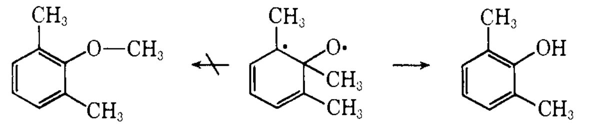
appreciable (less than 0.2%) 2,6-dimethylanisole, which might be expected by a simple 1,2 shift of methyl in the intermediate.



Preliminary investigation of nitrobenzene oxidation (at 100°) by the usual Hg-N_2O technique gave 20% phenol and 16% *o*-, 4% *m*-, and 60% *p*-nitrophenol. While such behavior can be rationalized by the known ability[8] of the nitro group to facilitate free-radical attack at the *ortho* and *para* positions, direct photolysis of nitrobenzene[13] under similar conditions in a helium atmosphere gave 28% nitrosobenzene, 51% phenol, and about the same ratio of nitrophenols (4% *o*-, 1% *m*-, and 16% *p*-).

Two chief limitations of the Hg-N_2O technique are formation of tar and direct photolysis. The amount of tar varies with the reactivity of the substrate; the weight ratio of tar to volatile product under comparable conditions was 0.2 for anisole and 2 for benzotrifluoride. The calculation of partial rate factors in the present work presumes that tar formation occurs nonselectively (if at all) from intermediates leading to the phenols. While this assumption has been shown to be valid in the attack of some radicals upon aromatic rings,[14] its application to the present case can be considered justified only by the consistent nature of the results which emerge. Direct photolysis of the substrate occurred with anisole and nitrobenzene; of the halobenzenes, chloro- and bromobenzene give rise to halobiphenyls so readily[15] that only fluorobenzene can be studied by the Hg-N_2O technique.

As far as we are aware, the present work constitutes the most extensive investigation of aromatic substitution in the gas phase. The absence of solvent effects and greater certainty about the identity of the reacting molecules (absence of molecular aggregates) should make this system more amenable to theoretical treatment than liquid-phase aromatic substitutions. In this respect a plot of the logarithm of the partial rate factors, for attack of O(^{3}P) upon nuclear C–H positions on the present alkylbenzenes, gives a fair linear plot *vs.* the ground-state electron density as calculated[16] for individual positions using the CNDO II approximation. This plot implies that the reaction of O(^{3}P) with aromatic hydrocarbons has an early transition state. The correlation further predicts that positions *ortho* to alkyl groups should be more reactive than *para* positions as found. More elaborate calculations involving the oxygen atom would appear worthwhile.

(13) A previous report on photolysis of nitrobenzene listed only nitrosobenzene and *p*-nitrophenol as products: S. H. Hastings and F. A. Matsen, *J. Amer. Chem. Soc.*, 70, 3514 (1948).

(14) D. H. Hey, M. J. Perkins, and G. H. Williams, *Chem. Ind.* (London), 83 (1963); R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, *J. Amer. Chem. Soc.*, **84**, 4152 (1962).

(15) *Cf.* N. Kharasch, R. K. Sharma, and H. B. Lewis, *Chem. Commun.*, 418 (1966).

(16) We are indebted to Mr. John M. McKelvey for assistance in these calculations.

Erling Grovenstein, Jr., Arthur J. Mosher
School of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

Received March 11, 1970

Reactions of Sulfur with Benzylamine[1]

Sir:

Primary amines have been successfully used in the Willgerodt-Kindler reaction[2] where, in addition to normal products, they can lead to novel types of compounds.[3] They have also been used as catalysts in various reactions between elemental sulfur and organic substrates.[4-6] Nevertheless, almost nothing is known of the reaction of sulfur with primary amines.[7,8] We describe here work showing thiodiamines[9] and arylimine polysulfides[10] to be interconverting intermediates in the reaction of sulfur with benzylamine.

With *excess* benzylamine sulfur serves, in an overall sense, as an oxidizing agent. The final products are ammonia, benzylammonium polysulfides, and N-benzylidenebenzylamine, as shown[11] in eq 1 where $x \simeq 6$–7. We propose (eq 2–6) to account for these products[12] where eq 4 is base catalyzed and eq 5 is catalyzed by

$$x\text{S} + 4\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \longrightarrow \text{C}_6\text{H}_5\text{CH}{=}\text{NCH}_2\text{C}_6\text{H}_5 + \text{NH}_3 + (\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3{}^+)_2\text{S}_x{}^{2-} \quad (1)$$

sulfide. Pertinent evidence in support of this scheme follows.

$$(a+1)\text{S} + 2\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \rightleftharpoons \text{H}_2\text{S} + \text{C}_6\text{H}_5\text{CH}_2\text{NHS}_a\text{NHCH}_2\text{C}_6\text{H}_5 \quad (2)$$

$$(x-1)\text{S} + 2\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 + \text{H}_2\text{S} \longrightarrow (\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3{}^+)_2\text{S}_x{}^{2-} \quad (3)$$

$$3\text{C}_6\text{H}_5\text{CH}_2\text{NHS}_a\text{NHCH}_2\text{C}_6\text{H}_5 \longrightarrow \text{C}_6\text{H}_5\text{CH}{=}\text{NS}_b\text{N}{=}\text{CHC}_6\text{H}_5 + 4\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 + (3a-b)\text{S} \quad (4)$$

$$\text{C}_6\text{H}_5\text{CH}{=}\text{NS}_b\text{N}{=}\text{CHC}_6\text{H}_5 + 2\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \rightleftharpoons 2\text{C}_6\text{H}_5\text{CH}{=}\text{NH} + \text{C}_6\text{H}_5\text{CH}_2\text{NHS}_b\text{NHCH}_2\text{C}_6\text{H}_5 \quad (5)$$

$$\text{C}_6\text{H}_5\text{CH}{=}\text{NH} + \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 \longrightarrow \text{C}_6\text{H}_5\text{CH}{=}\text{NCH}_2\text{C}_6\text{H}_5 + \text{NH}_3 \quad (6)$$

The initial steps (reactions 2 and 3) are written based on analogy with previous findings. Tertiary amines (when very pure) are known to be inert to sulfur[7,13] under normal conditions but lead to trialkylammonium polysulfides when hydrogen sulfide is added.[14] Secondary amines react with sulfur to give hydrogen sulfide (isolated as the alkylammonium polysulfide[15]) along

---

(1) Supported under a grant from the National Research Council, Canada.

(2) M. Carmack, *Org. Reactions*, 3, 83 (1946); F. Asinger and H. Offermanns, "Syntheses mit Ketonen, Schwefel und Ammoniak bzw. Aminen und Chemisches Verhalten der Reaktions Produkte," Opalden, W. Germany, 1966.

(3) F. Asinger and H. Offermanns, *Angew. Chem., Int. Ed. Engl.*, **6**, 907 (1967), and references cited therein.

(4) B. D. Vineyard, *J. Org. Chem.*, **32**, 3833 (1967).

(5) G. Petry and W. Scheele, *Kaut. Gummi Kunstst.*, 20, 518 (1967).

(6) F. Asinger, W. Schaefer, and H. Triem, *Monatsh. Chem.*, **97**, 1510 (1966).

(7) R. E. Davis and H. F. Nakshbendi, *J. Amer. Chem. Soc.*, **84**, 2085 (1962).

(8) A. P. Zipp and S. G. Zipp, *Sulfur Inst. J.*, 2 (1968).

(9) Houben-Weyl, "Methoden Organischen Chemie," Vol. XI, Pt. 2, Georg Thieme Verlag, Stuttgart, 1958, pp 744–751.

(10) Y. Sasaki and F. P. Olsen, *Chem. Commun.*, 1424 (1969).

(11) This experimentally verifiable equation is obtained by suitable combination of eq 2–6.

(12) Catenated sulfur species need not be of uniform chain length. The isolated benzylammonium polysulfide averaged about six to seven sulfurs per chain while the arylimine polysulfides appeared mainly with four sulfurs and somewhat less commonly with two or three. No estimate of the sulfur chain length in the thiodiamines is available.

(13) P. D. Bartlett, E. F. Cox, and R. E. Davis, *J. Amer. Chem. Soc.*, **83**, 103 (1961); P. D. Bartlett, R. E. Davis, and W. R. Roderick, *ibid.*, **83**, 109 (1961).

(14) H. Krebs, E. F. Weber, and H. Balters, *Z. Anorg. Allg. Chem.*, **275**, 147 (1954).

with tetraalkylthiodiamines,[16] while primary amines evolve hydrogen sulfide (isolated as the alkylammonium polysulfide[17]). The other product from the primary amine must also be a thiodiamine. Steps 2–4 were examined independently of steps 5 and 6 by adding a sulfide scavenger to suppress the sulfide-catalyzed reaction (5). The resulting products (in the presence of lead oxide) were benzylidenimine polysulfides.[10] The stoichiometry given in (7) accounts for over 90% of the

$$(b + 3)\mathrm{S} + 2\mathrm{C_6H_5CH_2NH_2} \longrightarrow \mathrm{C_6H_5CH{=}NS_bN{=}CHC_6H_5} + 3\mathrm{H_2S} \quad (7)$$

benzylamine under these conditions.[11] Benzylidenimine tetrasulfide exposed to benzylamine in the presence of lead oxide survived for at least 24 hr at room temperature with little change except for equilibration of the sulfur chain length (*i.e.*, tetrasulfide gave a mixture of sulfur and di-, tri-, and tetrasulfides). Small amounts of unsymmetrical mixed amine–imine polysulfides, $C_6H_5CH{=}NS_xNHCH_2C_6H_5$, were also formed under these conditions.

In the *absence* of lead oxide benzylidenimine tetrasulfide was quite reactive toward benzylamine, forming ammonia, N-benzylidenebenzylamine, and benzylammonium polysulfides (eq 8).[11]

$$3\mathrm{C_6H_5CH{=}NS_4N{=}CHC_6H_5} + 20\mathrm{C_6H_5CH_2NH_2} \longrightarrow 11\mathrm{NH_3} + 11\mathrm{C_6H_5CH{=}NCH_2C_6H_5} + 2(\mathrm{C_6H_5CH_2NH_3^+})_2\mathrm{S_6^{2-}} \quad (8)$$

Exchange of one amine for another (eq 5) has been previously observed in thiodiamines[18] and is expected to occur here in the presence of the excess benzylamine. The observed unsymmetrical material isolated in the presence of lead oxide is most likely an intermediate in this reaction. Benzylidenimine is quite reactive toward nucleophiles[20] and has been previously[21] proposed to react with benzylamine to give N-benzylidenebenzylamine and ammonia (eq 6). The other product in (5), a thiodiamine, decomposes according to (4) to regenerate more benzylidenimine polysulfide. The probable intermediacy of thiodiamines in the scheme was substantiated by examining the decomposition of an authentic sample of benzylamine disulfide (prepared from sulfur monochloride and benzylamine). Although fairly stable in the absence of base (eventually undergoing autocatalytic decomposition), the sample underwent rapid decomposition in the presence of small amounts of base at room temperature. The product of these decompositions was N-benzylidenebenzylamine and ammonia (about 80% of theory) along with smaller amounts of benzylidenimine tetrasulfide and benzylammonium polysulfides. As required by (2–6) the ammonia : benzylidenebenzylamine ratio as well as the benzylidenimine tetrasulfide : benzylammonium polysulfide ratio were both near 1:1. When the autocatalyzed decomposition was monitored by nmr, benzylamine and benzylidenimine tetrasulfide (about 4:1 molar ratios) were observed to increase to a maximum concentration in the early stages of the decomposition and later to decrease in amount as the concentration of N-benzylidenebenzylamine increased. A direct decomposition of the thiodiamine to sulfur, ammonia, and N-benzylidenebenzylamine was therefore eliminated.

Additional evidence for a benzylidenimine polysulfide–thiodiamine "cycle" was obtained by allowing *p*-methoxybenzylidenimine tetrasulfide to react with unsubstituted benzylamine. As required by (2–6), all of the amine obtained by hydrolysis of the N-benzylidenebenzylamine formed was unsubstituted; all of the *p*-methoxy substituent was present in the aldehyde. Not all of the aldehyde formed was substituted, however; the ratio of anisaldehyde to benzaldehyde was 1.3:1 (required by (2–6), 1.2:1).

The ease with which these reactions occur—a few hours or less at room temperature—suggests that they may well play a role in the various sulfur–primary amine reactions[2-6] involving organic substrates.

Fredric P. Olsen, Yukihiko Sasaki
Department of Chemistry, McMaster University
Hamilton, Ontario, Canada

Received January 17, 1970

---

[15] T. G. Levi, *Gazz. Chim. Ital.*, **60**, 975 (1930).

[16] H. Jenne and M. Becke-Goehring, *Chem. Ber.*, **91**, 1950 (1958); T. G. Levi, *Gazz. Chim. Ital.*, **61**, 286 (1931); P. Longi, R. Montagna, and R. Mazzocchi, *Chim. Ind.* (Milan), **47**, 480 (1965).

[17] M. G. Voronkov and A. Ya Legzdyn, *Zh. Org. Khim.*, **3**, 465 (1967).

[18] Either aniline with N-methylaniline disulfide or N-methylaniline with aniline disulfide results in rapid disproportionation to aniline, N-methylaniline, aniline disulfide, N-methylaniline disulfide, and the mixed aniline–N-methylaniline disulfide.[19]

[19] J. Barrick and F. P. Olsen, unpublished observations.

[20] T. L. Tolbert and B. Houston, *J. Org. Chem.*, **28**, 695 (1963).

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

Reactions of Organocopper Reagents with Oxiranes

Sir:

The nucleophilic ring opening of oxiranes by organometallic reagents is a useful synthetic method which has been limited in scope due to competing reactions arising from either the Lewis acidity or the basicity of the organometallic reagent.[1] We have found that lithium dimethylcuprate[2] and lithium diphenylcuprate[3] appear to be excellent reagents for the nucleophilic ring opening of oxiranes under mild conditions. Such reagents show promise of largely circumventing the side reactions encountered with other organometallic reagents.

Lithium dimethylcuprate reacts with propylene oxide and 1,2-epoxybutane to give the expected secondary alcohols as predominant products.

The reactions of cyclohexene oxide with some organocopper and organolithium reagents are summarized in Table I. These results indicate that lithium dialkylcuprates are more reactive toward oxiranes than the corresponding alkyllithiums and possibly are superior to the alkyllithiums with respect to yields of nucleophilic addition product. On the other hand, polymeric methylcopper[4] and methylcopper complexed with trimethyl phosphite[4] or tri-*n*-butylphosphine[2a] gave

---

[1] A. Rosowsky in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part I, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, pp 386–417.

[2] (a) H. O. House, W. L. Respess, and G. M. Whitesides, *J. Org. Chem.*, **31**, 3128 (1966); (b) H. Gilman, R. G. Jones, and L. A. Woods, *ibid.*, **17**, 1630 (1952).

[3] (a) G. M. Whitesides, W. F. Fischer, Jr., J. San Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969); (b) P. Rona, L. Tokes, J. Tremble, and P. Crabbe, *Chem. Commun.*, 43 (1969).

[4] H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **33**, 949 (1968).