ration of the filtrate under reduced pressure, was dissolved in petroleum ether and chromatographed on Merck acid alumina. Elution with the same solvent (50 ml.) gave unchanged hydrocarbon (5 mg.), and elution with chloroform (200 ml.) gave a solid (88 mg., λ^{CHCl_3} 2.70 and 2.90 μ), assumed to be the required diol and not further purified. To a solution of this diol (88 mg.) in acetic acid (20 ml.) was added freshly crystallized lead tetraacetate (180 mg.) in acetic acid (6 ml.). The mixture was allowed to stand at room temperature for 40 hr., diluted with water, and distilled. Sodium carbonate was added to the distillate, which was then redistilled and added to a solution of dimedone (60 mg.) in ethanol (2 ml.). A precipitate (17 mg.) formed and was collected and identified as formaldehyde dimedone by m.p. 192–193° and infrared comparison with authentic specimen. The residue from the initial distillation was extracted with ether; the extract was washed with sodium bicarbonate solution and water. Evaporation of the dried extract gave an oil (60 mg.) which was dissolved in petroleum ether and chromatographed on Savory and Moore alumina (7 g.). Elution with petroleum ether–benzene (1:1, 50 ml.) yielded a solid (26 mg.) which was crystallized from methylene chloride–methanol to give **3α-methylcholestan-4-one** as platelets, m.p. 90–92°, $[\alpha]_D$ +15° (c 1.3), λ^{KBr} 5.85 μ, R_f 0.45 (C_6H_6–$CHCl_3$, 1:1, as developing solvent on silica gel G).

Anal. Calcd. for $C_{28}H_{48}O$: C, 83.93; H, 12.08. Found: C, 84.11; H, 11.84.

Optical rotatory dispersion (O.R.D.)[18] in dioxane (c 0.045) gave: $[\alpha]_{345}$ −218°, $[\alpha]_{318.5}$ −980° (min.), and $[\alpha]_{278}$ +1420° (max.).

3β-Methylcholestan-4-one (19). A. By Alkylation of Cholestan-4-one.—Sodium methoxide (prepared from 385 mg. of sodium in 5 ml. of methanol) and ethyl formate (5 ml.) were added to a solution of cholestan-4-one[10] (455 mg.) in anhydrous ether (15 ml.), and the mixture was allowed to stand at room temperature for 5 days. Ether and buffered phosphate solution (pH 8, 40 ml.) were then added, and the aqueous layer was separated, acidified with 1 *N* hydrochloric acid, and extracted with ether. Evaporation of the washed and dried extract yielded the hydroxymethylene derivative, which was heated under reflux with a mixture of potassium carbonate (200 mg.) and methyl iodide (0.4 ml.) in dry acetone (10 ml.) for 16 hr. The mixture was then diluted with water and extracted with ether, and the extract was washed with 2 *N* sodium hydroxide solution and water and dried. The residue (290 mg.) obtained on evaporation was dissolved in petroleum ether and chromatographed on alumina (Savory and Moore, 20 g.). Elution with petroleum ether–benzene (1:1, 100 ml.) yielded a solid which, on crystallization from methylene chloride–methanol, gave **3β-methylcholestan-4-one** as needles (20 mg.), m.p. 118–119°, $[\alpha]_D$ +19° (c 0.8), λ^{KBr} 5.87 μ, R_f 0.53 (C_6H_6–$CHCl_3$, 1:1, as developing solvent and silica gel G as adsorbent).

Anal. Calcd. for $C_{28}H_{48}O$: C, 83.93; H, 12.08. Found: C, 84.20; H, 11.95.

O.R.D. in dioxane (c 0.031) gave: $[\alpha]_{345}$ −46°, $[\alpha]_{315.5}$ −680° (min.), and $[\alpha]_{275.5}$ +1380° (max.). Further elution with benzene gave a mixture of 3α- and 3β-cholestan-4-one (50 mg., R_f 0.45 and 0.53, respectively).

B. By Epimerization of 3α-Methylcholestan-4-one.—To 1% ethanolic potassium hydroxide solution (10 ml.) was added 3α-methylcholestan-4-one (14 mg.), and the mixture was heated under reflux for 1 hr. The solvent was then removed under reduced pressure, the residue was extracted with ether, and the extract was washed and dried. Evaporation gave a solid which was crystallized from methylene chloride–methanol to give 3β-methylcholestan-4-one as needles, m.p. 118–119°, with R_f and infrared spectrum identical with those of the specimen prepared as in A.

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[18] We are grateful to Mrs. Elke Mermelstein for O.R.D. data, determined on a Polaramatic 62 Bendix Ericsson polarimeter.

Bis(phenylsulfonyl)diazomethane[1]

J. DIEKMANN

Contribution No. 1044 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware

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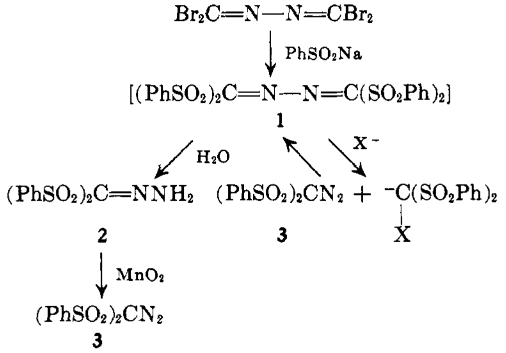
The preparation of the electrophilic bis(phenylsulfonyl)diazomethane (**3**) from carbonyl bromide azine is described. Photolysis of **3** is believed to give bis(phenylsulfonyl)carbene. A study of the reactions of this exceptionally electrophilic carbene and possible mechanisms are discussed.

A study of the reactions of divalent carbon has attracted the attention of many workers. In general, carbenes are highly reactive electrophilic reagents, although Wanzlick has rationalized reactions of bis[1,3-diphenylimidazolidinylidene-(2)] in terms of a nucleophilic diaminocarbene intermediate.[2] We were interested in studying the effect of strongly electron-withdrawing substituents on the reactivity of the divalent carbon atom in the hope of observing an exceptionally electrophilic carbene. The sulfonyl group is one of the strongest electron-withdrawing groups known and, therefore, we chose to prepare and study the reactions of bis(phenylsulfonyl)diazomethane (**3**), a possible source of bis(phenylsulfonyl)carbene.

Preparation.—A rapid reaction occurred upon treatment of carbonyl bromide azine with sodium benzenesulfinate in dimethylformamide. Addition of water precipitated bis(phenylsulfonyl)formaldehyde hydrazone (**2**) in 90% yield. Oxidation of **2** could be effected readily with active manganese dioxide or silver oxide to give bis(phenylsulfonyl)diazomethane in 55% yield. Bis(phenylsulfonyl)methane (**4**) was also isolated as a by-product; it was probably formed *via* a Wolff–Kishner-type reaction of **2** with the basic oxidizing agent.



In an attempt to prepare the intermediate tetrakis(phenylsulfonyl)formaldehyde azine (**1**), the reaction of carbonyl bromide azine with sodium benzenesulfinate was carried out in an anhydrous medium. Surprisingly, a good yield of **3** was isolated directly by this

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[1] A preliminary communication of this work appeared in *J. Org. Chem.*, **28**, 2933 (1963). The completed work was presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[2] H. W. Wanzlick, *Angew. Chem.*, **74**, 129 (1962).

procedure. Apparently the intermediate azine is very reactive toward nucleophiles present in the reaction mixture. An analogous base-catalyzed decomposition of benzal azine with phenyldiazomethane as a postulated intermediate has been reported by Zimmerman.[3]

Since the completion of this work the preparation of *p*-methoxybenzenesulfonyldiazomethane[4] and also **3** itself by a different route[5] have been reported. Bis(alkylsulfonyl)diazomethanes have also become accessible by an alternate route.[6]

Ionic Reactions of 3.—Bis(phenylsulfonyl)diazomethane (**3**) is very stable toward aqueous acids and also glacial acetic acid, from which it can be recrystallized. Nucleophiles, however, readily react with **3**. Reaction of **3** with triphenylphosphine gives a phosphazine, while phenylmagnesium bromide adds to **3**

$$(PhSO_2)_2CN_2 + Ph_3P \longrightarrow (PhSO_2)_2\bar{C}{-}N{=}N{-}\overset{+}{P}Ph_3$$

$$(PhSO_2)_2CN_2 + PhMgBr \xrightarrow{H_2O} (PhSO_2)_2C{=}N\overset{H}{N}Ph$$

with formation of a phenylhydrazone upon hydrolysis. We did not observe any reaction of **3** with a variety of olefins and acetylenes. Strating's monosulfonyldiazomethane, in contrast, reacts with aqueous acids at an appreciable rate.[7]

Photolysis of 3.—In addition to thermal stability, **3** possesses unusual photostability. A high light intensity is required for appreciable decomposition. Photolysis of **3** in the solid state proved to be very unrewarding as was photolysis of a heterogeneous mixture of **3** in alkanes and alkenes. Photolysis of a benzene solution of **3** gave a small amount of a white precipitate at the start. The solution developed a dark brown color, and photodecomposition of **3** stopped completely. For this reason we were unable to use aromatic compounds as solvents and reagents.

When **3** was photolyzed in ethanol we isolated the alkylation product bis(phenylsulfonyl)methyl ethyl ether (**5**) and the hydrogen abstraction product bis(phenylsulfonyl)methane (**4**). Since these products in-

$$\mathbf{3} \xrightarrow{CH_3CH_2OH} \underset{\mathbf{5}}{(PhSO_2)_2CHOCH_2CH_3} + \underset{\mathbf{4}}{(PhSO_2)_2CH_2}$$

dicated extensive involvement of the solvent as a reactant, we investigated the photolysis of **3** in different alcohols. The compositions of the product mixtures were determined by n.m.r. spectroscopy and are summarized in Table I.

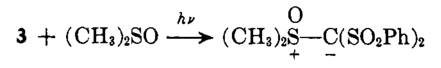
TABLE I

PHOTOLYSIS OF 3

	Products, %	
Solvent	Alkylation	Hydrogen abstraction
H_3COH	82	18
MeH_2COH	66	34
Me_2HCOH	15	85
Me_3COH	100	0

Irradiation of **3** in diethyl ether afforded the products **5** and ethylene. No detectable amount of **4** was formed in this reaction. Apparently the carbene could be trapped when photolysis of **3** was carried out in di-*n*-butyl sulfide and also dimethyl sulfoxide with resultant ylid formation. Photolysis of **3** in *n*-butyl mercaptan gave the corresponding thioether.

$$\mathbf{3} + [CH_3(CH_2)_3]_2S \xrightarrow{h\nu} [CH_3(CH_2)_3]_2\overset{+}{S}{-}\bar{C}(SO_2Ph)_2$$



$$\mathbf{3} + (CH_3)_2SO \xrightarrow{h\nu} (CH_3)_2\underset{+}{\overset{O}{S}}{-}\underset{-}{C}(SO_2Ph)_2$$

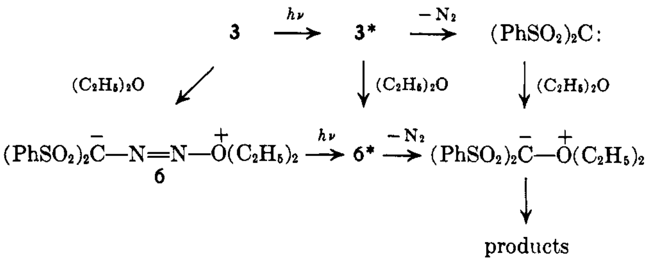
$$\mathbf{3} + CH_3(CH_2)_3SH \xrightarrow{h\nu} CH_3(CH_2)_3SCH(SO_2Ph)_2$$

Thermolysis of 3.—Decomposition of **3** below 100° neat or in solvents is negligible. Above 140°, decomposition of **3** is fairly fast, but unfortunately it is accompanied by formation of a brown tar in nearly all cases. Only dimethyl sulfide and di-*n*-butyl sulfide allowed the isolation of clean products, namely the respective ylids, while pyrolysis in aromatic solvents, monoglyme, or neat proved unrewarding.

Discussion

The stability of **3** toward electrophiles and ease of reaction with nucleophiles are in accord with the expectation that $(PhSO_2)_2\overset{-}{C}{-}\overset{+}{N}{\equiv}N$ is probably a good representation of **3**.

Photolytic decomposition of **3** can occur by several pathways as shown below for a solution of **3** in diethyl ether.



The absorption due to the diazo group at 380 mμ changes very little with different solvents such as methanol, benzene, and acetonitrile. Therefore, we rule out reaction of the solvent with ground state **3** to form oxazine **6** which then undergoes photolysis. The relative rates of nitrogen evolution do not exceed a factor of 2 for the various solvents examined. Since light absorption of the photostable **3** is not the limiting step, we would intuitively expect larger relative rate ratios if the solvents were to react with excited **3** to form the excited oxazine **6** which then undergoes decomposition. For these reasons, we suggest that photolysis of **3** leads to the carbene which then reacts with solvent. The carbene, a very strong electrophile, resembles a carbonium ion in its reactions. We have observed two types of reaction, alkylation and hydrogen abstraction. We think that the electrophilic carbene is stabilized by coordination with a nonbonded electron pair to form an ylid or by hydride abstraction to form **4** after subsequent protonation. Our failure to detect formation of **4** from the photolysis of **3** in diethyl ether argues against a radical pathway for the formation of **4** in alcohols. The increase in relative amounts of **4**, as seen from Table I, also parallels the ease of hydride abstraction. The

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[3] H. E. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, **82**, 5865 (1960).

[4] J. Strating and A. M. Van Leusen, *Rec. trav. chim.*, **81**, 966 (1962).

[5] F. Klages and K. Bott, *Ber.*, **97**, 735 (1964).

[6] U. Schöllkopf, private communication.

[7] B. Zwanenburg, J. B. F. N. Engberts, and J. Strating, *Tetrahedron Letters*, No. **11**, 547 (1964).

intermediate ylid may be stable as in the case of the sulfides and dimethyl sulfoxide. Where proton migration is feasible, an ether or thioether is obtained. The ylid from diethyl ether apparently suffers a Hofmann degradation. We never observed any C–H insertion of the carbene in its reactions with alcohols and ethers. In contrast, the reaction of methylene with methyl *n*-propyl ether in the gas phase yields 93.1% of C–H insertion products and only 6.9% of fragmentation products arising from coordination of methylene with the ether oxygen.[8]

It is interesting that photolysis of *p*-toluenesulfonyl azide gives products very similar to those from photolysis of **3**.[9] Decomposition of the azide in alcohols yields hydroxylamine derivatives, while decomposition in sulfides and sulfoxides affords stable sulfur ylids of the nitrene.

Experimental

Bis(phenylsulfonyl)formaldehyde Hydrazone.—To a solution of 3.72 g. (0.01 mole) of carbonyl bromide azine[10] in 50 ml. of dimethylformamide was added with stirring 6.56 g. (0.04 mole) of anhydrous sodium benzenesulfinate. The mixture was cooled by an ice–acetone bath. Stirring was continued for 30 min. Then a large excess of water was added, and the reaction mixture was stirred for another hour. The resulting solid was filtered and washed several times with water to give 3 g. (93%) of crude off-white product. On recrystallization from acetonitrile, white cubes were obtained, dec. pt. ~ 200°. The infrared spectrum is consistent with the hydrazone structure.

Anal. Calcd. for $C_{13}H_{12}N_2O_4S_2$ (324.38): C, 48.14; H, 3.73; N, 8.64; S, 19.77. Found: C, 48.39; H, 3.86; N, 8.87; S, 20.07.

Bis(phenylsulfonyl)diazomethane (3). A.—To a solution of 1 g. of the above hydrazone in 100 ml. of tetrahydrofuran was added 2 g. of active manganese dioxide. The suspension was stirred for 1 hr. and then filtered free of manganese oxide; the solvent was removed *in vacuo*. The solid residue was taken up in benzene and passed through a column containing acid-washed alumina. The yellow fractions were collected and, on removal of the solvent, there was obtained 0.53 g. (52%) of crystalline bis(phenylsulfonyl)diazomethane, m.p. 89–93°. Recrystallization from a benzene–cyclohexane mixture gave long, yellow rods, dec. pt. 99–100°, $\lambda_{\max}^{CH_3CN}$ 232 mμ (ϵ 17,200) and 375 mμ (ϵ 72).

Anal. Calcd. for $C_{13}H_{10}N_2O_4S_2$ (322.38): C, 48.44; H, 3.12; N, 8.69. Found: C, 48.32; H, 3.19; N, 8.50.

B.—To a solution of 3.72 g. (0.01 mole) of carbonyl bromide azine in 75 ml. of dry acetonitrile was added 8.55 g. (0.05 mole) of anhydrous sodium benzenesulfinate. Cooling was provided by an ice–acetone bath. The mixture was stirred for about 4 hr. and then filtered. The solvent was removed on a Rinco evaporator. The residual oil, 4 g., was taken up in benzene and chromatographed on acid-washed alumina with benzene. The first yellow fraction was collected, and removal of the benzene gave 3 g. (92%) of nearly pure product. Recrystallization from a benzene–cyclohexane mixture gave long, yellow rods, dec. pt. 99–100°.

Bis(phenylsulfonyl)methylazotriphenylphosphonium Ylid.—To a solution of 0.65 g. (2 mmoles) of bis(phenylsulfonyl)diazomethane in 10 ml. of benzene was added a solution of 0.52 g. (2 mmoles) of triphenylphosphine in 5 ml. of benzene. A yellow precipitate formed very fast and was collected by filtration after 10 min. It was washed with benzene several times. Thus there was obtained 1.05 g. (90%) of the desired phosphazine derivative, m.p. 194°.

Anal. Calcd. for $C_{31}H_{25}N_2O_4PS_2$ (584.66): C, 63.67; H, 4.31; S, 10.97. Found: C, 63.24; H, 4.11; S, 11.15.

Bis(phenylsulfonyl) Ketone Phenylhydrazone.—To 0.96 g. (3 mmoles) of **3** in 50 ml. of ether was added 2 ml. of 3 *M* phenylmagnesium bromide solution under nitrogen. The mixture was stirred for 30 min. and then poured into iced 1 *N* hydrochloric acid. Ether was added, and the organic layer was separated, washed with water, and dried over magnesium sulfate. Removal of the solvent gave a tan residue which was recrystallized from ethanol to give 0.64 g. (54%) of the desired product as yellow rods, m.p. 142–143°. Infrared bands at 3250 and 1525 cm.$^{-1}$ support the structure assignment.

Anal. Calcd. for $C_{19}H_{16}N_2O_4S_2$ (400.47): C, 56.98; H, 4.03; N, 7.00. Found: C, 56.99; H, 4.18; N, 6.58.

1,1-Bis(phenylsulfonyl)dimethyl Ether.—A solution of 0.32 g. (1 mmole) of **3** in 12 ml. of methanol was irradiated with an AH6 lamp[11] until nitrogen evolution stopped. The reaction took 90 min. and the mixture evolved 23 cc. of gas. The solvent of the colorless mixture was removed, and the residue was recrystallized from ethanol to give 0.2 g. (65%) of crystalline product, m.p. 179–180°.

Anal. Calcd. for $C_{14}H_{14}O_5S_2$ (326.38): C, 51.52; H, 4.33; S, 19.65. Found: C, 51.50; H, 4.41; S, 19.84.

Bis(phenylsulfonyl)methyl Ethyl Ether.—A solution of 0.32 g. (1 mmole) of **3** in 7 ml. of ether was irradiated with an AH6 lamp[11] until gas evolution stopped. The evolved gas (29 ml.) was collected over a 6-hr. period. Analysis of the gas by infrared and mass spectroscopy showed the presence of ethylene.

The nearly colorless ether solution was concentrated under a stream of nitrogen. White crystals appeared and were collected, yield 0.1 g. (30%), m.p. 128°. Recrystallization from ethanol gave crystals, m.p. 130°.

Anal. Calcd. for $C_{15}H_{16}O_5S_2$ (340.41): C, 52.93; H, 4.73; S, 18.84. Found: C, 52.99; H, 4.62; S, 18.78.

Examination of the nonvolatile part of the filtrate by n.m.r. and infrared analysis showed the absence of bands due to **4**.

Photolysis of 3 in Alcohols.—Solutions of **3** (1 mmole) in freshly distilled methyl, ethyl, isopropyl, and *t*-butyl alcohol were irradiated[11] until gas evolution stopped. The solvents were then removed *in vacuo*, and the total product mixture was dissolved in deuterated chloroform or deuterated acetone and analyzed with a Varian A-60 n.m.r. instrument (see Table II). In chloroform the $(PhSO_2)_2CHOR$ proton was observed near τ 4.8, while the $(PhSO_2)_2CH_2$ protons were observed near τ 5.2. In acetone the peaks were shifted to τ 4.2 and 4.6, respectively.

TABLE II

THE N.M.R. ANALYSIS OF PHOTOLYSIS PRODUCTS OF **3**

	Relative integration values	
Alcohol	$(PhSO_2)_2CHOR$	$(PhSO_2)_2CH_2$
Methyl	17	8
Ethyl	30	29
Isopropyl	23	137
t-Butyl	35	0

Bis(phenylsulfonyl)methylene Di-*n*-butylsulfonium Ylid. A.—A solution of 0.32 g. (1 mmole) of **3** in 40 ml. of *n*-butyl sulfide was irradiated with an AH6 lamp[11] for 4 hr., after which time gas evolution (22 ml.) stopped. A brown, solid product was collected by filtration, m.p. 133–135°, yield 0.25 g. Recrystallization from a benzene–cyclohexane mixture gave a white solid, m.p. 140°.

Anal. Calcd. for $C_{21}H_{28}O_4S_3$ (440.63): C, 57.24; H, 6.40; S, 21.83. Found: C, 57.51; H, 6.48; S, 21.29.

B.—A solution of 0.32 g. of **3** in 30 ml. of *n*-butyl sulfide was heated at 130° for 16 hr. Petroleum ether (20 ml.) was added to the cooled mixture, and 0.15 g. of white solid, m.p. 128–130°, was isolated. Recrystallization from a benzene–cyclohexane mixture gave 0.08 g. of product, m.p. 140°, m.m.p. 140° with sample from A.

Bis(phenylsulfonyl)methyl-*n*-butyl Sulfide.—A solution of 0.5 g. of **3** was heated in 20 ml. of *n*-butanethiol at 90° for 4 days. The solvent of the colorless product mixture was removed to afford a white solid residue, m.p. 133–135°. Recrystallization from a benzene–cyclohexane mixture gave 0.2 g. of product, m.p. 137–138°. Infrared and n.m.r. spectra unequivocally supported the assigned structure.

Anal. Calcd. for $C_{17}H_{20}O_4S_3$ (384.53): C, 53.10; H, 5.24. Found: C, 53.23; H, 5.42.

Bis(phenylsulfonyl)methylene Dimethylsulfonium Ylid.—A solution of 1 g. of **3** in 30 ml. of dimethyl sulfide was heated in a bomb at 130° for 5 hr. The volatile parts of the product mixture were removed *in vacuo*, and the residue was recrystallized

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[8] H. M. Frey, *Rec. trav. chim.*, **83**, 117 (1964).

[9] L. Horner and A. Christmann, *Ber.*, **96**, 388 (1963).

[10] J. Thiele, *Ann.*, **303**, 57 (1898).

[11] All irradiations were performed in a Pyrex vessel.

from a benzene–cyclohexane mixture to give 0.15 g. of white ylid, m.p. 210–212°.

Anal. Calcd. for $C_{15}H_{16}O_4S_3$ (356.48): C, 50.53; H, 4.53; S, 26.99. Found: C, 51.20; H, 4.56; S, 27.08.

Bis(phenylsulfonyl)methylene Dimethyloxosulfonium Ylid.—A solution of 0.5 g. of **3** in 40 ml. of dimethyl sulfoxide was heated under reflux for 60 hr. Water was added to the nearly colorless mixture, and an oil slowly settled out. The clear supernatant part was decanted and on standing deposited 0.05 g. of crystalline product, m.p. 178–179°.

Anal. Calcd. for $C_{15}H_{16}O_5S_3$ (372.48): C, 48.37; H, 4.33. Found: C, 48.81; H, 4.46.

Nucleophilic Displacement of Bromide by Thiosulfate Ion from 1,2-Aminobromopropanes

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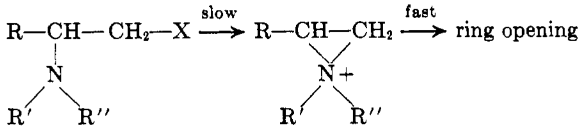
Received September 1, 1964

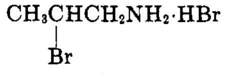
In the reaction of 2-amino-1-bromopropane hydrobromide (II) with 1 equiv. of sodium thiosulfate, the formation of only one product, 2-aminopropane-1-thiosulfuric acid (IV), is detected. Similar treatment of 1-amino-2-bromopropane hydrobromide (I) yields two products, namely, 1-aminopropane-2-thiosulfuric acid (III) and the rearranged product, IV. In order to determine whether an ethylenimonium ion is an intermediate in the formation of IV in the latter reaction, the ring opening of 2-methylethylenimine by thiosulfate ion was investigated. The direct displacement of bromide in I by thiosulfate ion without the intermediacy of the cyclic imonium ion accounts for the formation of III. The ratio of the rate constants for the intramolecular displacement *vs.* the intermolecular displacement was found to be 1.45.

In previous studies[2] of the reactions of 1,2-(tertiary-amino)haloalkanes evidence was presented that in solvolyses, dimerizations, and nucleophilic displacements, the rate-determining step in each case was the formation of the intermediate ethylenimonium ion. There



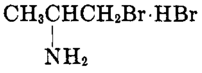
have been few reported investigations of such reactions in the case of (primary-amino)haloalkanes[3] since the studies have been complicated by the occurrence of side reactions, especially polymerization.[4] Also, earlier investigations[2d,f,5] of the nucleophilic displacement and rearrangement of aminohaloalkanes have been hampered by the lack of an adequate analytical technique. The marked similarity in the physical properties of the isomeric displacement products renders the separation of isomers and the determination of the reaction product composition difficult.

The reaction of an alkyl halide with sodium thiosulfate gives an alkyl thiosulfate (Bunte salt) and, similarly, aminoalkanethiosulfuric acids can be prepared by treating sodium thiosulfate with the corresponding aminohaloalkanes. The displacement of bromide from the isomeric primary-amino bromides, 1-amino-2-bromopropane hydrobromide (I) and 2-amino-1-bromopropane hydrobromide (II), with thiosulfate ion was selected for study. The products anticipated from these reactions, besides sodium bromide, were the isomeric compounds, 1-aminopropane-2-thiosulfuric acid (III) and 2-aminopropane-1-thiosulfuric acid (IV).



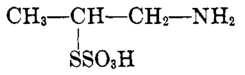
$CH_3\underset{\underset{\displaystyle Br}{|}}{C}HCH_2NH_2\cdot HBr$

I



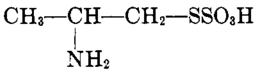
$CH_3\underset{\underset{\displaystyle NH_2}{|}}{C}HCH_2Br\cdot HBr$

II



$CH_3{-}\underset{\underset{\displaystyle SSO_3H}{|}}{CH}{-}CH_2{-}NH_2$

III



$CH_3{-}\underset{\underset{\displaystyle NH_2}{|}}{CH}{-}CH_2{-}SSO_3H$

IV

Experimental[6]

Bis(1-amino-2-propyl) Disulfide Dihydrochloride.—1-Amino-2-propanethiol hydrochloride (25.5 g., 0.2 mole), prepared by the method of Gabriel and Leupold[7] according to the modification of Mylius,[8] was dissolved in 100 ml. of water containing 20 ml. of 28% ammonia solution. To the cooled, magnetically stirred solution was added dropwise 5% aqueous hydrogen peroxide until the solution gave a negative nitroprusside test and liberated iodine from hydriodic acid. The solvent was evaporated under reduced pressure and the residue was recrystallized from methanol to give 22.8 g. (90.1% yield) of disulfide, m.p. 228–229° dec. (lit.[7] m.p. 213–214° dec.)

Anal. Calcd. for $C_6H_{18}Cl_2N_2S_2$: C, 28.45; H, 7.16; N, 11.06; S, 25.32. Found: C, 28.47; H, 7.28; N, 11.15; S, 25.69.

Bis(2-amino-1-propyl) Disulfide Dihydrochloride.—2-Amino-1-propanethiol hydrochloride[9] (25.5 g., 0.2 mole) prepared from 2-methylethylenimine was oxidized as above to give 22.7 g. (89.7% yield) of the disulfide, m.p. 224–225° dec. (lit.[9] m.p. 212° dec.)

Anal. Calcd. for $C_6H_{18}Cl_2N_2S_2$: C, 28.45; H, 7.16; N, 11.06; S, 25.32. Found: C, 28.19; H, 7.14; N, 11.02; S, 24.96.

1-Aminopropane-2-thiosulfuric Acid (III).—A solution of 7.6 g. (0.03 mole) of bis(1-amino-2-propyl) disulfide dihydrochloride and 6.24 g. (0.06 mole) of sodium bisulfite in 20 ml. of water was heated under reflux for 2.5 hr. It was cooled overnight and the product which crystallized was collected by filtration and recrystallized from water to give 2.5 g. (48.7%) of compound III, m.p. 184° dec.

Anal. Calcd. for $C_3H_9NO_3S_2$: C, 21.04; H, 5.30; N, 8.18; S, 37.45. Found: C, 20.96; H, 5.37; N, 8.33; S, 37.14.

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