Registry No.—I, 38896-59-2; II, 38896-60-5; III, 38896-61-6; IV, 38896-62-7; V, 38896-63-8; VI, 38896-64-9; VII, 38896-65-0; VIII, 38896-66-1; IX, 38896-67-2.

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The Oxidation of Benzylamines with Nitrosobenzene

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Aromatic amines react readily with nitrosobenzene to afford azobenzenes,[2] presumably through elimination of water from intermediate *N*-hydroxyhydrazines[3] (**1**, R = Ar). In view of this, we envisioned that the analogous reaction of nitrosobenzene with aliphatic amines might provide a convenient source of phenylazoalkanes (**2**, R = alkyl).[4] In fact, an early report is

$$ArNO + RNH_2 \longrightarrow Ar\overset{OH}{\overset{|}{N}}NHR \longrightarrow ArN{=}NR$$

1 **2**

available which describes the formation of toluene-α-azobenzene (**2**, R = benzyl) from nitrosobenzene and benzylamine in alcohol solvent.[5] However, a subsequent study of this reaction with a variety of benzylamines reported instead the production of aldehydes or ketones, azoxybenzene, and ammonia with no evidence for azo formation.[6] The mechanism postulated for this reaction involved transfer of an oxygen from a molecule of nitrosobenzene to the benzyl carbon with concurrent loss of ammonia and generation of azoxybenzene.[6]

In order to shed light on the above discrepancies and hopefully to divert the reaction to give phenylazoalkanes, the reaction was reinvestigated in a variety of solvents, including diethyl ether, benzene, and dimethyl sulfoxide (DMSO); the results are presented in Table I. In all cases the product profiles were nearly identical as determined by glpc and consisted of *N*-benzylbenzaldimine (**3**) and azoxybenzene, identified by nmr and mass spectral comparisons with authentic samples. In addition, structure **3** was confirmed by chemical methods (see Experimental Section). Repetition of the exact experimental conditions employed by previous workers[6] using a 2:1 mole ratio of nitrosobenzene to benzylamine in refluxing benzene gave glpc-determined yields of 78% azoxybenzene and 76% **3** in 9 hr (Table I). Conceivably, **3** may arise by condensation of initially produced benzaldehyde with remaining benzylamine. However, in no case was benzaldehyde detected by glpc under conditions where its presence would have been evident.[7] In addition, **3** reacts readily with 2,4-dinitrophenylhydrazine by an amine–imine exchange reaction to liberate benzylamine along with the corresponding 2,4-dinitrophenylhydrazone of benzaldehyde. This latter reaction would account for the identification of carbonyl compounds as primary products.[6] As an alternative, the mechanistic sequence depicted in Scheme I is suggested in which initial attack of benzylamine on nitrosobenzene occurs to furnish the hydroxylhydrazine species **4**. Elimination of phenylhydroxylamine (**5**), possibly *via* a Cope-type elimination (as in **6**),[8] affords benzaldimine[9] (**7**), which gives the observed imine **3** and ammonia upon exchange with benzylamine.[13] The azoxybenzene most probably arises by the well-known condensation of phenylhydroxylamine with nitrosobenzene.[10]

To provide evidence for the production and intermediacy of unsubstituted imines, the reaction of diphenylmethylamine with nitrosobenzene was investigated in hopes of detecting the fairly stable imine **8**[15] before exchange with starting amine. Indeed, in benzene at 70°, **8** was observed to be produced concomitantly with azoxybenzene. The imine **8** further reacted with benzylamine to afford *N*-benzyldiphenylmethyleneimine (**9**), which had been previously observed.[6] The production of various products was monitored by glpc and plotted in Figure 1. Furthermore, benzophenone was observed to be unreactive toward

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[1] National Science Foundation Undergraduate Research Participant, 1971.

[2] (a) P. Ruggli and J. Rohner, *Helv. Chim. Acta*, **25**, 1523 (1952); (b) W. Borsche and I. Exss, *Ber.*, **56**, 2353 (1923); see also (c) P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. II, W. A. Benjamin, New York, N. Y., 1966, pp 319–321, and references cited therein.

[3] P. Y. Sollenberger and R. B. Martin in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N. Y., 1968, p 395.

[4] Phenylazoalkanes may be prepared by oxidation of the corresponding hydrazines; see, for example, A. J. Bellamy and R. D. Guthrie, *J. Chem. Soc.*, 2788 (1965). The reaction of alkylzinc compounds with diazonium salts gives phenylazoalkanes, but the method is often unreliable; see D. Y. Curtin and J. A. Ursprung, *J. Org. Chem.*, **21**, 1221 (1956). See also ref 2c, p 219, for a review of preparative methods for azo compounds.

[5] P. Gallagher, *Bull. Soc. Chim. Fr.*, **29**, 683 (1921).

[6] (a) K. Suzuki and E. K. Weisburger, *Tetrahedron Lett.*, 5409 (1966); (b) *J. Chem. Soc. C*, 199 (1968).

[7] Benzaldehyde reacts with benzylamine to give the observed product *N*-benzylbenzaldimine under the reaction conditions, but sufficient amounts of benzaldehyde remain to be detectable by glpc. In addition, the reaction of nitrosobenzene with benzylamine at room temperature was followed by nmr (220 MHz). Even under such mild conditions benzaldehyde was not detected, only benzylbenzaldimine.

[8] A. C. Cope and E. R. Trumball, "Organic Reactions," Vol. XI, Wiley, New York, N. Y., 1960, p 361.

[9] Alternately, the breakdown of the first condensation intermediate **4** could involve an electron transfer to nitrosobenzene to afford an amino nitroxide (i) and nitrosobenzene radical anion; the latter species couple

$$Ar\overset{O\cdot}{\overset{|}{N}}NHCH_2Ar$$

i

$ArNH\cdot$

ii

readily to azoxybenzene (ref 10). The amino nitroxide i may fragment to furnish benzylamino radical ii [in analogy to the behavior of alkoxy nitroxides (ref 11)], which could disproportionate to benzylamine and benzaldimine (**7**) (ref 12). While nitrosobenzene has been documented as an electron acceptor (ref 13, 14), other experiments in our laboratory using such easily oxidized amines as *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine do not indicate this to be the general case in the presence of amines. In addition, the reaction of phenylhydroxylamine and nitrosobenzene generates a small concentration of monophenyl nitroxide as detected by esr. An examination of the reaction of nitrosobenzene with benzylamine demonstrated the same occurrence. The somewhat analogous reaction of benzyl alcohols with nitrosobenzene in the presence of base to yield benzaldehyde and azoxybenzene is also thought to proceed by an ionic mechanism; see J. Hutton and W. A. Waters, *J. Chem. Soc. B*, 191 (1968).

[10] G. A. Russell, E. J. Geels, F. T. Smentowski, K. Chang, J. Reynolds, and G. Kaup, *J. Amer. Chem. Soc.*, **89**, 3821 (1967).

[11] D. J. Cowley and L. H. Sutcliffe, *J. Chem. Soc. B*, 569 (1970).

[12] J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 6686 (1971); M. A. Ratcliff, Jr., and J. K. Kochi, *J. Org. Chem.*, **37**, 3268, 3275 (1972).

[13] H. Schecter, S. Rowalay, and M. Tubis, *J. Amer. Chem. Soc.*, **86**, 1701 (1964).

[14] F. T. Smentowski, *ibid.*, **85**, 3036 (1963).

[15] P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).

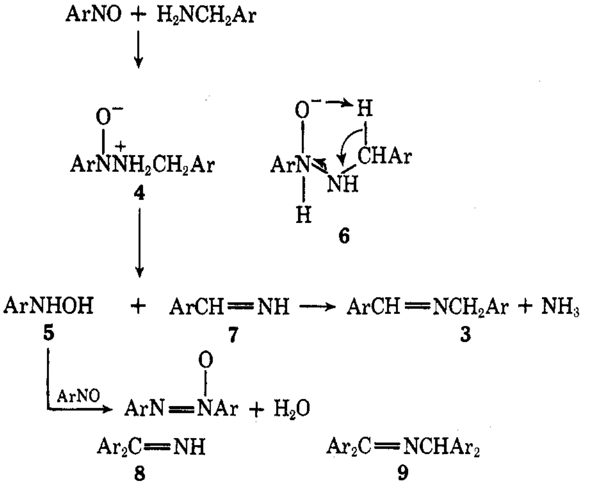
TABLE I

REACTION OF NITROSOBENZENE WITH BENZYLAMINES

Benzylamine	Ratio nitrosobenzene: benzylamine	Solvent	Temp, °C	Reaction time, hr	Products, % yield[a] Imine (isolated)	Products, % yield[a] Azoxybenzene (isolated)
Benzylamine	1.0	DMSO	25	48	77 (56)[b]	87 (44)
	2.0	Benzene	78	9	76[b]	78
	1.0	Benzene	25	72	75[b]	70
	1.0	Diethyl ether	25	72	44[b]	51
p-Methoxybenzylamine	2.0	Benzene	78	4.5	65[c]	82
Diphenylmethylamine	2.0	Benzene	70	0.5	56,[d] 3[e]	62
				1.0	57,[d] 11[e]	73
				1.5	68,[d] 15[e]	80
				2.7	52,[d] 34[e]	81
				3.2	48,[d] 37[e]	78
				19.5	35,[d] 57[e]	73

[a] Yields of products were determined by glpc using internal standards and detector response factors. [b] *N*-Benzylbenzaldimine. [c] *N*-(*p*-Methoxybenzyl)-*p*-methoxybenzaldimine. [d] Diphenylmethyleneimine. [e] *N*-Benzyldiphenylmethyleneimine.

SCHEME I



diphenylmethylamine in benzene, indicating that **9** does not arise by this route. On the other hand, **8**[15] reacted smoothly with diphenylamine to afford **9** and ammonia.

In conclusion, the primary products from the reaction of benzylamines with nitrosobenzene appear to be azoxybenzene and imines resulting from oxidation of the starting amines. This is followed by amine exchange to give substituted imines.

Experimental Section

Melting points and boiling points are uncorrected. Gas-liquid chromatographic separations were accomplished using either a 6 ft × 0.125 in. 3% OV-17 on 80/100 Chromosorb W (column A) or a 6 ft × 0.125 in. 10% OV-1 on 80/100 Chromosorb W column (column B). Nmr data were obtained on either a Varian A-60 or HR-220 instrument. Nitrosobenzene was sublimed prior to use. Benzylamine, *p*-methoxybenzylamine, and diphenylmethylamine were commercial materials, distilled before use. Authentic samples of products were either obtained commercially or prepared by standard procedures.

Reaction of Nitrosobenzene with Benzylamine. General Procedure.—Benzylamine (214 mg, 2 mmol) and nitrosobenzene (214 mg, 2 mmol, or 428 mg, 4 mmol; see Table I) were dissolved in 5 ml of the appropriate solvent, bibenzyl (184 mg, 1 mmol) was added as an internal standard, and the solution was kept at the appropriate temperature for the intervals listed in Table I. Analysis of the reaction mixtures was accomplished using column A and predetermined detector response factors for the products. As a typical procedure, a preparative reaction in DMSO is given. Nitrosobenzene (2.0 g, 18.7 mmol) and benzylamine (2.0 g, 18.7 mmol) in 50 ml of DMSO were kept at room temperature for 2 days, during which time the color gradually changed from green to orange. The mixture was diluted with water and extracted with ether; the ether solution was dried ($MgSO_4$) and concentrated on a rotary evaporator. Distillation of the residue afforded an orange oil (1.5 g), bp 85–100° (0.07 mm), consisting of *ca.* 44% azoxybenzene and 56% *N*-benzylbenzaldimine. The products were separated by glpc (3% OV-17 on 80/100 Chromosorb W) and identified by nmr and mass spectral comparisons with authentic samples. Further characterization of **3** was obtained by degradation and preparation of benzylamine picrate, mp 201–202° (lit.[16] mp 204–205°), and benzaldehyde phenylhydrazone, mp 156–157° (lit.[8] mp 156°).

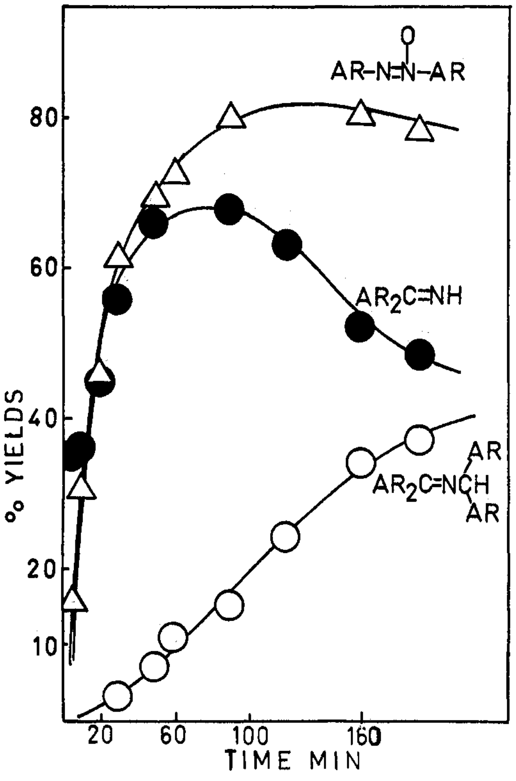


Figure 1.—Reaction of diphenylmethylamine with nitrosobenzene in benzene at 70°. The yields were determined by glpc (OV-1 column) using an internal standard and corrected for detector response.

Reaction of Diphenylmethylamine with Nitrosobenzene.—A solution of diphenylmethylamine (458 mg, 2.5 mmol), nitroso-

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[16] M. Pesez and J. Bartos, *Bull. Soc. Chim. Fr.*, 1122 (1963).

benzene (536 mg, 5.0 mmol), and *n*-tridecane (460.9 mg, 2.5 mmol, internal standard) in 5.5 ml of dry benzene was stirred under nitrogen at 70°. At appropriate intervals (Table I and Figure 1), the reaction solution was analyzed by glpc (column B) using predetermined detector response factors for the products which were identified by glpc retention times and, in the case of **8**, by preparative glpc and comparison with an authentic sample (see below).

Preparation of Imine 8.—The procedure described by Pickard and Tolbert[15] afforded **8** (66%), bp 127–129° (1.75 mm) [lit.[15] bp 127° (3.5 mm)].

Reaction of 8 with Diphenylmethylamine. Preparation of Imine 9.—A solution of **8** (1.83 g, 0.01 mol) and diphenylmethylamine (1.81 g, 0.01 mol) in 20 ml of dry benzene was refluxed for 30 hr. Removal of solvent on a rotary evaporator and recrystallization of the resulting white solid from ethanol gave 2.8 g (81%) of **9** as white flakes, mp 149–150° (lit.[6b] mp 153). An attempted preparation of **9** by refluxing benzophenone and diphenylmethylamine in benzene for 48 hr with azeotropic distillation of any water formed resulted in recovery of starting materials with no evidence of **9** detected by glpc.

Registry No.—**8** (Ar = Ph), 1013-88-3; **9** (Ar = Ph), 5350-59-4; nitrosobenzene, 586-96-9; benzylamine, 100-46-9; *p*-methoxybenzylamine, 2393-23-9; diphenylmethylamine, 91-00-9.

Dimerization of Phospholium Ions[1]

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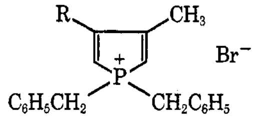
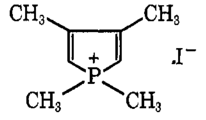
Quaternary salts have been prepared for many of the phospholes synthesized since the recognition of the existence of this ring system in 1959. In every case,[2] the salts have been assigned monocyclic structures with alkylation at phosphorus, although spectral changes in solutions of the benzyl bromide salt of 1-methylphosphole were suggestive of dimerization.[3] On the other hand, dimerization of phosphole 1-oxides can be quite rapid, and in some instances only the dimer can be isolated.[2] This behavior is consistent with the 4-π-electron system of the phosphole oxides and indeed might be expected for the phospholium salts as well. In characterizing some phospholes prepared in a recent study,[4] salts have been isolated which do indeed exhibit dimeric structure. They are described in this paper.

When monomeric structure is present in a salt, it is easily recognized from the simplicity of the proton nmr spectrum. Some examples are given in Table I. Furthermore, monomer character is also revealed by the presence of only one ^{31}P nmr signal; for a D_2O solution of **3**, for example, the signal appeared at −34.4 ppm.[5]

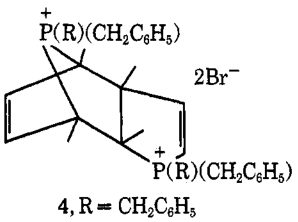


1, R = CH_3
2, R = H



3

The benzyl bromide salt (**4**) of 1-benzylphosphole, as well as the benzyl bromide salt (**5**) of 1-(2-phenylethyl)phosphole, had much more complex nmr spectra. They were incompatible with monomeric structure, but were suggestive of the molecular framework demonstrated[6] for phosphole oxide dimers. In particular, the presence of signals attributable to protons on saturated ring carbons (3.2–4.1 ppm) and the complexity of the *P*-benzyl signal point in this direction. Dimer structure imposes different character on the benzyl groups of each phosphorus atom; in **4**, all four benzyls are in structurally different environments, and in **5** stereoisomeric forms may be present. The *P*-benzyl absorption in both structures would then be a complex composite, rather than a doublet as observed in the monomer. The ^{31}P nmr spectrum for one salt (**4**) provided confirmation of the dimeric structure; two signals were observed (−51.6 and −53.1 ppm in $CDCl_3$), indicating that two structurally different phosphorus atoms were present. Furthermore, the signals were present in equal intensity.



4, R = $CH_2C_6H_5$
5, R = $CH_2CH_2C_6H_5$

It is of significance that we have encountered dimeric salts only for phospholes without a C substituent;[7] 3,4-dimethylphospholium ions (**1** and **3**) remain monomeric, probably through steric crowding encountered in the construction of the bicyclic structure. 3,4-Dimethyl substitution in phosphole oxides has been noted to reduce the east of dimerization in this family

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[1] Taken in part from the Ph.D. Dissertations of S. G. B. (1972) and J. F. E. (1971). Supported by Public Health Service Research Grant CA-05507 from The National Cancer Institute. The Bruker nmr system was purchased in part with funds from the National Science Foundation (Grant No. 10301).

[2] The earlier work has been reviewed: A. N. Hughes and C. Srivanavit, *J. Heterocycl. Chem.*, **7**, 1 (1970). See also ref 7, and F. Mathey and R. Mankowski-Favelier, *Org. Magn. Resonance*, **4**, 171 (1972).

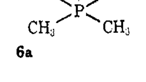
[3] L. D. Quin, J. G. Bryson, and C. G. Moreland, *J. Amer. Chem. Soc.*, **91**, 3308 (1969).

[4] L. D. Quin, S. G. Borleske, and J. F. Engel, *J. Org. Chem.*, **38**, 1858 (1973).

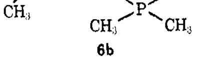
[5] All ^{31}P measurements in this study were performed under conditions of proton decoupling; this gives a sharp singlet and eliminates overlapping of two ^{31}P signals of similar chemical shift, as seen in the phosphole dimers. Spectra were determined at 36.4 MHz on a Bruker HFX-10 spectrometer.

[6] Y. H. Chiu and W. Lipscomb, *J. Amer. Chem. Soc.*, **91**, 4150 (1969).

[7] Two phosphole salts with one C substituent have been prepared that also appear to be dimeric from their ^{31}P nmr spectra. The methiodide (**6**) of 1,3-dimethylphosphole had 1:1 signals at −55.3 and −56.4 ppm (D_2O solution), and the methiodide of 1,2-dimethylphosphole had signals at −58.4 and −59.4 ppm (CF_3COOH solution), also 1:1 in intensity. The C substituent introduces the possibility of positional isomerism in the dimers (*e.g.*, **6a** and **6b** for **6**) and the exact structures of these salts remains unknown at this time.



6a



6b