portions required to give the final desired concentrations. All reaction times were measured from the time of addition of the DMSO. The DANSC concentration ranged from 0.6 to 1.8 × 10^{-4} *M*. The DMSO concentration was 6.2 *M* to give a large excess consistent with a pseudo-unimolecular reaction. All of the kinetic studies were made at room temperature, 27 ± 2°. Ether was chosen as a reaction solvent to prevent complicated side reactions.[5]

Identification of Reaction Products.—The increase in the absorbance at 316 mμ served to identify the DANSA formed in the reaction. It was further identified in a preparative experiment described later. The CDMS was identified by gas chromatography using a 4 ft × 6 mm column of Carbowax-20 M (5%), Haloport F (30–60 mesh) with programming at 11°/min from 60 to 170° on an F and M Model 500[16] gas chromatograph. The CDMS identification was confirmed by comparison of the peak and retention time with an authentic sample.

In a preparative experiment, the reaction mixture was allowed to stand for 24 hr at room temperature. A sample was removed and gas chromatographed as before. Only two peaks were observed and these were confirmed to be DMSO and CDMS with authentic samples treated the same way. The ether was removed from the remaining reaction mixture by gentle heating on a water bath and 1.0 ml of the residual solution was removed, diluted to 100 ml with DMSO, and examined spectrophotometrically. A single peak was observed at 322 mμ as evidence of the presence of DANSA. The remaining solution was treated according to the procedure of Laurence.[17] A solid material was obtained that when recrystallized from 0.1 HCl had a decomposition point of 292° uncor compared with 294° uncor for an authentic sample. Quantitative recovery of the DANSA was not made because of its extreme solubility in DMSO. The isolated material redissolved in DMSO showed only one absorbance peak at 322 mμ, substantiating the presence of DANSA. No "material" balance for the reaction was obtained.

Acknowledgment.—The author wishes to acknowledge the assistance of Mr. Robert A. Saperstein and to thank Mr. Phillip Albro and Dr. Charles K. Huston for the gas chromatography analyses.

[17] D. J. R. Laurence, S. O. Colowick, and N. O. Kaplan, Ed., "Methods of Enzymology," Vol. IV, Academic Press Inc., New York, N. Y., 1957, pp 208–210.

Deoxygenation of Nitro Groups. The Question of Nitrene Formation

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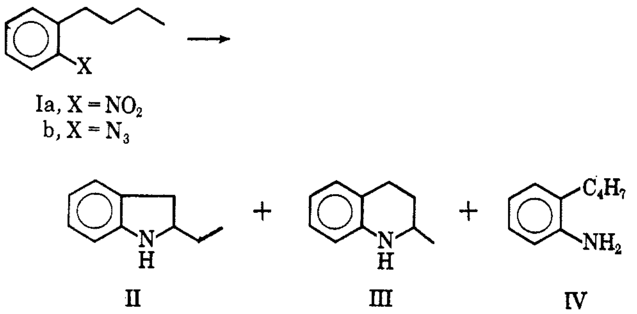
Reductive cyclization of aromatic nitro compounds has been achieved by a number of workers using several different reagents. Cadogan and co-workers,[1] and more recently Sundberg,[2] prepared heterocyclic compounds by heating the appropriate nitro compound in triethyl phosphite. Other investigators have accomplished similar reactions using such reagents as ferrous oxalate[3,4] or iron pentacarbonyl.[5] It has been postulated that all three reagents deoxygenate the nitro group to a nitrene intermediate,[1,3,5] though polar mechanisms have also been suggested[1a,2] for the triethyl phosphite reactions. Our present studies show that nitrenes are involved in the triethyl phosphite reactions but not in the ferrous oxalate case.

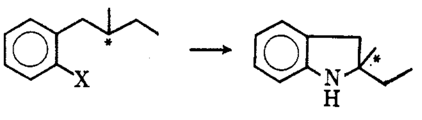
Apparently, the only support for the argument that a nitrene was involved in the above reactions was the fact that pyrolysis of the corresponding aromatic azides gave analogous products. It is generally agreed that nitrenes are involved in many azide decomposition reactions.[6] Since nitrenes formed from azides have been shown[6] to insert into the C–H bond of a saturated carbon atom, we believe that the most convincing evidence for intervention of a nitrene in the deoxygenation of a nitro group would be the formation of a carbon–nitrogen bond at a saturated carbon atom.

Sundberg has recently reported[7] that heating a solution of *o*-nitro-*n*-butylbenzene (Ia) in triethyl phosphite formed, in approximately 10% total yield, a mixture of compounds consisting of II, III, and IV in almost the same ratio as was formed from the solution phase decomposition[8] of the azide Ib. We wish to report that heating (+)-(*S*)-2-nitro-1-(2-methylbutyl)benzene (Va)[9] in triethyl phosphite resulted in a 25% yield of partially active (~50%) indoline VI. This compares favorably with our earlier finding[9] that solution-phase pyrolysis of azide Vb gave VI (60%) of 65% optical purity. Both of the above deoxygenation reactions meet our criterion for a nitrene reaction.



Ia, X = NO_2
b, X = N_3

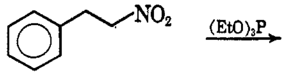
II III IV



Va, X = NO_2
b, X = N_3

VI

Heating the aliphatic nitro compound, 1-nitro-2-phenylethane (VII), in triethyl phosphite resulted in the formation of phenylacetonitrile presumably *via* the oxime since the nitrile could also be obtained by starting with the oxime (eq 1).



VII

$$\diagup CH_2CH_2NO \rightleftharpoons \diagup CH_2CH{=}NOH \rightarrow \diagup CH_2CN \qquad (1)$$

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[1] J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 4831 (1965); (b) P. J. Bunyan and J. I. G. Cadogan, *ibid.*, 42 (1963).

[2] R. J. Sundberg, *J. Org. Chem.*, **30**, 3604 (1965).

[3] R. A. Abramovitch, D. Newman, and G. Tertzakian, *Can. J. Chem.*, **41**, 2390 (1963); (b) R. A. Abramovitch and K. A. H. Adams, *ibid.*, **39**, 2516 (1961), (c) R. A. Abramovitch, Y. Ahmand, and D. Newman, *Tetrahedron Letters*, 752 (1961).

[4] R. H. Smith and H. Suschitzky, *Tetrahedron*, **16**, 80 (1961).

[5] J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965).

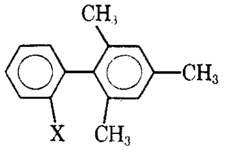
[6] R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964).

[7] R. J. Sundberg, *Tetrahedron Letters*, 477 (1966); (b) *J. Am. Chem. Soc.*, **88**, 3781 (1966).

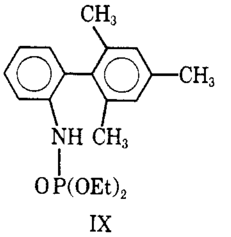
[8] G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, **29**, 3097 (1964).

[9] G. Smolinsky and B. I. Feuer, *J. Am. Chem. Soc.*, **86**, 3085 (1964).

Although products thought to be formed[10] from a nitrene intermediate can be obtained by thermally decomposing the biphenyl azide VIIIb, the corresponding nitrobiphenyl VIIIa gives presumably compound IX (see ref 1a) with triethyl phosphite.

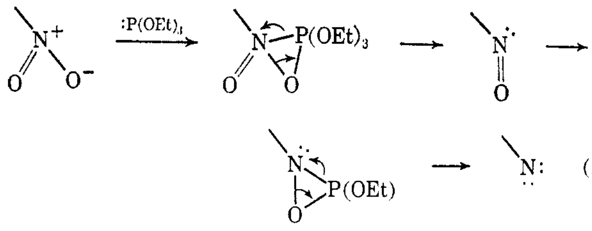


VIIIa, X = NO_2
b, X = N_3



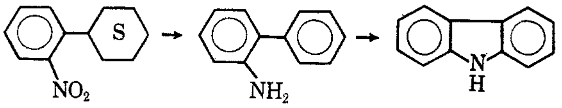
IX

We envision the deoxygenation of the nitro group by triethyl phosphite to be a two-step process involving first reduction to the nitroso stage and then to the nitrene (see eq 2). The concomitant formation of 2 moles of triethyl phosphate provides the driving force for this reaction. Sundberg[7b] has demonstrated that triethyl phosphite deoxygenates *o*-alkylnitrosobenzenes to give cyclic products.



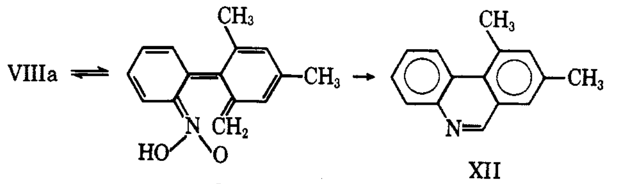
(2)

Abramovitch and co-workers[3] have suggested that the deoxygenative cyclization[3c] of 2,4,6-trimethyl-2′-nitrobiphenyl (VIIIa) or *o*-nitrophenylcyclohexane (X) with ferrous oxalate resulting in the formation of phenanthridine XII or carbazole, respectively, involves a nitrene intermediate. Indeed it would appear that these results fulfill our criterion for a nitrene reaction in that a new carbon–nitrogen bond has been formed in each case at a saturated carbon atom. However, we found that when nitro compound Va was heated with ferrous oxalate in diphenyl ether solution only a trace, if any, of indoline VI was formed. This apparent contradiction can be explained if the conversion of X to carbazole proceeds first by oxidation of the cyclohexane ring accompanied by reduction of some of the nitro compound followed by the known[4,11] cyclization reaction of the resulting 2-aminobiphenyl rather than by a nitrene reaction (eq 3). In addition, the formation of phenanthridine XII from nitrobiphenyl VIIIa can also be explained without invoking a nitrene by postulating that the nitro compound is reacting through its *aci* form XI just as has been shown[4] to be the case in the cyclization of 2-nitrodiphenylamine to phenazine N-oxide. Indeed, we have been able to achieve a 27% yield of carbazole and a 32% yield of phenanthridine XII merely by maintaining a diphenyl ether solution of X or VIIIa, respectively, at 350° for several hours. From the pyrolysis of cyclohexylnitrobenzene (X), 2-cyclohexylaniline (10%) and tetrahydrocarbazole (12%) were also obtained.



(3)

X



XI

XII

In conclusion, it seems clear from the experiments reported here and from the work of Sundberg[7] that nitrenes are frequently involved as intermediates in the triethyl phosphite deoxygenation of aromatic nitro compounds. On the other hand, this work and that of Smith and Suschitzky[4] clearly demonstrates that very similar thermal deoxygenative cyclization reactions of aromatic nitro compounds can be achieved with or without the addition of ferrous oxalate. Thus we feel there is no compelling reason to invoke a nitrene intermediate in these ferrous oxalate reductions.

Experimental Section

Reaction of (+)-(*S*)-2-Nitro-1-(2-methylbutyl)benzene (Va)[9] with Triethyl Phosphite.—A solution of 10.6 g (0.055 mole) of nitro compound Va[9] in 50 ml of triethyl phosphite was maintained at 145–150° for 18 hr in a nitrogen atmosphere. The triethyl phosphite was removed by distillation through a 2-ft spinning-band column operated at about 40 mm. When the boiling point reached 120°, distillation was discontinued, and the pot residue was taken up in benzene. The basic material (4.4 g) was extracted from the benzene solution with 3 *N* hydrochloric acid and isolated in the usual way. This mixture contained 50% (25% over-all yield) 2-ethyl-2-methylindoline (VI),[9] as shown by gas phase chromatographic analysis, which was isolated in pure form as described previously.[9] The molecular rotation $[M]_\lambda$, of the indoline was determined with a JASCO photoelectric spectropolarimeter at a concentration of 17.523 g/100 ml of cyclohexane and found to have the following values: −7.4° (589 mμ), −8.3° (546 mμ), −9.6° (500 mμ), −11° (436 mμ).

Reaction of 1-Nitro-2-phenylethane (VII)[12] with Triethyl Phosphite.—A solution of 8.5 g (0.056 mole) of nitro compound VII[12] in 50 ml of triethyl phosphite was maintained in a nitrogen atmosphere at a temperature of 145–150° for about 16 hr. The reaction solution was distilled through a 2 ft spinning-band column at about 25 mm. When the boiling point reached 110°, distillation was discontinued. The pot residue, a reddish, thick oil, was diluted with benzene and subjected to gas phase chromatographic analysis (10 ft $\times$ $^3/_8$ in. column, packed with 15% XF 1150 on 80–100 Chromosorb W-DMCS, operated at 180°) and found to consist mainly of phenylacetonitrile (identity established by comparison of the infrared spectrum with that of an authentic sample) contaminated with a trace of triethyl phosphate.

Reaction of Phenylacetaldehyde Oxime with Triethyl Phosphite.—A solution of 1.2 g (9.1 mmoles) of oxime in 10 ml of triethyl phosphite was heated for 21 hr in a nitrogen atmosphere at a temperature of 150°. The products were isolated as described above in the case of 1-nitro-2-phenylethane and shown to consist mainly of phenylacetonitrile.

Reaction of 2,4,6-Trimethyl-2′-nitrobiphenyl (VIIIa)[10] with Triethyl Phosphite.—A solution of 1.97 g (8.2 mmoles) of VIIIa[10] in 100 ml of triethyl phosphite was maintained in a nitrogen atmosphere at a temperature of 145° for 6.5 hr. The triethyl phosphite was removed by distillation at reduced pressure

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(10) G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4717 (1960). In contrast to the data reported in this reference, the 2,4,6-trimethyl-2′-nitrobiphenyl (VIIIa) was found to be crystalline with mp 42–44°.

(11) H. C. Waterman and D. L. Vivian, *J. Org. Chem.*, **14**, 289 (1949).

(12) W. Borsche and F. Sinn, *Ann.*, **553**, 260 (1942).

[bp 60° (25 mm)]. When the triethyl phosphite ceased distilling, heating was discontinued and the pressure was reduced to about 1 mm and maintained for about 1 hr in order to remove the remaining solvent. The red pot residue was heated with 125 ml of 1 *N* sodium hydroxide at about 70° overnight. The aqueous mixture was extracted with ether, and the ether phase was washed with dilute hydrochloric acid, dried over sodium carbonate, and evaporated. The residue was chromatographed on a column of 30 g of Merck alumina. A trace of 2-amino-2′,4′,6′-trimethylbiphenyl[11] (identified by comparison of its infrared spectrum with that of an authentic sample[11]) was eluted with 1:2 (v/v) benzene–petroleum ether (bp 30–60°). A red, viscous material was finally washed from the column with 2% 2-propanol in benzene. This substance, presumed to be IX, sublimed at 100° (0.001 mm) to give 450 mg (18%) of pale yellow, oily crystals. The compound showed strong absorption in the infrared (CCl_4 solution) at 3400, 1030, and 970 cm.$^{-1}$ The nmr spectrum (in CCl_4 solution) exhibited a 6 H triplet centered at 1.20 ($J = 7$ cps), a 6 H singlet at 1.95, a 3 H singlet at 2.25, two, a 2 H each, overlapping quartets centered at 3.86 and 4.03 ($J = 7$ cps each), a 1 H doublet centered at 4.73 ($J = 8.5$ cps), and a complex multiplet of 6 H in the region 6.7 to 7.5 ppm from a TMS internal standard.

Reaction of (+)-(*S*)-2-Nitro-1-(methylbutyl)benzene (Va)[9] with Ferrous Oxalate.[3]—To a mixture of anhydrous ferrous oxalate (3 g) in diphenyl ether (20 ml) maintained in a nitrogen atmosphere just below the boiling point, was added 3 g (0.016 mole) of nitrogen compound Va.[9] A vigorous reaction occurred while the temperature was maintained at the boiling point for 0.5 hr. The cooled reaction mixture was filtered with the aid of a Hyflo Super Cel bed, and the products (0.52 g) were separated from the diphenyl ether by column chromatography as described previously.[13] A gas chromatographic analysis, using an instrument equipped with a flame ionization detector (6 ft × $^{1}/_{8}$ in. column packed with 10% Ucon Polar on 80–100 Chromosorb W–DMCS) indicated that the product consisted of at least 12 compounds including about 15% unreacted nitro compound, 5% corresponding amine, and no more than 1%, if any, 2-ethyl-2-methylindoline (VI).[9]

Pyrolysis of 2,4,6-Trimethyl-2′-nitrobiphenyl (VIIIa)[10] in Diphenyl Ether.—A solution of 576 mg (2.4 mmoles) of VIIIa[10] in 20 ml of dry diphenyl ether was sealed under vacuum in an ampoule and heated for 2 hr in a sand bath at 350°. The resulting dark solution was transferred to a column packed with 120 g of Merck alumina. The diphenyl ether was eluted with petroleum ether (bp 30–60°); 206 mg of darkly colored, crystalline material was obtained with 4% 2-propanol in benzene. This crystalline product was sublimed [110–120° (0.1 mm)] overnight. The sublimate (156 mg, 32%) was recrystallized from carbon tetrachloride and shown to be 8,10-dimethylphenanthridine (XII) by comparison of its melting point, mixture melting point, and infrared spectrum with that of an authentic sample.[10]

Pyrolysis of *o*-Nitrophenylcyclohexane (X)[14] in Diphenyl Ether.—A solution of 1.9 g (9.3 mmoles) of X in 25 ml of dry diphenyl ether sealed under vacuum in an ampoule was heated for 1 hr in a sand bath at 350°. The resulting dark solution was transferred to a column packed with 60 g of Merck alumina. The diphenyl ether was eluted with petroleum ether (bp 30–60°); 334 mg of a mixture of 2-cyclohexylaniline and tetrahydrocarbazole was eluted with benzene; 423 mg (27%) of carbazole (identified by melting point, mixture melting point, infrared, and ultraviolet spectra of a recrystallized sample with that of an authentic sample) was eluted with 10% 2-propanol in benzene; finally a dark tar was obtained with 20% 2-propanol in benzene.

The 2-cyclohexylaniline was separated from the tetrahydrocarbazole by an acid-extraction procedure, weighed 150 mg (9.3%), and was identified by comparison of its infrared spectrum with that of an authentic sample.[13] The sublimed [75° (0.003 mm)] tetrahydrocarbazole weighed 184 mg (12%) and had a melting point and infrared spectrum identical with those of an authentic sample.

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(13) G. Smolinsky, *J. Am. Chem. Soc.*, **83**, 2489 (1961).

(14) H. A. Mayes and E. E. Turner, *J. Chem. Soc.*, 503 (1929).