

rine trifluoride was shut off and the system was flushed with nitrogen in order to eliminate all of the chlorine trifluoride before opening the tube. All the reactions were carried out at room temperature.

In all attempts, praseodymium sesquioxide yielded the trifluoride as the reaction product. Higher oxides of praseodymium, Pr_2O_3 and Pr_2O_5 , were treated with chlorine trifluoride but, likewise, the trifluoride was the only product obtained. Neodymium sesquioxide, under similar conditions, also yielded only the trifluoride.

Bromine Trifluoride.—Bromine trifluoride was obtained likewise from the Harshaw Chemical Company. It was of technical grade and probably contained bromine pentafluoride and hydrogen fluoride as impurities.

About 5 ml. of the bromine trifluoride was poured into a platinum crucible and the rare earth compound was slowly added. The reaction mixture was allowed to stand in the hood until the excess of the bromine trifluoride had evaporated and its last traces were removed by placing the crucible in a vacuum desiccator over barium oxide for a few hours.

Freshly ignited oxides did not react noticeably with bromine trifluoride. When the oxides were exposed to the air for some time so that they absorbed some moisture, the reaction was very vigorous and was accompanied by evolution of heat and light. Small amounts of the rare earth trifluoride were formed, but usually the reaction was not complete even with excess of the bromine trifluoride.

Hydrated oxalates reacted very violently giving a mixture of the trifluoride and some carbon. No reaction was observed between the rare earth trifluorides and the bromine trifluoride. An attempt was made to facilitate the reaction by heating the bromine trifluoride-rare earth oxide mixture to about 100–150°. The reaction was somewhat more vigorous, but the products were contaminated by a brown residue which was the product of the attack of bromine trifluoride on the platinum crucible. This result contradicts the observation of Sharp and Emeleus³ that bromine trifluoride does not attack platinum.

About 20 ml. of bromine trifluoride was distilled at room temperature, under vacuum, in a Vycor apparatus. The distillate, which had a much lighter color than the original material, was allowed to react with platinum foil. Slow reaction was observed at room temperature and the platinum was dissolved when the mixture was heated to approximately 50°. The reaction product was a brown compound containing platinum, bromine and fluorine. Its exact composition could not be determined.

In the course of this investigation, it was necessary to prepare rare earth trifluorides by a precipitation reaction. Addition of equimolar amount of fluoride ion to rare earth ion in solution produced only a highly dispersed gelatinous precipitate which was impossible to filter or centrifuge. A crystalline, easily filtrable precipitate was, however, obtained by dissolving the rare earth nitrate in 95% alcohol and slowly adding to it a 40% solution of hydrofluoric acid until the precipitation was complete. Analysis of the resulting product showed that it was the anhydrous salt rather than the monohydrate which is the usual form of the rare earth trifluoride obtained under similar conditions.

(3) A. G. Sharp and H. J. Emeleus, *J. Chem. Soc.*, 2135 (1948).

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Addition Compound of Dicyclohexylamine and Hydrogen Peroxide

BY THEODORE WAGNER-JAUREGG

It is known that dicyclohexylamine forms a crystalline monohydrate and monoalcoholate, melting at 23 and 28°, respectively. We have found that by treating the base with 30% H_2O_2 at room temperature, a stable addition compound can be obtained, with a melting point of 88–90°. The empirical formula of this complex was found to be $2(\text{C}_6\text{H}_{11})_2\text{NH}\cdot\text{H}_2\text{O}_2$, which indicates that each of the two hydroxyl groups of hydrogen peroxide is coordinated with one $>\text{NH}$ group.

The analytical values for such a complex are close to those for dicyclohexylhydroxylamine, $(\text{C}_6\text{H}_{11})_2\text{NOH}$. That the new substance is not this hydroxylamine derivative but the addition compound mentioned above has been established by the following facts: Free dicyclohexylamine can be liberated from the addition compound by gently warming with diluted sodium hydroxide. Upon the reaction of the H_2O_2 base complex with oxalic, hydrochloric or hydroiodic acid the corresponding dicyclohexylamine salts are obtained; in the latter case the expected amount of iodine is liberated.

No similar hydrogen peroxide complexes could be obtained with cyclohexylamine, dodecylamine or di-*n*-heptylamine.

The new substance might be useful for technical applications, where an oxidant is needed in the presence of a strong base, to neutralize formed acids. It further could be of value for analytical or preparative purposes as a source of hydrogen peroxide in solid form.

Twenty ml. of dicyclohexylamine was mixed with 40 ml. of 30% hydrogen peroxide. Immediate reaction with slight rise of temperature took place yielding a solid mass. Next morning the material was filtered with suction, washed with a very small amount of water, and dried over P_2O_5 in a vacuum desiccator. The yield was almost quantitative.

The product was soluble in alcohol or ether at room temperature, or in boiling petroleum ether, insoluble in water. For purification it was dissolved in a small amount of warm alcohol and precipitated by the addition of water. After recrystallization from boiling petroleum ether fine needles with a melting point of 88–90° were obtained.

Anal. Calcd. for $(\text{C}_{12}\text{H}_{23}\text{N})_2\cdot\text{H}_2\text{O}_2$ (396.6): C, 72.8; H, 12.2; N, 7.1; equiv. wt., 396.6; H_2O_2 , 8.6. Found: C, 73.0; H, 12.2; N, 7.1; equiv. wt., 404; H_2O_2 , 8.1.

On boiling with 20% HCl the substance yielded dicyclohexylamine hydrochloride; m.p. 326° (uncorrected, with decomposition).

Anal. Calcd. for $\text{C}_{12}\text{H}_{23}\text{N}\cdot\text{HCl}$ (217.6): C, 66.3; H, 11.12; Cl, 16.3. Found: C, 66.24; H, 10.96; Cl, 16.7.

Dicyclohexylamine oxalate was formed by precipitation of the substance with oxalic acid in ether; m.p. 206° (uncorrected).

Anal. Calcd. for $\text{C}_{12}\text{H}_{23}\text{N}\cdot\text{C}_2\text{H}_2\text{O}_4$ (271.2): N, 5.17. Found: N, 5.23.

By dissolving the substance in diluted H_2SO_4 and addition of KI, iodine was liberated and a salt precipitated, which after several recrystallizations from hot water formed colorless flat prisms, decomposing about 300°.

Anal. Calcd. for $\text{C}_{12}\text{H}_{23}\text{N}\cdot\text{HI}$ (309.1): I, 41.1. Found: 41.3.

Acknowledgments.—A sample of dicyclohexylamine was kindly supplied by Monsanto Chemical Co., Organic Chemicals Division, St. Louis, Mo. I wish to thank Mr. B. Hackley, Jr., and Mr. R. Proper for technical assistance.

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Derivatives of β -Hydroxypropyl Sulfides. II. Alkylthioalkoxypropanols

BY EDWARD G. RIETZ, THOMAS K. TODSEN, ARTHUR S. LEON AND C. B. POLLARD

In the course of an investigation of the reactions of 1-alkylthio-2,3-epoxypropanes,¹ it was found

(1) T. K. Todsén, C. B. Pollard and E. G. Rietz, *THIS JOURNAL*, **72**, 4000 (1950).

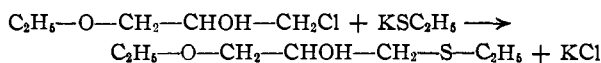
TABLE I
 ALKYLTHIOALKOXYPROPANOLS [R'SCH₂CH(OH)CH₂OR]

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 C₇H₁₆SO₂: 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

BY WILLIAM B. WHEATLEY AND LEE C. CHENEY

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).