block temperature (17 mm.). The infrared spectrum of this material was identical to that of a known sample.

The phenylurethan was prepared using the same procedure described earlier, m.p. 89.5–90° (lit.[11] 93°) after crystallization from hexane.

Preparation of Benzyl Methyl Ketone-carbonyl-O^{18}.—In a manner entirely similar to that used for the preparation of III, 26.8 g. (0.20 mole) of benzyl methyl ketone was allowed to exchange with H_2O^{18}. The ketone was distilled, b.p. 87–89° (12 mm.), yield 22.3 g.

Preparation of Benzylmethylcarbinol-hydroxyl-O^{18}.—The labeled ketone obtained above was reduced with lithium aluminum hydride as described in the preparation of V. From 21.6 g. of ketone there was obtained 16.8 g. of alcohol, b.p. 91–92° (12 mm.).

The phenylurethan was prepared and after crystallization from hexane had m.p. 91–92°.

Preparation of IXa.—The labeled alcohol, benzylmethylcarbinol, 13.6 g. (0.10 mole), was allowed to react with 25.6 g. (0.10 mole) of *p*-bromobenzenesulfonyl chloride in pyridine. The ester was isolated in the usual manner. The crude material was crystallized from acetone–hexane to afford 19.3 g. of IXa, m.p. 77–78°.

Solvolysis of IXa.—A solution of 9.24 g. (0.052 mole) of IXa in 500 ml. of dry acetic acid was heated at 99.8° for ten minutes. The recovered ester was obtained in the usual manner. The yield was 5.29 g., m.p. 77.5–78°.

Cleavage of IXa.—The ester, 3.17 g., was reduced with 1.30 g. of sodium to give benzylmethylcarbinol, b.p. 120°, block temperature (12 mm.). The infrared spectrum of this material indicated that it was contaminated with a small amount of some carbonyl-containing compound.

The phenylurethan was prepared, m.p. 89–90°, after crystallization from hexane.

Preparation of VI.—α-Methylhomoanisaldehyde,[12] 50.0 g. (0.31 mole), was stirred with 37.0 g. of acidified H_2O^{18}, *ca.* 1.5 atom % O^{18}. After 12 hr., the aldehyde was extracted with ether. The ether solution was dried over sodium sulfate. The ether solution of the labeled aldehyde was added to 5.77 g. (0.15 mole) of lithium aluminum hydride in 150 ml. of ether. The alcohol was isolated as described for V, b.p. 128° (5 mm.), $n^{20}D$ 1.5319.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.96; H, 8.48.

The phenylurethan was prepared and had m.p. 69–70° after crystallization from hexane.

Anal. Calcd. for $C_{17}H_{19}O_3N$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.68; H, 6.66; N, 5.20.

Preparation of VIII.—The alcohol VI (10.0 g., 0.060 mole) was allowed to react with 11.40 g. (0.060 mole) of *p*-toluenesulfonyl chloride in dry pyridine. The ester VIII was isolated as an oil and was used as such in the solvolysis experiments.

Rearrangement of VIII.—VIII (18.1 g., 0.057 mole) was allowed to rearrange in 834 ml. of dry acetic acid for 19 hr. at 49.5–49.8°. The mixture of esters obtained from this reaction deposited X on cooling. The crude X was purified by crystallization from hexane to give 2.39 g. (13.1%) of pure X, m.p. 78–80° (lit.[6] 80°).

Cleavage of X.—X (2.11 g., 0.0068 mole) was cleaved with 1.26 g. (0.055 mole) of sodium in liquid ammonia to give 0.81 g. (72%) of XII, b.p. 77–80° (0.4 mm.), $n^{25}D$ 1.5240 (lit. b.p. 119° (4 mm.), $n^{25}D$ 1.5261).

The α-naphthylurethan was prepared and after crystallization from acetone–hexane had m.p. 99–100°.

Anal. Calcd. for $C_{21}H_{21}O_3N$: C, 75.20; H, 6.31. Found: C, 75.48; H, 6.36.

The *p*-nitrobenzoate was prepared by allowing the alcohol to react with *p*-nitrobenzoyl chloride in pyridine. The ester was purified by crystallization from hexane, m.p. 76–77.5°.

Anal. Calcd. for $C_{17}H_{17}O_5N$: C, 64.75; H, 5.43. Found: C, 64.49; H, 5.73.

Preparation of *p*-Methoxybenzylmethylcarbinol-hydroxyl-O^{18}.—*p*-Methoxybenzyl methyl ketone was allowed to exchange with H_2O^{18} and was then reduced with lithium aluminum hydride. Two samples of this alcohol were prepared, XIIa and b. XIIa had b.p. 113–118 (5 mm.), $n^{25}D$ 1.5308; and XIIb, b.p. 106–110° (4 mm.), $n^{25}D$ 1.5300.

Preparation of Xa and Xb.—These substances were prepared in the same manner as the other esters; Xa, m.p. 78–80°, Xb, m.p. 78–80°.

Solvolysis of Xa and Xb.—A solution of 7.31 g. (0.029 mole) of Xa in 340 ml. of dry acetic acid was heated 6.6 hr. at 49.7–50.1°. The recovered ester was purified by crystallization from acetone–hexane, m.p. 78–80°. The Xb which was recovered had m.p. 77–80°.

Cleavage of Xa and Xb.—Xa (3.38 g., 0.011 mole) was reduced with 1.95 g. (0.085 mole) of sodium in liquid ammonia to yield 1.36 g. (77%) of the alcohol, b.p. 82°, block temperature (0.6 mm.), $n^{25}D$ 1.5258.

The α-naphthylurethan had m.p. 99–101°.

Xb was reduced to give recovered XIIb, b.p. 62–64° (0.7 mm.), $n^{25}D$ 1.5258. The *p*-nitrobenzoate had m.p. 76–78°.

NEW BRUNSWICK, N. J.

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[11] I. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1953, p. 318.

[12] A. Sosa, *Ann. chim.*, **13**, 97 (1940).

[CONTRIBUTION FROM RESEARCH LABORATORIES, EASTMAN KODAK CO.]

A New Method for the Preparation of Ethylene Sulfide[1]

BY DELBERT D. REYNOLDS

RECEIVED MAY 7, 1957

A new method for the preparation of ethylene sulfide is described. It involves pyrolysis of monothiolethylene carbonate. The yields range from 80–88% and the ethylene sulfide is very pure, since the only by-product is carbon dioxide. The monothiolethylene carbonate is new.

Like ethylene oxide and ethylene imine, ethylene sulfide is an important organic intermediate. It polymerizes readily to yield polyethylene sulfide, which, in turn, can be converted to derived polymers. It is an excellent mercaptoethylating agent[2] and is an intermediate for numerous syntheses.[3] Several methods of synthesis have been reported in the literature. One of these involves the reaction of 2-chloroethylmercaptan with sodium bicarbonate.[4] The 2-chloroethylmercaptan is not readily available, and of greater importance is the fact that the ethylene sulfide must be separated by fractionation to free it from water. This is difficult because of the ease with which it polymerizes.

The second method[3] involves the reaction of ethylene oxide with potassium thiocyanate. The

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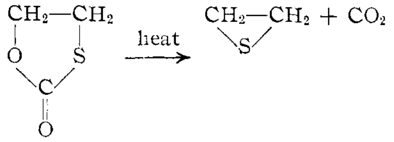
[1] Communication No. 1900 from the Kodak Research Laboratories.

[2] H. R. Snyder and W. Alexander, THIS JOURNAL, **70**, 217 (1948).

[3] G. I. Braz, *J. Chem. Soc., U.S.S.R.*, **21**, 757 (1951).

[4] U. S. Patent 2,183,860, W. Coltof, Dec. 19, 1940; British Patent 508,932, N. V. de Bataafsche Petroleum Maatschappij, July 7, 1939; Dutch Patent 47,835, N. V. de Bataafsche Petroleum Maatschappij, Feb. 15, 1940.

starting materials are readily available, but, after a long preparation which involves a low temperature reaction, ether extractions, and purification by distillation, a low yield is obtained. Yields ranging from 25–50% have been reported, but the method has met with little success in these Laboratories. A method has now been discovered whereby ethylene sulfide can be obtained in high yield by decomposition of monothiolethylene carbonate. The reaction is



The ethylene sulfide is pure as obtained since the only by-product is carbon dioxide. The reaction is not accompanied by polymerization and there is practically no residue. The monothiolethylene carbonate is prepared readily by the reaction of commercially available 2-mercaptoethanol with phosgene.

Among other advantages of the process is the fact that the monothiolethylene carbonate is a high-boiling, stable liquid which can be prepared and kept until ethylene sulfide is needed. Then it is only necessary to heat this intermediate in a suitable apparatus in which the ethylene sulfide can be collected. Since ethylene sulfide cannot be kept because of its tendency to polymerize, this provides a quick and convenient source of it.

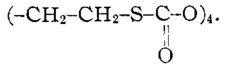
The monothiolethylene carbonate can serve as a mercaptoethylating reagent, as will be shown in a subsequent publication.

The addition of a small amount of an alkaline catalyst, such as sodium carbonate, during the preparation of ethylene sulfide results in a smooth and rapid decomposition. On the other hand, the addition of, *e.g.*, 1% *p*-toluenesulfonic acid inhibits the decomposition. The optimum amount of sodium carbonate is 1%, based on the monothiolethylene carbonate. Larger quantities cause too rapid decomposition and polymerization. Volatile catalysts cause polymerization of the ethylene sulfide in the distillation column.

When the procedure for preparing monothiolethylene carbonate is modified by stirring the pyridine, 2-mercaptoethanol, and ethyl acetate together and adding the phosgene–ethyl acetate solution, the yield of monothiolethylene carbonate is decreased and the amount of polymer is increased accordingly. If the pyridine and pyridine hydrochloride are not thoroughly removed by washing, the monothiolethylene carbonate may decompose near the end of the step in which the ethyl acetate is being removed.

Experimental

Monothiolethylene Carbonate.—Two hundred and thirty seven grams of pyridine and one hundred grams of ethyl acetate were stirred together at 10°. A solution of 150 g. of phosgene in 300 ml. of ethyl acetate was cooled to −15° and 158 g. of 2-mercaptoethanol was added to it. This cold solution was added gradually to the stirred pyridine solution. The reaction temperature was maintained at 15–20°. After all the phosgene had been added, the reaction mixture was stirred for an additional 30 minutes at 35°, after which it was washed by stirring rapidly in an equal volume of cold water containing 10 ml. of concentrated hydrochloric acid. The ethyl acetate layer was washed with an equal volume of cold water, dried over anhydrous magnesium sulfate, and then ethyl acetate was removed by distillation under reduced pressure. The oily residue was then distilled through a 10-in. Vigreux column equipped with a variable-reflux take-off head; yield, 80 g., b.p. 50–60° at 1.0–1.5 mm., n^{25}_D 1.5104; residue of polymer 47 g. Redistillation of the monothiolethylene carbonate gave 75 g. (48.1%), b.p. 47–50° at 0.08 mm., n^{25}_D 1.5104. Analysis indicated the polymer is



$$(\text{-CH}_2\text{-CH}_2\text{-S-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-O})_4.$$

Anal. Calcd. for $C_3H_4SO_2$: C, 34.6; H, 3.8; S, 30.7. Found: C, 34.6; H, 3.9; S, 31.1. Found for the polymeric residue: C, 34.4; H, 4.2; S, 30.1; mol. wt., 415.

Ethylene Sulfide.—Thirty-six grams of monothiolethylene carbonate and 0.36 g. of anhydrous sodium carbonate was heated to 200°. The decomposition proceeded smoothly to yield ethylene sulfide which was collected in a Dry-Ice trap (19.0 g., 88%, n^{25}_D 1.4898). There was no polymerization and practically no residue remaining in the flask.

Numerous other runs were made in which the yields varied from 80–88%.

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[Contribution from the Petroleum and Chemical Research Department of the M. W. Kellogg Co.]

The Chemistry of *p*-Xylylene.[1] I. The Preparation of Solutions of Pseudodiradicals[2]

By L. A. Errede[3] and B. F. Landrum

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A method has been developed for the preparation of relatively stable solutions of pseudodiradicals such as *p*-xylene, 2-chloro-*p*-xylylene and 2-methyl-*p*-xylylene. It involves the fast flow pyrolysis of the parent aromatic hydrocarbon under low pressure and subsequent instantaneous condensation of the pyrolysis products into a solvent maintained at 78°. Polymerization occurs rapidly when the solutions are warmed to room temperature. The corresponding *p*-xylylene diiodides are obtained, however, when these solutions are added at −78° to an excess of iodine.

Introduction

Szwarc[4] was the first to observe that the fast flow pyrolysis of *p*-xylene at low pressure leads to the formation of a white polymeric material having the postulated structure of poly-*p*-xylylene. He suggested[5] that the polymer is formed *via* a series of gas phase reactions whereby C–H bonds of *p*-xylene are cleaved thermally to give *p*-xylyl radicals that disproportionate on collision to produce

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(1) Also named *p*-quinodimethane and 1,4-dimethylene-2,5-cyclohexadiene.

(2) Presented at the 131st Meeting of the American Chemical Society, Miami, Florida, April, 1957.

(3) To whom inquiries should be sent, Minnesota Mining and Manufacturing Co., St. Paul 6, Minn.

(4) M. Szwarc, *Nature*, **160**, 403 (1947).

(5) M. Szwarc, *J. Chem. Phys.*, **16**, 319 (1951).