

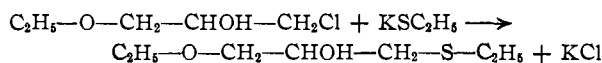
TABLE I
 ALKYLTHIOALKOXYPROPANOLS [R'SCH₂CH(OH)CH₂OR]

R'	R	°C.	B.p.	Mm.	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁵	Yield, %	Analyses, %					
								MRD		Carbon		Hydrogen	
							Found	Calcd.	Found	Calcd.	Found	Calcd.	
Et	Me	92.5-92.8		9	1.4734	1.0322	62	40.86	41.05	48.24	47.97	9.52	9.39
Et	Et	136-137		40	1.4679	1.0037	34	45.49	45.66	50.78	51.16	10.06	9.81
Et	Pr	78-78.5		2	1.4661	0.9837	65	50.20	50.28	53.97	53.89	10.62	10.18
Et	Bu	85.5-86.5		2	1.4652	0.9695	69.5	54.91	54.90	55.91	56.20	10.47	10.48
Pr	Me	65-66		2	1.4719	1.0095	49	45.55	45.66	50.98	51.16	10.14	9.81
Pr	Et	69.5-70		1.5	1.4670	0.9850	63	50.22	50.28	53.71	53.89	10.49	10.18
Pr	Pr	81-81.5		1.5	1.4641	.9676	31	54.85	54.90	56.22	56.20	10.68	10.48
Pr	Bu	90.5-91		1.5	1.4639	.9578	67	59.44	59.52	58.35	58.21	11.04	10.75

that these compounds reacted readily with alcohols to give mixed ether derivatives of 1-mercaptoglycerol. Synthesis of sulfur-oxygen di-ethers has been reported previously by Clarke, who treated 1-iodo-2-methoxyethane in methanol with sodium methyl mercaptide to obtain 1-methylthio-2-methoxyethane,² and by Kretov, who studied the action of zinc and alcohols upon mustard gas.³

A modification of the method of Swern, Billen and Knight⁴ was used in this work. Although work in this Laboratory has produced some evidence that the 1-alkylthio-2,3-epoxypropanes, like epichlorohydrin, react under the influence of either acid or basic catalysts to form secondary alcohols, a basic catalyst was used here to assure the formation of secondary alcohols.

The secondary alcohol structure of the addition products was proved by synthesis of an ethylthio-1-ethoxypropanol from 1-ethoxy-3-chloro-2-propanol and potassium ethylmercaptide. The product obtained in this reaction is identical with that obtained by the addition of ethanol to 1-ethylthio-2,3-epoxypropane.



Conceivably the above reaction could proceed *via* epoxide formation to yield the isomeric 2-ethylthio-1-propanol but the identity of the product actually obtained in the reaction with that obtained from 1-ethylthio-2,3-epoxypropane necessarily requires that both ethylthio- and ethoxy-groups are situated on primary carbon atoms.

A series of eight 1-alkoxy-3-alkylthio-2-propanols has been prepared by the reaction of alcohols with 1-alkylthio-2,3-epoxypropane. The derivatives have been characterized and their physical constants are given in Table I.

Experimental

Preparation of 1-Alkoxy-3-alkylthio-2-propanols from 1-Alkylthio-2,3-epoxypropanes.—A 1.6-g. portion of metallic sodium was added to two moles of the alcohol contained in a 500-ml., 3-necked, round-bottomed flask equipped with thermometer, stirrer and reflux condenser. A 0.25-mole portion of the 1-alkylthio-2,3-epoxypropane was added dropwise through the condenser to the stirred solution. No temperature change was observed during one hour. The mixture was then refluxed, with stirring, for five hours; the product neutralized with 6 *N* sulfuric acid; five grams of anhydrous potassium carbonate added; and the mixture

(2) H. T. Clarke, *J. Chem. Soc.*, **101**, 1806 (1912).

(3) A. E. Kretov, *J. Russ. Phys.-Chem. Soc.*, **61**, 2345 (1929).

(4) D. Swern, G. N. Billen and H. B. Knight, *THIS JOURNAL*, **71**, 1152 (1949).

allowed to stand overnight. The solid was filtered off and the filtrate distilled under reduced pressure.

Preparation of 1-Ethoxy-3-ethylthio-2-propanol from 1-Ethoxy-3-chloro-2-propanol.—A 65-g. portion of ethyl mercaptan was added to a cold solution of 160 ml. of water containing 60 g. of potassium hydroxide. This solution was added dropwise during the course of an hour to 137 g. of 1-ethoxy-3-chloro-2-propanol under vigorous stirring. Stirring was continued for four hours after addition whereupon the product was removed. The aqueous solution was extracted with ether and the ether extract combined with the bulk of the product. Distillation yielded 98 g. of material (60% yield) possessing the following constants: b.p. 137° at 40 mm., *d*₄²⁵ 1.0038, *n*_D²⁰ 1.4690.

Anal. Calcd. for C₇H₁₈SO₂: C, 51.16; H, 9.81. Found: C, 51.19; H, 9.92.

Preparation of the 3,5-Dinitrobenzoate of 1-Ethoxy-3-ethylthio-2-propanol.—The 3,5-dinitrobenzoate of 1-ethoxy-3-ethylthio-2-propanol was prepared in the usual manner. The products produced by the dinitrobenzoylation of the compounds obtained from 1-ethylthio-2,3-epoxypropane and from 1-ethoxy-3-chloro-2-propanol gave identical derivatives melting at 59°. The mixed melting point was also 59°.

Anal. Calcd. for C₁₄H₁₈N₂SO₇: C, 46.91; H, 5.06. Found: C, 46.61; H, 5.10.

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Alkylation with γ -Dialkylaminoneopentyl Chlorides¹

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Neopentyl halides are traditionally unreactive with respect to displacement reactions and subject to rearrangements. Recent evidence has shown, however, that under suitable experimental conditions these halides do react with a velocity of the same order as other primary halides and not necessarily with rearrangement.² This is true particularly if a second functional group is present in the molecule; e.g., hydroxyl,³ halogen⁴ or amino (see below).

The situation with respect to neopentyl alcohol is analogous; pentaglycol,⁴ pentaglycerol⁵ and pen-

(1) Presented before the Division of Organic Chemistry of the American Chemical Society, Chicago, Ill., September 6, 1950.

(2) I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 157 ff. (1946); F. G. Bordwell, M. Knell and B. M. Pitt, *Abstracts of Papers*, 117th Meeting of the A.C.S., p. 67L (1950). Cf. F. C. Whitmore and G. F. Fleming, *J. Chem. Soc.*, 1289 (1934).

(3) J. Barbieri and J. Matti, *Bull. soc. chim.*, [5] **5**, 1565 (1938).

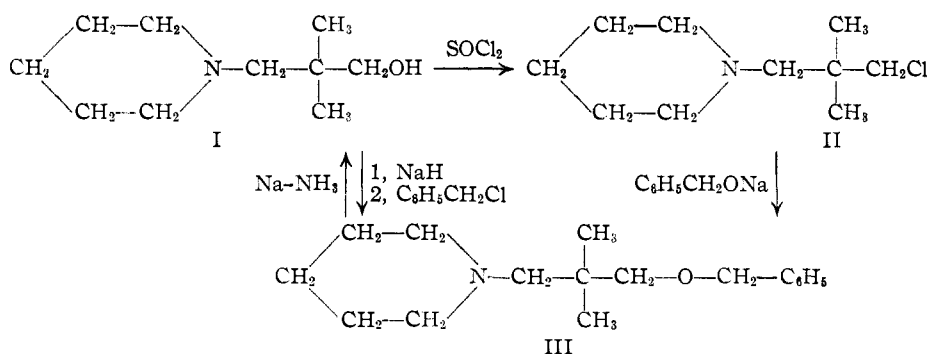
(4) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, *THIS JOURNAL*, **70**, 946 (1948); A. H. Blatt, "Organic Syntheses," Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 477.

(5) J. M. Derfer, K. W. Greenlee and C. E. Boord, *THIS JOURNAL*, **71**, 157 (1949).

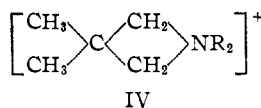
taerythritol⁶ react readily and without rearrangement with phosphorus tribromide, and a paper just published describes the conversion of neopentyl alcohol to neopentyl bromide.⁷

Some time ago we considered the use of γ -dialkylaminoneopentyl chlorides as alkylating agents. These basic alkyl chlorides, which are prepared by treating the basic alcohols with thionyl chloride,⁸ have been used without apparent difficulty to alkylate a variety of compounds, but proofs of structure of the alkylated products were not given.⁹ We proposed to determine whether alkylation occurred with or without rearrangement.

The reactions involved in our work are outlined



The γ -1-piperidylneopentyl chloride (II) reacted with sodium benzoxide to give a basic ether (III) identical with that obtained from I by treatment with sodium hydride followed by benzyl chloride. The ether prepared by the first route was cleaved by sodium in liquid ammonia to give an amino alcohol identical with the starting material. Thus we feel justified in concluding that a simple γ -dialkylaminoneopentyl chloride does in fact alkylate with retention of the intact carbon skeleton. Probably a cyclic trimethyleniminium ion (IV) is involved in these alkylations.^{10,11}



(6) A. H. Blatt, "Organic Syntheses," Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 476.

(7) L. H. Sommer, H. D. Blankman and P. C. Miller, *THIS JOURNAL*, **73**, 3542 (1951). Cf. F. C. Whitmore and H. S. Rothrock, *ibid.*, **54**, 3431 (1932).

(8) C. Mannich and G. Baumgarten, *Ber.*, **70**, 210 (1937).

(9) See, *inter alia*, O. Yu. Magidson, N. M. Delektorskaya and I. M. Lipovich, *Arch. Pharm.*, **273**, 74 (1934); F. F. Blicke and C. Otsuki, *THIS JOURNAL*, **63**, 1945 (1941); F. Schönhöfer, *Z. physiol. Chem.*, **274**, 1 (1942); British Patent 608,208, Sept. 10, 1948 (C. A., **43**, 2647 (1949)).

(10) Mannich and Baumgarten (ref. 8) prepared cyclic trimethyleniminium halides from the basic neopentyl chlorides.

(11) The following limitation was pointed out by a referee. Assuming the cyclic ion IV to be an intermediate, our evidence does not establish whether the carbon atom attached to the oxygen in the ether III is the same carbon atom originally attached to the chlorine in the basic alkyl chloride II. Because of the symmetry of the trimethyleniminium ion IV, cleavage of either carbon-nitrogen bond results in the same product. By analogy with the alkylation of diphenylacetone nitrile with *p*-dimethylaminoisopropyl chloride (R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 72-73); alkylation with a γ -dialkylaminoneopentyl chloride bearing an additional α - or γ -substituent could result in a mixture of two isomeric products through the formation of an

Experimental¹²

γ -1-Piperidylneopentyl Benzyl Ether (III). Preparation from II and Benzyl Alcohol.—Thirty-six grams (0.16 mole) of the hydrochloride of II⁸ was stirred for ten minutes with 20 ml. (0.2 mole) of 56% potassium hydroxide and 50 ml. of toluene. The toluene layer was decanted and the aqueous slurry was stirred in turn with three 40-ml. portions of fresh toluene. The combined toluene decantates were dried by shaking for three hours over anhydrous potassium carbonate. A solution of 16.2 g. (0.15 mole) of benzyl alcohol in 100 ml. of toluene was added dropwise to a stirred suspension of 3.7 g. (0.15 mole) of sodium hydride in 100 ml. of toluene, under a nitrogen atmosphere. The mixture was refluxed for an hour to ensure complete conversion of the alcohol to the insoluble sodium benzoxide. To this suspension was then added dropwise the filtered toluene solution of II. The reaction mixture was stirred at reflux overnight. Water was added to the cooled mixture until all sodium chloride dissolved. The toluene layer was shaken with saturated sodium chloride solution, then filtered through anhydrous potassium carbonate. There was obtained on distillation 30.9 g. of III, b.p. 124-127° at 2 mm., n_D^{25} 1.4996 (79% yield).

Anal. Calcd. for $C_{17}H_{27}ON$: C, 78.1; H, 10.4. Found: C, 78.4; H, 10.6.

A flavianate was obtained by heating equivalent amounts of III and flavianic acid (2,4-dinitro-1-

naphthol-7-sulfonic acid) in isopropyl alcohol; m.p. 116.0-117.5° after recrystallization from ethyl acetate.

Anal. Calcd. for $C_{27}H_{33}O_9N_3S$: C, 56.3; H, 5.8; N, 7.3. Found: C, 56.4; H, 5.9; N, 7.1.

γ -1-Piperidylneopentyl Benzyl Ether (III). Preparation from I and Benzyl Chloride.—A mixture of 25.6 g. (0.15 mole) of I¹³ and 3.7 g. (0.15 mole) of sodium hydride in 150 ml. of toluene was stirred and refluxed for two hours under a nitrogen atmosphere. To the resulting clear solution was added dropwise 19.0 g. (0.15 mole) of benzyl chloride. After being stirred and refluxed overnight, the reaction mixture was cooled and water added to dissolve the sodium chloride. The toluene layer was dried as described above, then distilled. There was obtained 32.6 g. of III, b.p. 146-153° at 5 mm., n_D^{25} 1.5000 (83% yield).

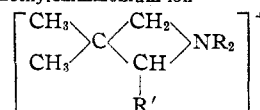
Anal. Calcd. for $C_{17}H_{27}ON$: C, 78.1; H, 10.4. Found: C, 78.1; H, 10.6.

The flavianate melted at 116.0-117.5° alone and when mixed with the flavianate of III prepared by the other route.

Anal. Calcd. for $C_{27}H_{33}O_9N_3S$: C, 56.3; H, 5.8; N, 7.3. Found: C, 56.3; H, 5.9; N, 7.6.

Hydrogenolysis of III.—In a 500-ml. three-necked flask was placed 19.6 g. (0.075 mole) of III prepared as described from II and benzyl alcohol. The flask was immersed in trichloroethylene in a dewar flask and equipped with a stirrer and condenser filled with Dry Ice and trichloroethylene. Approximately 100 ml. of liquid ammonia was collected in

unsymmetrical trimethyleniminium ion



Therefore the present evidence allows us to conclude only that a simple γ -dialkylaminoneopentyl chloride of the type $R_2N-CH_2-C(CH_3)_2-CH_2Cl$ alkylates without rearrangement; chlorides of the type $R_2N-CHR'-C(CH_3)_2-CH_2Cl$ or $R_2N-CH_2-C(CH_3)_2-CHR'Cl$ could well alkylate with rearrangement.

(12) Melting points are corrected. The authors are indebted to Mr. Richard M. Downing for the microanalyses reported.

(13) The preparation by the crossed Cannizzaro (L. C. Cheney, *THIS JOURNAL*, **73**, 685 (1951)) or $LiAlH_4$ (K. Hayes and G. Drake, *J. Org. Chem.*, **15**, 873 (1950)) appears superior to the sodium amalgam reduction⁸).

the flask; III appeared to be only slightly soluble in the ammonia. Stirring was begun, and a small piece of sodium added; the blue color faded very slowly. On the addition of 50 ml. of dry ether, a homogeneous solution resulted. Subsequent addition of sodium was followed by rapid disappearance of the blue color. Sodium was added until the blue color persisted for 15 minutes; 6.9 g. (0.3 mole) was required. Sixteen grams (0.3 mole) of ammonium chloride was added portionwise, followed by 100 ml. of dry ether. The flask was removed from the cooling bath and the ammonia allowed to evaporate. Water was added until two clear layers resulted. The aqueous layer was withdrawn and extracted twice with ether. These ether extracts, together with the original ether layer, were shaken with saturated sodium chloride solution and filtered through anhydrous sodium sulfate. Distillation gave 11.1 g. of I, b.p. 94–98° at 8 mm., n_D^{25} 1.4640 (87% yield). The hydrochloride melted at 208.0–209.5°, alone and when mixed with an authentic sample of the hydrochloride of I.

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NEW COMPOUNDS

6-*p*-Toluenesulfonyldiisopropylidene-D-galactose

6-*p*-Toluenesulfonyldiisopropylidene-D-galactose Diethylmercaptopal.—One and one-half grams (0.0034 mole) of 6-*p*-toluenesulfonyl-D-galactose diethylmercaptopal was suspended in 25 ml. of dry, redistilled acetone containing 2% by weight of sulfuric acid. Five and one-half grams of anhydrous copper sulfate was added and the mixture shaken for fifty hours. The suspension was filtered, an excess of finely divided anhydrous sodium carbonate introduced, and the mixture shaken for nine hours. After filtration, the solution was treated with norite for two hours at room temperature, centrifuged clear, and the solvent removed under reduced pressure. A brown sirup weighing 0.7 g. (39%) was obtained which crystallized spontaneously on standing. By dissolving in petroleum ether and storing for several days in the ice box, a small quantity of long white needles were obtained. These were thought to be a monoacetone product and were removed by centrifugation. On further standing, 6-*p*-toluenesulfonyldiisopropylidene-D-galactose diethylmercaptopal crystallized as flat plates. It was recrystallized in a similar manner to constant properties. The rotation of this material, m.p. 53°, was $[\alpha]_D^{25}$ -36.4° in chloroform (c 3.06).

Anal. Calcd. for $C_{28}H_{38}O_7S_2$: C, 53.1; H, 6.92. Found: C, 52.8; H, 7.02.

1-Bromo-2,3-isopropylidenglycerol.—Fifty-seven grams (0.66 mole) of anhydrous lithium bromide was dissolved in 150 ml. of dry acetone. To the viscous liquid which resulted was added 66.8 g. (0.22 mole) of 1-*p*-toluenesulfonyl-2,3-isopropylidenglycerol. The clear solution was heated to refluxing and after a few minutes a crystalline precipitate began to appear, which soon filled the entire flask. Fifty milliliters of dry acetone was added and the mixture refluxed for two hours. The following day, 100 ml. of dry acetone was introduced and the solid filtered off. The weight of white flaky lithium *p*-toluenesulfonate obtained was 31 g. The acetone was removed from the filtrate under reduced pressure and the resulting sirup extracted with portions (100 ml. each) of ether under reflux. After drying over sodium sulfate, the ether was removed from the combined extracts under reduced pressure and the remaining liquid distilled through a small column. The total yield of 1-bromo-2,3-isopropylidenglycerol of b.p. 45° (4 mm.), n_D^{25} 1.4601, and m.p. -23°, was 6.9 g. (14%).

Anal. Calcd. for $C_8H_{11}O_2Br$: C, 37.0; H, 5.68. Found: C, 37.3; H, 5.62.

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Studies in Silico-organic Compounds. XX. Preparation of a Silahydrocarbon and a Dichloride

The preparation of two new organic compounds of silicon, 2,2,5,5-tetramethyl-2,5-disilohexane and di-*n*-butyldichlorosilane, is herein described.

Sodium metal (9.2 g., 0.4 mole) was cut into small pieces and placed in 100 cc. of anhydrous amyl ether. Bromomethyltrimethylsilane (66.8 g., 0.4 mole) was added dropwise with stirring. As no apparent reaction was taking place after about one fourth of the bromomethyltrimethylsilane had been added, the reaction mixture was heated. The mixture soon began to turn blue and maintained a temperature of 50° without heating during the addition of the remainder of the bromide. The reaction mixture was then heated to the melting point of sodium and a sharp rise to 130° was noted. A cooling bath was applied and the temperature maintained at 105° for four hours. This temperature was chosen as the bromomethyltrimethylsilane boils at 115° and its loss was to be prevented. A Dry Ice-acetone trap had been placed at the condenser exit to catch any escaping low boiling material. Examination of the contents of the trap showed it contained 5 cc. of a low boiling liquid. This liquid was identified as tetramethylsilane by its refractive index (found) n_D^{25} 1.3580 (literature),¹ n_D^{20} 1.3591.

2,2,5,5-Tetramethyl-2,5-disilohexane was isolated, b.p. 150.5–151.5° (750 mm.), n_D^{25} 1.4170, d_4^{25} 0.7457, 14.3 g., yield 40%.

Anal. Calcd. for $C_8H_{20}Si_2$: Si, 32.18; mol. wt., 174.37; *MR*, 58.43. Found: Si, 31.84; mol. wt., (cryoscopic in benzene) 174.0; *MR*, 58.81.

From the interaction of 170 g. (1.0 mole) of tetrachlorosilane and 3 moles of *n*-butylmagnesium bromide in absolute ether, there were obtained tri-*n*-butylchlorosilane and di-*n*-butyldichlorosilane. The flask was cooled during the reaction with an ice-bath and the Grignard reagent added dropwise with stirring. After addition, the system was heated and stirred for eight hours, then filtered with suction and distilled. Tri-*n*-butylchlorosilane, b.p. (found and literature)² 142–144° (29 mm.), n_D^{25} 1.4460, 27.0 g., yield 11.5%; di-*n*-butyldichlorosilane, b.p. 109.0–109.5° (28 mm.), n_D^{25} 1.4430, d_4^{25} 0.9850, 75.5 g., yield 35%.

Anal. Calcd. for $C_8H_{18}Cl_2Si$: Si, 13.16; Cl, 33.26; *MR*, 57.32. Found: Si, 12.77; Cl, 32.83; *MR*, 57.34.

(1) H. H. Anderson, *THIS JOURNAL*, **69**, 3049 (1947).

(2) H. Gilman and H. J. Marshall, *ibid.*, **71**, 2066 (1949).

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The Coördination Compound of Boron Trifluoride with Tri-*n*-butylamine

$(C_4H_9)_3N:BF_3$ was prepared in a manner similar to that described by Kraus and Brown¹ in the case of the preparation of $(C_2H_5)_3N:BF_3$.

When 5 ml. of freshly distilled boron trifluoride etherate was added to a solution of 8.5 ml. of anhydrous tri-*n*-butylamine (dried over anhydrous sodium sulfate) in dry diethyl ether at -78°, a white precipitate was formed. However, this solid completely dissolved in the ether when the solution was warmed to room temperature. Addition of petroleum ether (b.p. 30–60°) yielded a precipitate of white crystals (7.1 g.) which were filtered off and washed several times with petroleum ether. These crystals may be crystallized from pure petroleum ether and melt at 59–61°.

Anal. Calcd. for $C_{12}H_{27}N:BF_3$: C, 56.93; H, 10.75; N, 5.53. Found: C, 55.60; H, 10.64; N, 5.35.

The infrared spectrum of $(C_4H_9)_3N:BF_3$ in chloroform was obtained with a Baird spectrophotometer. The principal bands in the range of 2–16 μ are: 3.54, 6.80, 7.24, 8.78, 9.00, 10.75, 11.10 and 11.84 μ .

The coördination compound of tri-*n*-butylamine with boron trifluoride is very soluble in benzene, chloroform, carbon tetrachloride and ether at room temperature, but is sparingly soluble in petroleum ether. The colorless

(1) C. A. Kraus and E. H. Brown, *THIS JOURNAL*, **51**, 2690 (1929).