phenylindanone (V), m.p. 82–83° (recrystallized from 95% ethanol). Its infrared spectrum showed principal bands at 698, 710, 740, 760, 1222, 1492, 1605, 1702, 2915, and 3030 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.68; H, 6.17.

Dehydrogenation of I through Disodio Salt II to Form X.—To a stirred solution of 24.4 g. (0.1 mole) of 2,3-dibromo-2,3-dimethylbutane (IX)[25] in dry ether was added, during 30 min., a solution of 0.05 mole of disodio salt II in 200 ml. of liquid ammonia. The red color of II was discharged immediately, but the reaction mixture soon darkened. The resulting brown mixture was stirred for 30 min., and the ammonia was replaced by ether. The resulting yellow-green suspension was filtered, and the solvent was removed from the filtrate. The residue was placed immediately on an alumina column. The column was eluted immediately[26] with hexane to remove the excess dibromide IX, and then with 20% benzene–hexane to remove 3-phenylindenone (X), which was obtained as a yellow-orange oil on evaporation of the solvent, yielding 4.1–5.2 g. (40–50%). Its infrared spectrum (liquid film) showed principal bands at 693, 752, 765, 1621, and 1713 cm.$^{-1}$. Compound X produced an emerald green color with concentrated sulfuric acid.[14] Compound X (0.67 g.) was treated with 0.6 g. of *p*-nitrophenylhydrazine in ethanol–hydrochloric acid[27] at 40° for 45 min. to afford *p*-nitrophenylhydrazone XI in 90–92% yield. After recrystallization from acetonitrile, XI melted at 266–267°, lit.[13] m.p. 266–267°. Compound XI produced a blue color with aqueous sodium hydroxide.[13]

Anal. Calcd. for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31. Found: C, 74.01; H, 4.56; N, 12.28.

Independent synthesis of XI was effected from 2-bromo ketone XII[12] and the *p*-nitrophenylhydrazine reagent.[27,13] The product had m.p. 266–267°, undepressed on admixture with a sample of XI prepared from X as described above. Infrared spectra of the two samples were identical.

Attempted Preparation of X from 3-Hydroxy Ester XIII.—A 0.3-g. sample of ethyl 3-hydroxy-3,3-diphenylpropionate (XIII)[28] was dissolved in 3 ml. of concentrated sulfuric acid to produce the emerald-green color indicative of the formation of 3-phenylindenone (X, see above) but, on standing 24 hr. at room temperature as described by de Fazi,[14] the color changed to brown. There was isolated only a white powder, m.p. 205–235° (recrystallized from 95% ethanol), which was presumably a mixture of α- and γ-diphenyltruxones, m.p. 253 and 224°, respectively.[29] Similar results were obtained with ester XIII and with the corresponding acid employing 96% sulfuric acid for 30 min. or 3 hr. and 90% sulfuric acid for 12 hr. When the ester was treated with 80% or 60% sulfuric acid for 12 hr., and with polyphosphoric acid for 3 or 12 hr., the emerald-green color failed to appear, and the only product isolated was 3-phenylcinnamic acid. When the acid corresponding to XIII was treated similarly, it was largely recovered.

Dehydrogenation of 2,3-Diphenylindanone to Form XVI.—2,3-Diphenylindanone was prepared in 60% yield from 2,3,3-triphenylpropionic acid[30] through its acid chloride, which was cyclized with aluminum chloride.[16,22] The product melted at 99–100°, lit.[16] m.p. 100–101°.

A dry, ethereal solution of 1.42 g. (0.005 mole) of 2,3-diphenylindanone was added dropwise to a stirred suspension of 0.01 mole of sodium amide in 150 ml. of liquid ammonia; the mixture was stirred for 30 min. To the resulting deep red solution containing XV was added, with stirring, a dry, ethereal solution of 1.22 g. (0.005 mole) of dibromide IX. After 60 min., the ammonia was replaced by ether, and the mixture was filtered. The solvent was removed from the filtrate, and the residue recrystallized from hexane to give 0.99 g. (70%) of 2,3-diphenylindenone (XVI) as red needles, m.p. 152–153°, lit.[31] m.p. 150–151°.

Dehydrogenation of 2,3,3-Triphenylpropionitrile to Form XVII.—2,3,3-Triphenylpropionitrile[8] (3.55 g., 0.0125 mole) was converted to its dipotassio salt VII,[32] which was treated with a molecular equivalent of dibromide IX essentially as described above for disodio salt XV. During the addition of IX, the red color of VII changed to intense purple, which faded to brown when the addition was complete. There was obtained 2.45 g. (70%) of 2,3,3-triphenylacrylonitrile (XVII), m.p. 165–166°, lit.[32] m.p. 165°.

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[25] This compound was prepared by bromination of 2,3-dimethylbutane, as described by A. V. Grosse and V. N. Ipatieff [*J. Org. Chem.*, **8**, 438 (1943)], and purified by chromatography on alumina.

[26] When the product was allowed to remain on the column overnight, the yellow-orange band became dark green and the yield of X was reduced considerably.

[27] Concentrated hydrochloric acid was added to a suspension of *p*-nitrophenylhydrazine (0.6 g.) in 95% ethanol until solution was achieved; then 5 drops more of the acid were added.

[28] W. R. Dunnavant, and C. R. Hauser, *J. Org. Chem.*, **25**, 503 (1960).

[29] R. de Fazi, *Gazz.*, **57**, 551 (1927).

[30] W. R. Dunnavant and C. R. Hauser, *Org. Syn.*, **40**, 38 (1960).

[31] G. Heyl and V. Meyer, *Ber.*, **28**, 2776 (1895).

[32] W. G. Kofron, W. R. Dunnavant, and C. R. Hauser, *J. Org. Chem.*, **27**, 2737 (1962).

The Reaction of Chloramine with Alkyl Sulfides[1]

JOSEPH A. COGLIANO AND GEORGE L. BRAUDE

The Research Division, W. R. Grace and Company, Washington Research Center, Clarksville, Maryland

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Organic sulfides react with chloramine to give a series of compounds having the probable general formula, $(R_2\overset{+}{S}NH\overset{-}{N}H)_2$, bis(iminodialkylsulfilimine) and its salts. It is postulated that a sulfiliminium salt is initially formed from sulfide and chloramine and then aminated by another mole of chloramine as is shown. The

$$R_2S + NH_2Cl \longrightarrow (R_2\overset{+}{S}\text{–}NH_2)\overset{-}{Cl} \xrightarrow{NH_2Cl} (R_2\overset{+}{S}\text{–}NH\overset{-}{N}H)_2HCl$$

labile hydrogen chloride can be removed completely by sublimation in the presence of sodium methylate to give the free base, $(R_2\overset{+}{S}NH\overset{-}{N}H)_2$. In solution and especially in the solid phase, this dimer is postulated as consisting of two betaine-type monomeric units held together in a six-membered ring by electrostatic attraction or by resonance stabilization. The monomer is capable of existence in the vapor phase.

Organic sulfides have, for many years, been known to react with aromatic N-chlorosulfonamides such as chloramine B and T to form sulfilimines.[2,3]

$$R_2S + p\text{-}CH_3C_6H_4SO_2NClNa \longrightarrow p\text{-}CH_3C_6H_4SO_2NSR_2 + NaCl$$

In a recent series of papers, Appel[4] described the preparation of similar compounds from chloramine, NH_2Cl, and O-aminosulfonic acid, NH_2OSO_3H.

$$R_2S + NH_2X \longrightarrow [R_2\overset{+}{S}NH_2]\overset{-}{X}$$

Previous to the publication of these studies, we treated sulfides with chloramine in the expectation of

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[1] Presented before the Organic Division at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[2] A. S. Ash, F. Challenger, and D. Greenwood, *J. Chem. Soc.*, 1877 (1951).

[3] F. G. Mann and W. J. Pope, *ibid.*, 1052 (1922).

[4] R. Appel, *et al.*, *Ann.*, **618**, 53 (1958); *Angew. Chem.*, **71**, 701 (1959); *Chem. Ber.*, **95**, 849 (1962).

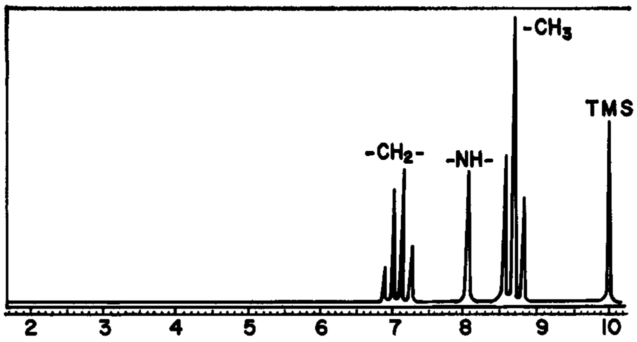


Fig. 1.—N.m.r. spectrum of bis(iminodiethylsulfilimine); solvent, carbon tetrachloride; filter band width, 4 c.p.s.; R_f field, 0.02 mg.; sweep time, 500 sec.; sweep width, 500 c.p.s.; sweep offset, 0.0 c.p.s.; and spectrum amperes, 1.0.

obtaining sulfilimines in analogy to the bimolecular displacement reaction of chloramine with tertiary amines.[5,6]

$$R_3N + NH_2Cl \longrightarrow [R_3\overset{+}{N}NH_2]\overset{-}{Cl}$$

Instead of the expected 1:1 addition product, $[R_2\overset{+}{S}NH_2]\overset{-}{Cl}$, two moles of chloramine reacted with one mole of sulfide to form a hydrochloride of bis(iminodialkylsulfilimine).[7]

$$2R_2S + 4NH_2Cl \longrightarrow [(R_2\overset{+}{S}NH\overset{-}{N}H)_2]HCl + 3HCl$$

Discussion

The preparation of the ethyl sulfide adduct was studied in detail to ascertain the properties of this general class of compounds. The reactions and proposed structures are summarized in Chart I. Similar compounds were obtained with dimethyl and di-*n*-butyl sulfides, indicating the generality of this reaction.

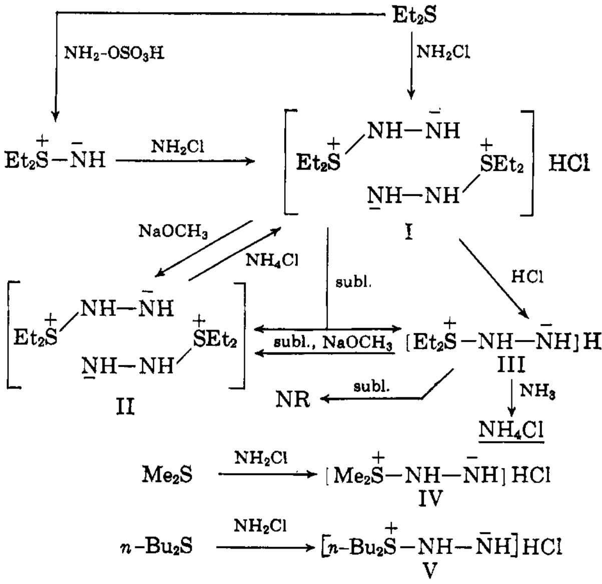
Addition of a mole of hydrochloric acid to bis(iminodiethylsulfilimine) hydrochloride (I) yielded iminodiethylsulfilimine hydrochloride (III). Both compounds could be converted to the free base, bis(iminodiethylsulfilimine) (II). Disproportionation occurs during vacuum sublimation of I to give II and III. In presence of sodium methoxide, only II is obtained (III is inert under these conditions unless a base is present to react with the hydrogen chloride allowing II to sublime).

The exact number of hydrogens could not be ascertained by elemental analysis. The area of the peaks of the proton magnetic resonance spectrum of II was measured and corresponded to 3:1:2 for CH_3, NH, and CH_2, respectively (see Fig. 1). This indicates a 1:1 ratio of nitrogen-bonded protons to ethyl groups (and therefore to nitrogen).

The position of the proton absorption was similar to that of the nitrogen-bonded proton of morpholine indicating a cyclic structure. This was substantiated by the infrared spectrum, in which the positions of the bands and their relative sharpness was typical for cyclic structures (see Fig. 2). In addition, no bands indicative of a primary amino group were detected.

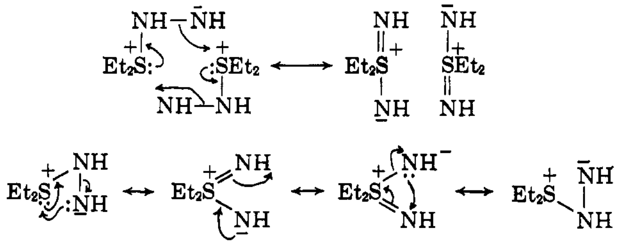
Ebullioscopic molecular weight determinations of II in benzene gave 158, a value intermediate between the monomer (mol. wt. 120.2) and dimer (mol. wt. 240.4). Mass spectrometry was indicative of a monomer since the last significant peak appeared at *m/e* of 120. The rate of effusion of the compound corresponded to a molecular weight of approximately 100.

CHART I



The proposed structure for this group of compounds as shown in Chart I is in agreement with these data. The dimers thus can be visualized as two betaine-type monomeric units held together either by electrostatic attraction or by resonance stabilization. In solution and especially in the vapor phase, this dimeric structure is largely destroyed.

Several alternate resonance structures can be visualized for the monomeric and the dimeric compounds.



Reaction Mechanism.—To understand the route of formation of these compounds and their structure, diethylsulfilimine was prepared from ethyl sulfide and O-aminosulfonic acid as described by Appel.[4] Its further reaction with chloramine to give I established diethylsulfilimine as a probable intermediate.[8]

The initial reaction is probably the formation of a sulfilimine salt from the sulfide and chloramine, which then is aminated by another mole of chloramine to give the iminosulfilimine salt (as shown below). Since

$$R_2S \xrightarrow{NH_2Cl} [R_2\overset{+}{S}\text{-}NH_2]\overset{-}{Cl} \xrightarrow{NH_2Cl} [R_2\overset{+}{S}\text{-}NHN\overset{-}{H}]HCl$$

the hydrogen chloride is labile in all these compounds, it is not known whether the sulfilimine or sulfiliminium chloride is the reactive species. The free sulfilimine,

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(5) G. M. Omietanski and H. H. Sisler, *J. Am. Chem. Soc.*, **78**, 1211 (1956).

(6) G. L. Braude and J. A. Cogliano, *J. Chem. Soc.*, 4172 (1961).

(7) Proposed nomenclature.

(8) Appel treated alkyl sulfides with chloramine in the presence of ether and obtained sulfilimines. We have shown that under these conditions the dialkylsulfilimine hydrochloride precipitates in the course of the reaction, because it is insoluble in nonpolar solvents. This material thus cannot undergo the further reaction with chloramine to the iminosulfilimine compounds which we have obtained in such solvents as alcohols.

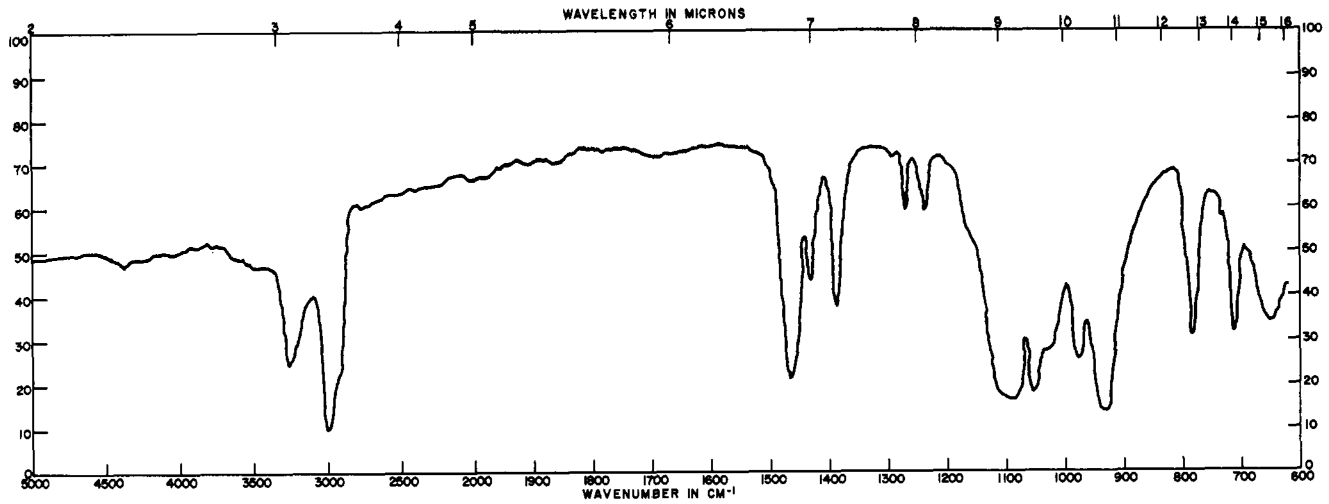
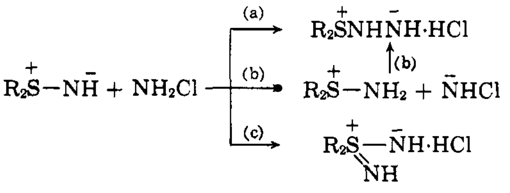


Fig. 2.—Infrared spectrum of bis(iminodiethylsulfilimine) in Nujol mull.

being a strong base, may abstract a proton from chloramine to give the chloramide ion which then reacts with the sulfiliminium salt (mechanism b). An alternate route may involve the displacement on nitrogen as in mechanism a or on sulfur, as in c.



$$R_2\overset{+}{S}-\overset{-}{N}H + NH_2Cl \begin{cases} \xrightarrow{(a)} R_2\overset{+}{S}NH\overset{-}{N}H\cdot HCl \\ \xrightarrow{(b)} R_2\overset{+}{S}-NH_2 + \overset{-}{N}HCl \\ \xrightarrow{(c)} R_2\overset{+}{S}(=NH)-\overset{-}{N}H\cdot HCl \end{cases}$$

Experimental

Bis(iminodiethylsulfilimine) Hydrochloride (I). A. From Chloramine and Diethyl Sulfide.—A stream of chloramine in excess ammonia, prepared by the method of Sisler[9] and filtered free of ammonium chloride, was introduced into 2 l. of 2-propanol containing 90 g. (1.0 mole) of diethyl sulfide at the rate of 0.01 mole/min. An external water bath was used to maintain the solution near room temperature. Three moles of chloramine was added over a 5-hr. period. Absorption was quantitative as evidenced by the absence of chloramine in the vented gas from the reaction vessel. The reaction mixture was filtered, and the filtrate was evaporated under vacuum to give 147 g. of a brownish oil. The oil was diluted with 75 g. of acetone and crystallized by cooling to 8–10° for 1 week. The precipitate obtained was filtered, washed with 2-propanol, and dried, yielding 32 g. (23% yield) of colorless crystals, m.p. 91–93°. Recrystallization from 2-propanol–acetone raised the melting point to 94.2–95.8° (decompn. 186°).

Anal. Calcd. for $C_8H_{25}ClN_4S_2$: C, 34.70; H, 9.10; Cl, 12.81; N, 20.23; S, 23.16. Found: C, 34.73; H, 9.57; Cl, 12.97; N, 20.19; S, 23.55.

This compound was found to contain one acidic and one basic group per molecule by titration, did not react with benzaldehyde, and displayed no oxidizing (KI) or reducing (KIO_3) properties in aqueous solution. The pure crystals were soluble in water (hygroscopic) and hot 2-propanol or methanol, and insoluble in carbon tetrachloride, acetone, ether, hexane, and benzene.

The product was prepared also more conveniently without removal of ammonium chloride from the chloramine-containing gas stream. In a concentric submerged spray nozzle, chlorine gas was introduced into the reaction solution through the central opening at the rate of 3 g. of chlorine per minute. Gaseous anhydrous ammonia was simultaneously added through the outer nozzle at the rate of 7 g. per minute. The solution contained 90 g. (1.0 mole) of diethyl sulfide in 2 l. of 2-propanol. The gas introduction was continued until a total of 385 g. (5.4 moles) of chlorine was added. The reaction mixture was filtered and washed with 2-propanol. The combined filtrates were concentrated under vacuum to a sirupy slurry weighing 144 g. Crystals deposited on cooling were filtered, yielding 38.8 g. of bis(iminodiethylsulfilimine) hydrochloride, m.p. 91.5–96°. A second crop of 5.5 g. was obtained on further evaporation of the filtrate and addition of acetone. The over-all yield was 44.3 g. (32%). Mixture melting point of the recrystallized material with a known sample of I proved the compounds to be identical.

B. From Diethylsulfilimine.—Following the method described by Appel,[4] a solution of 12.7 g. (0.141 mole) of ethyl sulfide in 100 ml. of methanol was added to 100 ml. of methanol containing 3.3 g. (0.143 g.-atom) of sodium. Fifty milliliters of methanol containing 9.1 g. (0.08 mole) of O-aminosulfonic acid then was introduced slowly over a 15-min. period. Slight heating was noticed during the addition. The mixture was heated to reflux, cooled, and filtered. The filtrate was evaporated under vacuum to give 7.3 g. of a brownish oil.

To check its composition, a portion of this oil (2.0 g.) was treated in 10 ml. of water with 10 ml. of a picric acid solution saturated at 50°. Orange-yellow needles were precipitated, m.p. 113.5–114.5°. The melting points for the picric acid salt of diethylsulfilimine are reported to be 111 and 115°.[4]

A 5.3-g. sample of the crude diethylsulfilimine as prepared above was dissolved in 2-propanol and treated with 0.3 mole of gaseous chloramine in excess ammonia. The resulting slurry was filtered to remove the ammonium chloride, and the filtrate was evaporated under vacuum. Excess acetone was added, precipitating 2 g. of white crystals, m.p. 89–93°. Recrystallization from 2-propanol–acetone raised the melting point to 92.5–95°. The ionic chloride content of this sample was 12.5% (calcd. for $C_8H_{25}ClN_4S_2$, 12.8%).

Bis(iminodiethylsulfilimine) (II). A. By Reaction of I with Sodium Methoxide.—A 73-ml. portion (0.05 mole) of a 0.68 *N* solution of sodium methoxide in 2-propanol was treated with 13.7 g. (0.05) of I dissolved in 2-propanol. The sodium chloride was filtered and the solvent was evaporated at room temperature under vacuum. The residue was recrystallized from acetone to give hygroscopic crystals melting at 43–49° which could easily be sublimed at 80° under vacuum.

In an attempt to duplicate this experiment on a larger scale, 420 ml. (0.25 mole) of 0.6 *N* sodium methoxide in methanol was added to a methanolic solution containing 68.6 g. (0.25 mole) of I. Upon evaporation under vacuum, 92 g. of oil was obtained. The oil was transferred to a distillation flask and heated under 10-mm. pressure. Rapid decomposition occurred causing disruption of the apparatus.

B. By Sublimation of I.—A 4-g. sample of bis(iminodiethylsulfilimine) hydrochloride (I) was placed in a sublimation apparatus and heated to 80° at 0.1 mm. A low melting (47.5–49°) solid slowly sublimed (*ca.* 1.5 g.).

Anal. Calcd. for $C_4H_{12}N_2S$: C, 39.96; H, 10.06; N, 23.30; S, 26.67. Found: C, 39.76; H, 9.68; N, 23.13; S, 26.87.

The sublimation residue crystallized after standing for 1 week. On recrystallization from hot 2-propanol, a white solid, m.p. 76.5–77.5, was obtained; it was believed to be iminodiethyl-

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[9] H. H. Sisler, F. T. Neth, R. S. Drago, and D. Yaney, *J. Am. Chem. Soc.*, **76**, 3906 (1954).

sulfilimine hydrochloride (III). A known sample of III had a melting point of 75–77°.

Potentiometric titration of II with perchloric acid in glacial acetic acid gave an equivalent weight of 118.9 (calcd. 120.2). Only one of the nitrogens in the monomeric unit is thus basic. A molecular weight determination, run with 0.45 g. of II in 10.21 g. of benzene, gave a freezing depression of 1.43° (calcd. mol. wt. 158).

Reaction of II. A. With Hydrochloric Acid: Formation of Iminodiethylsulfilimine Hydrochloride (III).—To 1.79 g. (0.0075 mole) of the chloride-free sublimate in 10 ml. of 2-propanol was added 7 ml. (0.0067 mole) of a 0.96 *N* 2-propanol solution of hydrochloric acid. Ether (20 ml.) precipitated crystals which were filtered and recrystallized from 2-propanol–ether to give a white crystalline solid, m.p. 75–77°. A test for ionic chloride gave 22.3% (calcd. for $C_4H_{13}ClN_2S$: 22.6%).

B. With Ammonium Chloride: Formation of Bis(iminodiethylsulfilimine) Hydrochloride (I).—A sample of the chloride-free solid was dissolved in excess 2-propanol. Ammonium chloride was added and the mixture was heated repeatedly on the steam bath followed by partial vacuum stripping. After cooling, seeding with a known sample of I produced crystals having a melting point of 90–91°. This compound required 92.5% of theoretical equivalent of base in aqueous titration.

Iminodiethylsulfilimine Hydrochloride (III).—A solution of 2.74 g. (0.01 mole) of I in a few milliliters of 2-propanol was treated with 10 ml. (0.0096 mole) of 0.96 *N* hydrochloric acid in 2-propanol. Ether was added to precipitate the product, which was recrystallized from 2-propanol–ether to give colorless crystals of III, m.p. 75–77°. Analysis gave 22.4% ionic chloride (theoretical: 22.6%).

Addition of ammonia into a 2-propanol solution of III precipitated ammonium chloride. No solid could be obtained from the filtrate. It is believed that an equilibrium is present between the free base and the monochloride, and possibly the dichloride, in the presence of ammonia. This mixture then depresses the melting point of II, making the isolation of the solid difficult. The free base (II) is probably present in the largest concentration, since ammonia appears to be a strong enough base to precipitate ammonium chloride from I.

Compound III did not sublime on heating to 85° under 0.1-mm. pressure except when solid sodium methylate was mixed with the crystals beforehand. Under these conditions, II was obtained.

Iminodimethylsulfilimine Hydrochloride (IV).—Gaseous chloramine (1.65 moles) in excess ammonia was treated with 2 l. of 2-propanol containing 31 g. (0.5 mole) of dimethyl sulfide, as described above for diethyl sulfide. The reaction was maintained at room temperature for 45 min. and filtered to remove ammonium chloride. The filtrate then was evaporated to dryness, yielding a viscous residue which slowly crystallized. The melting point was 111–113° (decompn. 172°).

Anal. Calcd. for $C_2H_9ClN_2S$: C, 18.67; H, 7.05; N, 21.78; S, 24.93. Found: C, 18.39; H, 6.53; N, 21.71; S, 25.20.

Iminodi-*n*-butylsulfilimine Hydrochloride (V).—Filtered chloramine (2.9 moles) was bubbled through 146 g. (1 mole) of *n*-butyl sulfide in 1 l. of 2-propanol, as described above. The reaction mixture was filtered, and the filtrate was evaporated under vacuum at room temperature to give a semisolid material. A 20-g. sample (about 0.05 mole) of this material was dissolved in 100 ml. of cold 2-propanol, heated to 45°, and filtered. The clear filtrate was then combined with 40 ml. (0.04 mole) of a 2-propanol solution of hydrochloric acid. Upon cooling, 4.5 g. of flat white plates were obtained. These plates were recrystallized from warm 2-propanol, m.p. 131–132°.

Anal. Calcd. for $C_8H_{21}ClN_2S$: C, 45.15; H, 9.95; Cl, 16.66; N, 13.17; S, 15.07. Found: C, 44.49; H, 9.98; Cl, 16.59; N, 12.71; S, 15.20.

Reaction of Dioctyl Sulfide with Chloramine.—An 81-g. sample (0.32 mole) of dioctyl sulfide dissolved in 244 g. of 2-propanol was treated with 2.25 moles of filtered chloramine at room temperature. The ammonium chloride was filtered from the reaction mixture at room temperature and the filtrate was evaporated under vacuum to give a waxy solid. Attempts to isolate a crystalline product so far have been unsuccessful.

Acknowledgment.—The authors are indebted to J. N. Lomonte, J. L. McClanahan, and G. L. Kearns of W. R. Grace and Company for infrared, nuclear magnetic resonance, and mass spectrographic studies and to H. H. Sisler and G. A. Russell for their valuable comments.

Competing Reactions in the Ozonation of Anthracene

PHILIP S. BAILEY, PER KOLSAKER, BISWAJIT SINHA, JOSEPH B. ASHTON, FRANK DOBINSON, AND JOHN E. BATTERBEE

Department of Chemistry, The University of Texas, Austin, Texas 78712

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Evidence is presented that in protolytic solvents anthraquinone is derived from ozonation of anthracene by two different routes. The first requires three mole-equivalents of ozone and the evolution of three mole-equivalents of molecular oxygen. The second involves the 1,4-addition of a single ozone molecule. In non-protolytic solvents, anthraquinone is produced only by the first route. The second route leads to phthalic acid. Phthalic acid is also produced, in both solvent types, *via* a minor competing bond attack on an outer ring. The solvent effect observed is of a different type than originally suggested. A strong ozone concentration effect also exists.

Anthracene (I) was first ozonized in 1907, in chloroform solution, but no identifiable products were obtained.[1] Roitt and Waters[2] obtained anthraquinone (XI) from ozonation of anthracene in acetic anhydride, but they neither reported the yield nor proved that ozone rather than oxygen was the oxidizing agent. Certain aspects of the ozonation of anthracene were discussed in two preliminary communications from this laboratory.[3-5] The first one[3] showed that ozone was the reactant and proposed that the production of anthraquinone involves the 1,4-addition of one mole-equivalent of ozone to the reactive 9- and 10-positions of anthracene. The second communication[4] reported the evolution of molecular oxygen during the ozonation of anthracene and suggested that three mole-equivalents of ozone are required per mole of anthraquinone produced.[6] The second paper[4,5b] also reported a solvent effect which was thought to control the ratio of atom attack (leading to anthraquinone) to bond attack (leading to phthalic acid) of ozone on anthracene.

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(1) E. Molinari, *Ber.*, **40**, 4160 (1907).

(2) I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 3060 (1949).

(3) P. S. Bailey and J. B. Ashton, *J. Org. Chem.*, **22**, 98 (1957).

(4) F. Dobinson and P. S. Bailey, *Chem. Ind.* (London), 632 (1961).

(5) See also: (a) P. S. Bailey, S. S. Bath, and J. B. Ashton, *Advan. Chem. Ser.*, **21**, 143 (1959); (b) P. S. Bailey, paper presented before the Petroleum Division at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962; preprints, Petroleum Division, American Chemical Society, Vol. 7, No. 4, C-151.

(6) P. G. Copeland, R. E. Dean, and D. McNeil [*J. Chem. Soc.*, 3858 (1961)] also report molecular oxygen to be a product of the ozonation of anthracene.