$C(CH_3)_3]$; 3.45 (broad s, ∼2 H, NH_2), 6.67 (d, $J = 9$ Hz, 2 H), 6.93 (d, $J = 9$ Hz, 2 H); mass spectrum (relative intensity) 165 (6), 109 (100); acetyl derivative mp 131–132° (lit.[23] mp 130°). Treatment of the acetyl derivative with hydrochloric acid gave 4-hydroxyacetanilide, mp 164–165° (lit.[24] mp 166°), which was identified by spectral comparison with an authentic sample.

Deoxygenation of *p*-Nitrosotoluene in Methanol.—A solution of TEP (10.0 ml) in methanol (600 ml) was stirred at room temperature and a solution of *p*-nitrosotoluene (2.0 g, 16.5 mmol) was added dropwise over 3 hr. The solution was then stirred at room temperature for 1 hr followed by addition of water (50 ml). The resulting solution was concentrated at room temperature to about 100 ml with a rotary evaporator. The residue was diluted with water (500 ml) and thoroughly extracted with hexane. Evaporation of the hexane gave a mixture containing 0.3 g (17%) of 2-methoxy-4-methylaniline (**13**) by nmr analysis. A sample purified by glpc using an Apiezon-KOH column gave a pure sample: nmr (CCl_4) δ 2.15 (s, 3 H), 3.45 (broad, 2 H), 3.80 (s, 3 H), and 6.52 (s, 3 H). An acetyl derivative was prepared, mp 127–129° (lit.[25] mp 131°). The water solution remaining after hexane extraction was extracted with ether. Evaporation of the dried ether extract gave a mixture of triethyl phosphate and 4-methoxy-4-methyl-2,5-cyclohexadienone (**14**) containing 0.5 g of **14** (23%) by nmr analysis. Crystallization from hexane gave pure **14**: mp 61–63° (lit.[26] mp 62–63°); nmr (CCl_4) 1.48 (s, 3 H), 3.27 (s, 3 H), 6.35 (d, 2 H), and 6.85 (d, 2 H).

Deoxygenation of Nitrosobenzene in Methanol–Diethylamine Mixtures.—A solution of nitrosobenzene (0.45 g, 4.2 mmol) in benzene (20 ml) was added dropwise over a period of 1 hr to a cooled (0°) solution of TEP (2.1 ml, 12 mmol) in the methanol–diethylamine mixtures indicated in Figure 2. After the reaction was complete, the solvent was removed on a rotary evaporator and the residue was analyzed for *o*-anisidine, *p*-anisidine, and 2-diethylamino-3*H*-azepine by glpc. The glpc analysis indicated the presence of a fourth volatile product which was isolated by preparative glpc using a 5-ft 5% SE-30 on Chromosorb G column. Spectral data indicated this to be 1,1-diethyl-2-phenylhydrazine and the identification was confirmed by comparison with an authentic sample prepared by the procedure of Fratzl and Berger.[6] The hydrazine was not detected at concentrations below 5 mol % diethylamine. The maximum yield observed was 8% at 40 mol % diethylamine.

Deoxygenation of Nitrosobenzene in Ethanol–Diethylamine Mixtures.—The reaction procedure was identical with that described for methanol–diethylamine mixtures. Results of glpc analysis for *p*-phenetidine and 2-diethylamino-3*H*-azepine are shown in Figure 3. Traces of 1,1-diethyl-2-phenylhydrazine were detected by tlc.

Deoxygenation of Nitrosobenzene in Ethanol Containing Sodium Ethoxide.—A solution of nitrosobenzene (0.225 g, 2.1 mmol) in benzene (10 ml) was added slowly to ethanol (67 ml) containing sodium ethoxide (11.7 mmol, prepared by dissolution of 0.27 g of sodium) and TEP (1.0 ml). No *p*-phenetidine was detected by glpc using the standard conditions of analysis.

Photolysis of Phenyl Azide in Methanol, Ethanol, Methanol–Acetic Acid, and Ethanol–Acetic Acid.—A solution of phenyl azide (1.0 g, 8.4 mmol) was irradiated using a 200-W Hanovia mercury lamp (filtered through Pyrex) for 9 hr in 180 ml of the appropriate solvent. More than 90% of the azide decomposed in each run. The solvents were removed using a rotary evaporator and the residue was analyzed by glpc. The results for the four solvent systems are described individually below.

A. Methanol.—No *o*-anisidine or *p*-anisidine was detected. 2-methoxy-3*H*-azepine[27] was formed in 11% yield and identified by spectra data.

B. 9:1 (v/v) Methanol–Acetic Acid.—No *o*-anisidine or *p*-anisidine was detected. A 9% yield of 2-methoxy-3*H*-azepine was indicated by glpc.

C. Ethanol.—No *o*-phenetidine or *p*-phenetidine was detected. A volatile product, tentatively identified as 2-ethoxy-3*H*-azepine, on the basis of spectral data was detected, but the yield was not determined.

D. 9:1 (v/v) Ethanol–Acetic Acid.—No *o*- or *p*-phenetidine was detected. Qualitative glpc indicated that 2-ethoxy-3*H*-azepine had been formed, but the yield was not determined.

Registry No.—**1**, 586-96-9; triethyl phosphite, 122-52-1; **9a**, 67-56-1; **9b**, 64-17-5; **9c**, 109-86-4; **9d**, 67-63-0; **9e**, 75-65-0; **12**, 623-11-0.

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Structure–Reactivity Studies of Deoxygenation Reactions

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The rates of deoxygenation by triethyl phosphite in methanol have been measured for nitrosobenzene, six monosubstituted derivatives, and 2-nitrosomesitylene. The rate of deoxygenation is enhanced by electron-withdrawing substituents and correlated best ($\rho = 1.83$, $r = 0.994$) in the Hammett equation using σ^+ substituent constants. Nitrosomesitylene is slightly more reactive than nitrosobenzene and the lack of a steric hindrance to deoxygenation points to nucleophilic attack by phosphorus at oxygen. Rates of deoxygenation of nitrobenzene and eight derivatives are reported. The rate of deoxygenation is enhanced by electron-withdrawing substituents. The question of isolation of triethyl *N*-arylphosphorimidates from thermal deoxygenation reactions is considered in light of these rate data.

The deoxygenation of aromatic nitroso and nitro compounds by trivalent derivatives of phosphorus has attained important synthetic potential for the preparation of a variety of benzoazoles,[1] trialkyl *N*-arylphosphorimidates,[2] dialkyl *N*-arylphosphoramidates,[3] nucleophilic aromatic substitution products,[4] and several types of rearranged heterocyclic nitrogen system.[2,3] During the course of the investigations which have explored the synthetic scope of the deoxygenation reaction, there have been relatively few rate studies which could provide data for more detailed mechanistic discussion of the deoxygenation reaction. Cadogan has reported a comparison of the reactivity of *o*-nitrobiphenyl with its 4-bromo and 4′-methyl derivatives.[5] Half-

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[1] J. I. G. Cadogan, *Quart. Rev., Chem. Soc.*, **22**, 222 (1968); *Synthesis*, **1**, 11 (1969).

[2] (a) R. J. Sundberg, *J. Org. Chem.*, **30**, 3604 (1965); (b) R. J. Sundberg, *J. Amer. Chem. Soc.*, **88**, 3781 (1966); (c) R. J. Sundberg, B. P. Das, and R. H. Smith, Jr., *ibid.*, **91**, 658 (1969).

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lives of 50, 17, and 50 min, respectively, at 145.5° in triethyl phosphite (TEP) were reported. Cadogan and Cooper[6] have also reported a study of the rate of deoxygenation of *o*-nitrosobiphenyl by TEP in triethyl phosphate. Rate data in the temperature range 278–332°K led to values for E_a of 11.56 kcal mol^{-1} and $\Delta S^{\ddagger}$ of −29 eu at 298°K.

In the present work we have studied the rate of deoxygenation of eight substituted nitrosobenzenes by TEP in methanol and of nine aromatic nitro compounds in excess TEP. This study has provided the first quantitative data on the sensitivity of the deoxygenation reaction to ring substitution.

Results

The aromatic nitroso compounds reported in Table I were deoxygenated in methanol with sufficient excess of TEP to provide pseudo-first-order kinetics. The rates of disappearance of the nitroso compounds were followed by the decrease in absorbance at the absorbance maximum of the nitroso compound in the range 283–342 nm. The rate constants were evaluated from the absorbance data by the Guggenheim method.[7] A first-order dependence of [TEP] was established for nitrosobenzene and *p*-nitrosotoluene. The derived rate constants and relative reactivity of the compounds studied are shown in Table I.

TABLE I
RATES OF DEOXYGENATION IN METHANOL

R	Registry no.[a]	Max (nm)	$k\psi$ sec^{-1} [b] × 10^4	k_2 sec^{-1} mol^{-1} l. × 10^2	Relative rate
p-OCH$_3$	1516-21-8	345	0.33	0.868	0.057
p-CH$_3$	623-11-0	315	1.80	4.74	0.31
m-CH$_3$	620-26-8	286	3.83	10.1	0.67
H	586-96-9	283	5.75	15.1	1.00
m-CO$_2$CH$_3$	26960-97-4	283	36.3	95.6	6.3
m-Cl	932-78-5	282	37.5	98.7	6.5
p-CO$_2$CH$_3$	13170-28-0	286	76.6	202	13.3
2,4,6-Tri-CH$_3$	1196-12-9	321	7.47	19.7	1.30

[a] Registry no. are for nitrosobenzene with substituents. [b] Temperature 29.9°; [TEP] = 3.80 × 10^{-3} *M*.

Rate data recorded in Table II indicate the sensitivity of the deoxygenation of nitrosobenzene to changes of the solvent media to ethanol or ethanol containing 1% acetic acid. Rate-temperature results for *p*-nitrosotoluene are reported in Table III. From this data a value of E_a of 9.7 kcal/mol and a $\Delta S^{\ddagger}$ of −35 eu are calculated at 30.0°. These activation data are quite comparable to the results Cadogan and Cooper[6] obtained for *o*-nitrosobiphenyl.

TABLE II
RATES OF DEOXYGENATION OF NITROSOBENZENE IN OTHER SOLVENTS

Solvent	$k\psi$ sec^{-1} × 10^4
MeOH	5.75
EtOH	5.40
EtOH–1% HOAc	5.80

The nitroso compounds, with the exception of *p*-methoxynitrosobenzene, gave a satisfactory Hammett correlation with σ, yielding a ρ value of 3.08. An excellent correlation, which included *p*-methoxynitrosobenzene, was found with σ$^+$ with ρ equal to 1.83. These correlations are shown in Figure 1 and 2, respectively.

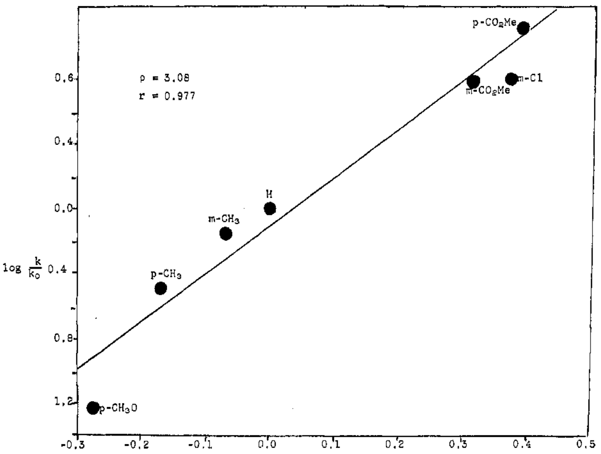
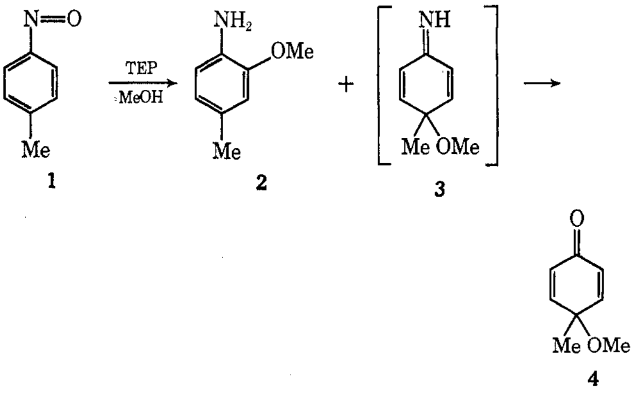


Figure 1.—Hammett correlation of rates of deoxygenation of nitrosoaromatics with σ.

TABLE III
TEMPERATURE DEPENDENCE OF DEOXYGENATION OF *p*-NITROSOTOLUENE

Temp, °C	$k\psi$ sec^{-1} × 10^4	k_2 sec^{-1} mol^{-1} l. × 10^2
24.0	1.29	3.39
27.0	1.56	4.10
29.9	1.80	4.74
34.7	2.25	5.92

The principal products of the deoxygenation of nitrosobenzene in methanol are *o*- and *p*-anisidine.[4c] The absorption spectrum found at the end of typical rate runs in consistent with the formation of *p*-anisidine as the major reaction product. The final absorption spectrum for *m*-nitrosotoluene is very similar indicating that 3-methyl-4-methoxyaniline is the major product in this reaction. The final absorption spectrum for *p*-nitrosotoluene is much different. Product isolation studies in this system have shown that 2-methoxy-4-methylaniline and 4-methoxy-4-methyl-2,5-cyclohexadienone are major products.[4c]



The final absorption spectrum [λ_{max} 228 nm (ε 13,600), 290 (s) (1120)] for the deoxygenation of *p*-nitrosotoluene is very similar to that reported for **4**,[8] indicating that **4**, or conceivably the precursor **3**, is the principal product formed under the conditions of the

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(6) J. I. G. Cadogan and A. Cooper, *J. Chem. Soc. B*, 883 (1969).

(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 49.

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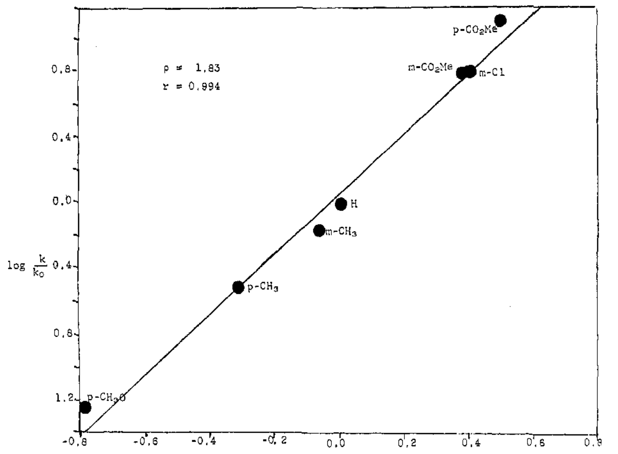


Figure 2.—Hammett correlation of rates of deoxygenation of nitrosoaromatics with σ^+.

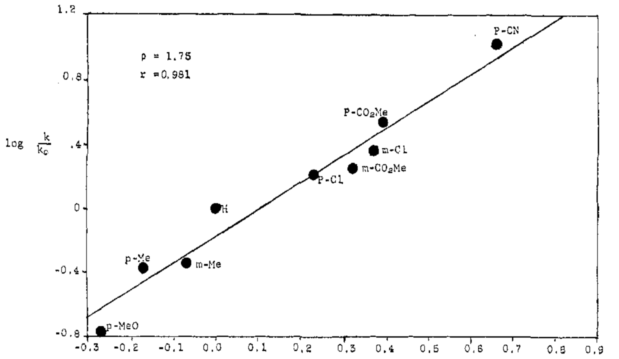


Figure 3.—Hammett correlation of rates of deoxygenation of nitroaromatics with σ.

kinetic experiment. The products formed from the other nitroso compounds have not been studied. The satisfactory Hammett relationship indicates that no change in the nature of the rate-determining step has occurred in the range of substituent groups studied, however.

The rate of deoxygenation of 2-nitrosomesitylene was studied in order to assess the steric effect of the two ortho substituents. Nitrosomesitylene was found to be surprisingly reactive toward deoxygenation as the reaction proceeded slightly faster than that of nitrosobenzene despite the presence of the electron-donating methyl substituents.

The rates of deoxygenation of the nitro compounds in triethyl phosphite were followed by gas chromatography. Pseudo-first-order rate constants were derived from the resulting data. These rates are summarized in Table IV.

Hammett plots of the rate data *vs.* σ and σ^+ are shown in Figures 3 and 4. The correlation with σ (correlation coefficient 0.981) is somewhat more satisfactory than with σ^+ (correlation coefficient 0.961).

In contrast to nitrosomesitylene, the deoxygenation of nitromesitylene is subject to some steric hindrance. It was not included in the present study but data from preparative runs give a half-life of about 4 hr at 156°.

The product mixtures obtained from thermal deoxygenations of nitro compounds in triethyl phosphite are complex and include triethyl *N*-arylphosphorimidates and products derived from them,[2,3] as well as products resulting from rearrangement of the original aromatic ring.[2c,3] Although, as described in the discussion section, we have repeated some of our earlier product studies, no new product studies on the reaction were carried out in the course of this work.

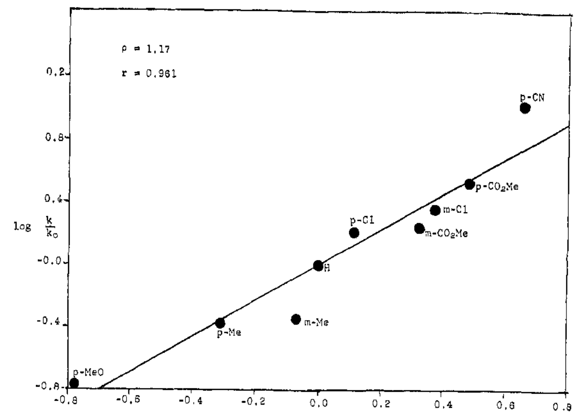


Figure 4.—Hammett correlation of rates of deoxygenation of nitroaromatics with σ^+.

TABLE IV

RATES OF DEOXYGENATION OF NITROAROMATICS IN TRIETHYL PHOSPHITE AT 130.0 ± 0.1°

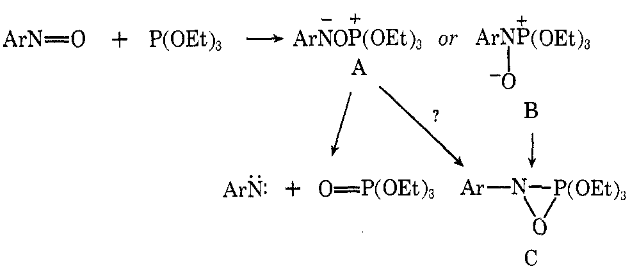
R	Registry no.[a]	k_ψ (hr^{-1}) × 10	$t_{1/2}$ (hr)	Relative rate
p-MeO	100-17-4	0.80 ± 0.05	8.6	0.17
p-Me	99-99-0	2.11 ± 0.12	3.3	0.45
m-Me	99-08-1	2.33 ± 0.07	2.9	0.50
H	98-95-3	4.68 ± 0.40	1.5	1.00
p-Cl	100-00-5	8.14 ± 0.20	0.85	1.74
m-CO$_2$Me	618-95-1	8.79 ± 0.31	0.79	1.88
m-Cl	121-73-3	11.5 ± 0.2	0.60	2.46
p-CO$_2$Me	619-50-1	16.9 ± 0.3	0.41	3.61
p-CN	619-72-7	51.5 ± 1.1	0.13	11.0

[a] Registry no. are for nitrobenzene with substituents.

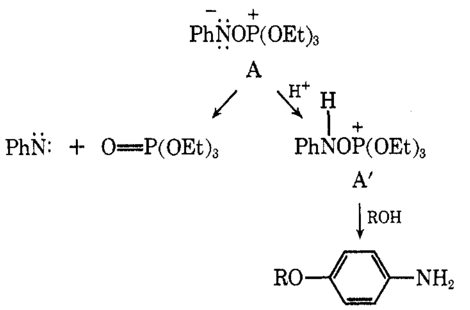
Discussion

In the preceding paper,[4c] evidence was presented pointing to the existence of an intermediate in the deoxygenation of nitrosobenzene which could give either phenylnitrene by α elimination or aromatic nucleophilic substitution products. The intermediate was considered to be the zwitterion A (Scheme I). We can now consider this intermediate and its role in the deoxygenation reaction in terms of the rate studies presented in this paper.

SCHEME I



The response of the deoxygenation rates to substituents in the nitroso compounds shows that the rate of deoxygenation is accelerated by electron-withdrawing substituents. These data, along with studies of Cadogan and Todd[5] which have established that highly nucleophilic phosphorus compounds are the most reactive deoxygenating agents, indicate that nucleophilic attack by phosphorus on the nitroso compounds occurs in the deoxygenation reaction. The initial nucleophilic attack could conceivably be at oxygen or nitrogen. Furthermore, either of the resulting zwitterionic intermediates A and B might form the cyclic pentacovalent phosphorus intermediate C prior to expulsion of triethyl phosphate. Any of these schemes is compatible with the observed substituent effects, provided the initial nucleophilic attack by phosphorus is rate determining. The evidence that the deoxygenation eventually leads to aryl nitrenes has been discussed elsewhere.[1,2b–c,3,9] Our studies[4c] of the products of deoxygenation in alcoholic solvents have established that the type of products formed in the reaction is very sensitive to the nature of the reaction media. Changes in solvent media which would increase the rate of protonation of a dipolar intermediate, such as A, divert the reaction from its normal nitrenoid course and lead, instead, to nucleophilic aromatic substitution.[4c]

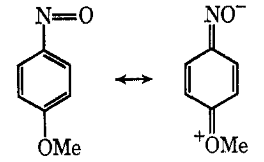


A dipolar intermediate such as A provides an attractive explanation for this feature of the reaction. Its conjugate acid A′ is an aniline derivative with an excellent leaving group, triethyl phosphate, bonded to nitrogen. Protonation of C could also lead to aromatic nucleophilic substitution, but protonation of the intermediate B would not be expected to lead directly to aromatic substitution although it could do so indirectly *via* a cyclic form.

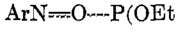
The rate of deoxygenation of nitrosobenzene is relatively unaffected by changes in solvent which have a major effect on product composition. Nucleophilic aromatic substitution accounts for >60% of the nitrosobenzene in methanol, but less than 5% of the total product in ethanol.[4c] The rates of deoxygenation in the two solvents are within 10% of one another. Addition of acetic acid to ethanol induces nucleophilic aromatic substitution in >50% yield[4c] but increases the rate of deoxygenation by less than 10%. These results indicate that the product-determining step in deoxygenation, protonation, or α elimination, follows the rate-determining step which must be formation of A (or B or C).

The insensitivity of the deoxygenation reaction to steric hindrance which is dramatically indicated by the fact that nitrosomesitylene is slightly more reactive than nitrosobenzene can not easily be reconciled with the formation of B in the rate-determining step of the reaction. Nucleophilic attack at nitrogen would be expected to be subject to large steric hindrance. Base-catalyzed hydrolysis of mesitoate esters, for example, is about 10^5 times slower than comparable hydrolyses of benzoate esters.[10,11] The reason for the small rate enhancement present in nitrosomesitylene is not entirely clear. It may be associated with steric inhibition of resonance in nitrosomesitylene. Such an effect is known to be present[12] and the resulting higher ground-state energy of the nitroso compound may result in increased reactivity.

The Hammett correlation for the nitroso deoxygenations is significantly improved by use of σ^+ values in place of σ values. This points to a high contribution from resonance interactions in the overall substituent effect.[13] The intermediate A cannot account for the large resonance effect associated with σ^+ correlations. However, the ground-state nitroso compounds present the opportunity for direct conjugation of the nitroso group with the substituents and such conjugation is known to significantly effect the spectral[14] properties of the nitroso compounds. We suggest that the σ^+ correlation reflects the fact that this direct conjugation is decreased in the transition state leading to A.



In summary, we propose that the transition state for deoxygenation of aromatic nitroso compounds can be represented as D. A similar proposal has been made by Cadogan and Cooper[8] on the basis of their studies on *o*-nitrosobiphenyl. In accord with expectation for an exothermic reaction with a low energy of activation,[15] the transition state probably occurs early on the reaction coordinate and there appears to be minimal steric resistence to the approach by phosphorus in the transition state. There is no evidence in the present data that indicates that the reaction proceeds to a cyclic intermediate C but the possibility can not be finally ruled out.



$$\mathrm{Ar}\overset{\delta^-}{\mathrm{N}}\!\!=\!\!\mathrm{O}\text{---}\overset{\delta^+}{\mathrm{P}}(\mathrm{OEt})_3$$

D

The electronic substituent effects in the nitro deoxygenations are generally similar to those observed with the nitroso compounds. There is a moderate steric effect observed in the deoxygenation of nitromesitylene. Although quantitative rate data were not obtained, preparative scale runs indicate a half-life of about 40 hr at 156° for nitromesitylene. The steric effect thus decreases the reactivity relative to nitrobenzene by a factor of roughly 100. Again, this seems much too small for a nucleophilic attack on nitrogen. The increase in steric sensitivity may reflect the fact that nitrogen is trisubstituted in the nitro system but only disubstituted

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(13) C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

(14) I. C. Calder and P. J. Garratt, *Tetrahedron*, **25**, 4023 (1969); B. G. Gowenlock and W. Lüttke, *Quart. Rev., Chem. Soc.*, **12**, 321 (1958).

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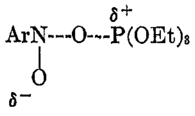
in the nitroso case. The transition state for deoxygenation of nitrobenzene may be represented as E. It is as-



$$\mathrm{Ar}\underset{\substack{|\\ \mathrm{O}\\ \delta-}}{\mathrm{N}}\text{---}\mathrm{O}\text{---}\overset{\delta+}{\mathrm{P}}(\mathrm{OEt})_3$$

E

sumed that the deoxygenation of nitroaromatics leads to nitroso compounds which are rapidly deoxygenated,[1,2b,16] but, as Cadogan[1] has pointed out, the evidence for this assumption is indirect at this point.

We believe that the rate data presented here affords a partial explanation for the differences in products reported in our studies of the deoxygenation of nitro compounds as compared with those of Cadogan. Cadogan has reported the deoxygenation of a number of alkyl and alkoxynitroaromatics and found dialkyl *N*-arylphosphoramidates and dialkyl *N*-alkyl-*N*-arylphosphoramidates as the major products.[3] In contrast, our studies of similar compounds have lead usually to the isolation of trialkyl *N*-arylphosphorimidates.[2a-c] Cadogan has noted this difference. We have confirmed the isolation of trialkyl *N*-arylphosphorimidates from deoxygenation of several representative (specifically *o*-ethylnitrobenzene, 3,4-dimethylnitrobenzene, and 2,3-dimethylnitrobenzene). We have usually[2b,c] isolated triethyl *N*-arylphosphorimidates by direct distillation of the reaction mixture after a *4–5-hr reflux* period. Cadogan's coworkers have used *11–17 hr* reflux periods. With half-lives of the nitrotoluenes in the range of 0.5–1.0 hr at 156° (the reflux temperature of triethyl phosphite), it is clear that the more extended reflux periods provide the opportunity for subsequent conversion of the initially formed *N*-arylphosphorimidates to the dialkyl *N*-arylphosphoramidates isolated by Cadogan and coworkers. We suspect that this difference in length of reflux contributes to the difference in product distribution noted in the two laboratories. In our hands[2c] only such unreactive compounds as *p*-nitroanisole and nitromesitylene give rise to much dealkylation of the phosphorimidate during the time required for deoxygenation. It should be noted that trimethyl *N*-arylphosphorimidates are quite thermally labile.[17]

Experimental Section

Nitrosoaromatics.—With the exception of *p*-nitrosoanisole, all of the nitroso compounds were prepared from the corresponding nitro compounds by reduction with zinc followed by oxidation of the crude arylhydroxylamine with ferric chloride.[18] 2-Nitrosomesitylene was prepared following the procedure of Bamberger and Rising.[19] We were able to prepare only impure *p*-nitrosoanisole from *p*-nitroanisole. Pure *p*-nitrosoanisole was obtained by oxidation of *p*-anisidine with persulfuric acid.[20] Potassium persulfate (57 g) was slowly added to cooled concentrated sulfuric acid (80 ml). A solution of *p*-anisidine (12 g) in water (1500 ml) was brought to pH 6 with 6 *N* acetic acid and cooled to 5°. The solution of persulfuric acid was poured on to ice, neutralized with potassium carbonate, and finally made slightly acidic with dilute acetic acid. This solution was added all at once at 5° to the solution of *p*-anisidine. After 0.5 hr, the precipitated nitroso compound was extracted with hexane. The hexane extract was diluted with methanol and a methanol–hexane azeotrope was removed (bp 50°). The concentrated hexane solution was steam distilled, yielding blue crystalline *p*-nitrosoanisole, contaminated with 15% *p*-nitroanisole. The product was purified by sublimation.

Triethyl Phosphite.—Commercial triethyl phosphite (Mobil Chemicals) was stored over sodium metal and then distilled through a Vigreux column under nitrogen at atmospheric pressure.

Kinetic Measurements on Nitroso Compounds.—Solutions of the nitroso compounds with absorbance of ~0.9 were prepared in methanol and exactly 3 ml was pipetted into a cell thermostated at 29.9° in a Beckman DU spectrophotometer. At $t = 0$, triethyl phosphite was added from a microsyringe and the cell was shaken. The cell was quickly returned to the thermostat and absorbance *vs.* time measurements were recorded for several half-life periods. Straight lines were obtained plotting log $(A_t - A_{t+c})$ *vs.* time according to the Guggenheim method.[7] The pseudo-first-order rate constants were evaluated from the slope of the line, slope = $-k/2.303$. Most runs gave good straight lines for two to three half-lives when subjected to standard first-order analysis but precise determination of $A_{s\infty}$ was difficult because of slow drift, and the Guggenheim method was used to circumvent this problem. The concentration of triethyl phosphite was calculated from the volume of triethyl phosphite delivered by the calibrated syringe (2–92 µl). The chloro- and carbomethoxy-substituted compounds were deoxygenated at [TEP] = 3.80×10^{-3} mol/l. The nitrosotoluenes were deoxygenated at several TEP concentrations ranging from [TEP] = 1.52×10^{-2} to 3.04×10^{-2} mol/l. and showed first-order dependence on [TEP] in this range. Nitrosobenzene was deoxygenated at [TEP] = 3.80×10^{-3} and 7.60×10^{-3} mol/l. and showed first-order dependence on TEP. For *p*-nitrosoanisole, [TEP] = $1.52 \times 10^{-2} - 1.75 \times 10^{-2}$ mol/l. were used.

The procedures for studies in ethanol and solutions containing acetic acid were identical with those described for methanol.

Kinetic Measurements on Nitro Compounds.—Samples of 0.003–0.012 mol of the nitro compound were diluted to 25 ml with *triethyl phosphite. The resulting solution was sealed in a series* of 10–15 Pyrex ampoules. These were immersed in a oil bath at 130° and t_0 was taken at the point at which the bath and tubes had been at constant temperature (130 ± 0.1°) for 3 min. Tubes were removed at t_0 and subsequent time intervals, cooled in ice water, and stored for analysis at the end of the run. The amount of unreacted nitro compound was determined by the peak height method using a Wilkens A-90-P gas chromatograph and a 5-ft SE-30 column. Plots of log c_0/c *vs.* time showed first-order behavior and rate constants were obtained from the best least squares line using data for several half-life periods.

Preparative Thermal Deoxygenations.—Three nitroaromatics (2-ethylnitrobenzene, 3,4-dimethylnitrobenzene, and 2,3-dimethylnitrobenzene) were deoxygenated by refluxing with triethyl phosphite. The nitroaromatic (0.10 mol) was dissolved in triethyl phosphite (1.0 mol) and heated at reflux under nitrogen for 4–5 hr. Three fractions were collected by direct vacuum distillation of the reaction mixture. Recovered triethyl phosphite was obtained at 25–40° (0.1–0.2 mm), followed by triethyl phosphate, bp 55–65° (0.1–0.2 mm), and the trialkyl phosphorimidate, bp 120–140° (0.1 mm). Yields were 60, 78, and 79%, respectively, for the three nitro compounds (reported[2] 44, 60, 79%, respectively). The infrared spectra showed no NH absorption. The nmr spectra were in accord with expectation and in particular the integration gave the expected values for the $-OCH_2CH_3$ and $-OCH_2CH_3$ signals indicating three ethoxy groups attached to phosphorus. There were no NCH_2CH_3 signals evident in the nmr. The only indication of any impurities is the presence of weak phosphoryl absorption in the infrared near 1250 cm^{-1}. Since phosphoramidates show strong absorptions in this region, the distilled samples are believed to be >90% pure.

Similar thermal deoxygenations of 2-nitromesitylene lead to substantial recovery of nitromesitylene (9 hr, 90% recovery; 43 hr, 52% recovery; 96 hr, 21% recovery). The products of such deoxygenations have been previously described.[2c]

Registry No.—Triethyl phosphite, 122-52-1.

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