigation an attempt was made to prepare ketothiol  $1^4$  by heating a solution (CCl<sub>4</sub>) of O-isopropyl S-phenacyl dithiocarbonate (2a) in contact with 70% perchloric acid. Upon neutralization and workup of the reaction mixture, a fair yield of 4-phenyl-1,3-dithiol-2-one (3a) was obtained. Further investigation of this reaction led to a general preparation of 1,3-dithiol-2ones 3a-f and 5a-d from the readily accessible  $\beta$ -keto Oisopropyl dithiocarbonates 2a-f and  $4a-d.^5$ 



The 1,3-dithiol-2-ones described herein should also serve as useful precursors of the corresponding 2-hydroxy-1,3-dithiolium cations, which are of some theoretical interest.3,6

## Experimental Section<sup>7</sup>

O-Isopropyl S-Phenacyl Dithiocarbonate (2a). Potassium O-isopropyl xanthate<sup>8</sup> (11.3 g) was treated in small quantities during 10 min with a solution of  $\alpha$ -bromoacetophenone (12.0 g) in acetone (140 ml). The solvent was removed in vacuo. Water was added to the solid residue and the resulting suspension was acidified with dilute HCl and extracted with diethyl ether. The combined extracts were washed with water followed by brine and dried (MgSO<sub>4</sub>). The solvent was removed in vacuo, yielding 14.9 g of crude **2a:** mp 65-67°; purity (pmr assay) *ca.* 90%; pmr (CDCl<sub>3</sub>) 1.33 (d, 6, *J* = 6.5 Hz), 4.60 (s, 2), 5.70 (h, 1, *J* = 6.5 Hz), 7.27-7.63 (m, 3), and 7.88-8.08 (m, 2); ir (CCl<sub>4</sub>) 1690, 1240, 1090, 1053, and 686 cm<sup>-1</sup>. Recrystallization from diethyl ether afforded 12.7 g (83%) of pure 2a, mp 68-69°. An analytical sample exhibited mp 68-69°. Anal. Calcd for C12H14O2S2: C, 56.66; H, 5.55. Found: C, 56.72; H, 5.46. O-Isopropyl S-(p-Phenylphenacyl) Dithiocarbonate (2b).

Potassium  $\overline{O}$ -isopropyl xanthate (3.0 g) was treated (10 min) in small quantities with a solution of  $\alpha$ -bromo(p-phenyl)acetophenone (4.0 g) in acetone (40 ml). Work-up as described for 2a yielded 5.0 g of crude product. Recrystallization from diethyl