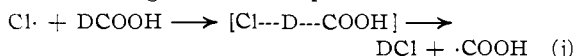
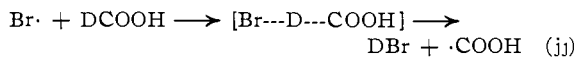


from the bonding in the normal reactants. Therefore this reaction and the similar chlorination of formic acid could both be expected to show much smaller carbon-13 isotope effects than those theoretically calculated assuming complete loss of the carbon-to-hydrogen bond in proceeding to the activated state. This was borne out in the chlorination of formic-C<sup>13</sup> acid at 20° since the theoretically calculated maximum value of  $k_{12}/k_{13}$  was 1.032 and the net experimental value was only 1.006. In the case of the bromination reaction at 45° the net experimental value of  $k_{12}/k_{13}$ , 1.023, was much closer to the theoretically calculated value, 1.029, as might be expected if the activated state for the bromine reaction retained considerably less residual carbon-to-hydrogen bond strength than the activated state for the chlorine reaction. The much slower bromine reaction having the higher activation energy might be expected to retain less of its carbon-hydrogen bond strength at the higher energy level of its activated state. In other words it appears that the carbon-hydrogen bond must be stretched more before cleavage can be effected by a bromine atom than before the corresponding cleavage can occur under the influence of a more active chlorine atom.

Assuming this to be the correct explanation of the difference in degree of isotope fractionation with the two types of halogen atoms, it is interesting to speculate upon what might be the relative hydrogen rate isotope effects due to deuterium or tritium labeling in the same pair of reactions; that is



and



It would seem that  $(k_{\text{H}}/k_{\text{D}})_{\text{Cl}}$  might bear about the same relation to  $(k_{\text{H}}/k_{\text{D}})_{\text{Br}}$  as  $(k_{12}/k_{13})_{\text{Cl}}$  was found to bear to  $(k_{12}/k_{13})_{\text{Br}}$ . Whether or not this would be found to be the case might depend upon the importance of the X—H bond in the activated state. It is planned to study these deuterium (and/or tritium) isotope effects and to compare them with the corresponding carbon-13 (and possibly the carbon-14) effects. Although there is considerable uncertainty in calculating theoretical values of either carbon or hydrogen isotope effects, it may well be that the ratio of the carbon isotope effect to the hydrogen isotope effect would be easier to predict than either effect individually. If so, it may be of value to compare ratios such as

$$\left[ \frac{k_{\text{H}}/k_{\text{D}}}{k_{12}/k_{13}} \right]_{\text{Cl}} \quad \text{and} \quad \left[ \frac{k_{\text{H}}/k_{\text{D}}}{k_{12}/k_{13}} \right]_{\text{Br}}$$

**Acknowledgment.**—G. A. Ropp acknowledges the support of the U. S. Public Health Service in providing the Special Fellowship which made possible a 1955–1956 visit to the Physical Chemistry Laboratory, Oxford University, Oxford, England, where most of this research was carried out. He also wishes to thank his sponsor, Professor Cyril N. Hinshelwood, whose generous cooperation and encouragement made the visit and this research possible.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

## An Oxygen-18 Tracer Study of the Rearrangements of 2-Phenyl-1-propyl *p*-Bromobenzenesulfonate and 2-*p*-Methoxyphenyl-1-propyl *p*-Toluenesulfonate<sup>1</sup>

By DONALD B. DENNEY AND BERNARD GOLDSTEIN

RECEIVED APRIL 26, 1957

2-Phenyl-1-propyl *p*-bromobenzenesulfonate, which was specifically labeled in the ether oxygen of the ester group with oxygen-18, was allowed to rearrange in acetic acid to give 1-phenyl-2-propyl *p*-bromobenzenesulfonate. The ester was reduced with sodium in ammonia to afford benzylmethylcarbinol. The oxygen-18 content of this molecule showed that during the rearrangement partial equilibration of the label took place. In a similar manner 2-*p*-methoxyphenyl-1-propyl *p*-toluenesulfonate was rearranged to give 1-*p*-methoxyphenyl-2-propyl *p*-toluenesulfonate. The oxygen-18 content of the alcohol, obtained by the reductive cleavage of the *p*-toluenesulfonate, showed that during this transformation the three oxygens of the *p*-toluenesulfonate moiety became equivalent.

The mechanism of solvolytic reactions has received a great deal of attention. The reviews<sup>2</sup> of this subject are numerous and cover it in great detail. Recently Winstein<sup>3</sup> and his co-workers have investigated a considerable number of these reactions with a view toward elucidating the role of ion pairs in these systems. In the course of their investigations they found that 2-phenyl-1-propyl

*p*-bromobenzenesulfonate (VII) rearranged in acetic acid to give 1-phenyl-2-propyl *p*-bromobenzenesulfonate (IX).<sup>4</sup> They observed that the addition of *p*-bromobenzenesulfonate ion to the reaction mixture did not cause a common ion rate suppression, but rather only a normal salt effect was observed. On the basis of these results and other data, they suggested that the rearrangement of VII to IX proceeded through an ion pair, which was held together by coulombic attraction and also possibly by some covalent bonding. They have called ion pairs of this sort "internal" or "intimate."

They have also investigated the solvolysis of 2-

(1) Presented at the Sixth Conference on Reaction Mechanisms, Swarthmore College, Sept. 12–15, 1956.

(2) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956); J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956; C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(3) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *This Journal*, **78**, 328 (1956), and references cited there.

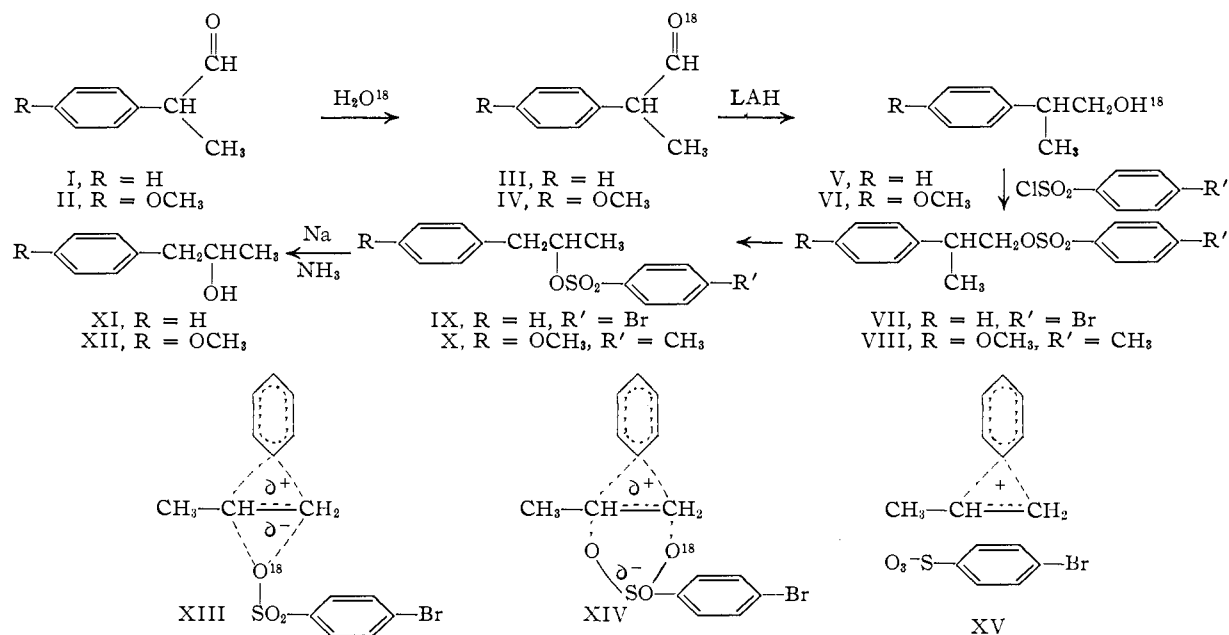
(4) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2171 (1952).

*p*-methoxyphenyl-1-propyl *p*-toluenesulfonate (V-III). They found that there was no common ion rate depression in this reaction; however, in the presence of lithium perchlorate they observed a large rate enhancement, which was not due to a normal salt effect.<sup>5</sup> They suggested that VIII undergoes ionization to an ion pair in which some solvent molecules are interposed between the two ions. They have called such ion pairs "external" or "solvent separated." During the course of the work reported here, it has been found that X can be isolated from the acetolysis of VIII.

It was the purpose of the investigation reported here to study the rearrangements of oxygen-18 labeled VII and VIII. If the ion pair from VII has the structure XIII, then in the product all of the oxygen-18 will still be retained as the ether oxygen. A structure as represented by XIV must also be considered for the ion pair. It leads to IX in which none of the excess oxygen-18 is retained as ether oxygen.

toluenesulfonates quite smoothly to the parent alcohols.<sup>7</sup> Under these conditions IX and X were converted to the alcohols XI and XII. The oxygen-18 analytical results for these compounds can be found in Table I.

After the solvolysis of VII both recovered VII and IX were obtained. The recovered VII was converted back to V which was shown to have the same oxygen-18 content as the original V. These results show that there is no equilibrating return from the ion pair back to VII. The alcohol XI which was obtained from IX had only 57% of the excess oxygen-18 which was originally incorporated in V. Thus there has been considerable equilibration of the oxygen-18 during this transformation. The observed equilibration could have arisen during the conversion to IX or by subsequent equilibrating ion pair formation and return. Of course both of these paths could contribute to the over-all equilibration. In order to examine the behavior of IX under these conditions, IXa of known oxygen-



Still another possibility is represented by XV in which all of the oxygens become equivalent. XV leads to IX in which one-third of the oxygen-18 is retained in the ether position. In an entirely analogous manner, intermediates from VIII can be considered. The possibility exists that more than one of these paths can operate; if such is the case then intermediate amounts of equilibration will be found.

The necessary labeled compounds were prepared as indicated in the flow sheet. The solvolytic conditions were those employed by Winstein and his co-workers.<sup>4-6</sup> In order to determine the fate of the oxygen-18, it was necessary to have a specific method of degrading IX and X. It was shown earlier that sodium in liquid ammonia reduces *p*-

18 content was synthesized by an independent route. This material was solvolyzed until 25% of the starting IXa had been destroyed. This material was then cleaved back to the original alcohol XIa. It was found that some equilibration had occurred. Using the data of Winstein and Schreiber<sup>4</sup> it can be calculated that during the conversion of VII to IX 69% of IX which is formed is decomposed to the acetate. Using the data obtained on the equilibration of IXa, one can calculate that 42% of the equilibration observed in IX is caused by ion pair formation from IX itself. The remaining 58% presumably arises during the rearrangement of VII to IX.<sup>8</sup> These findings show that there is a

(7) D. B. Denney and B. Goldstein, *J. Org. Chem.*, **21**, 419 (1956).

(5) S. Winstein, A. Fainberg and G. Robinson, *Chem. and Ind.*, 664 (1954).

(6) S. Winstein, K. Schreiber and M. Brown, *THIS JOURNAL*, **74**, 1140 (1952).

(8) The question should be asked as to whether these losses of oxygen-18 can be occurring by some other means than those considered. Since it has been shown that VII can be treated under these solvolysis conditions, recovered and converted back to V without loss of oxygen-18, it appears that the losses are not by some "washout" or by the reduction procedure.

TABLE I

Compound	Atom% O <sup>18</sup> in labeled position <sup>a</sup>
$\alpha$ -Naphthylurethan of V	1.28; 1.31
$\alpha$ -Naphthylurethan of V from VII	1.32
V recovered from VII	1.31; 1.29
Phenylurethan of XI	0.82; 0.83
Phenylurethan of XIa	1.24; 1.24
Phenylurethan of XIa from 1Xa	1.18; 1.16
Phenylurethan of VI	1.19; 1.19
<i>p</i> -Nitrobenzoate of XII	0.50; 0.57
	0.52; 0.56
<i>p</i> -Nitrobenzoate of XIIb <sup>b</sup>	1.05; 1.03
<i>p</i> -Nitrobenzoate of XIIb from Xb	0.77
XIIa	1.09; 1.09
XIIa from Xa	0.81; 0.76

<sup>a</sup> The analyses were carried out using the method of W. E. Doering and E. Dorfman, *THIS JOURNAL*, **75**, 5595 (1953), as modified by D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957). In general we have found that analyzing solid samples gives better results than liquid samples. This undoubtedly occurs because the solid materials can be freed from oxygen-containing impurities much more easily than liquids, especially when only small quantities of sample are available. <sup>b</sup> The XIIa and XIIb series represent the same compounds but with different amounts of oxygen-18.

high degree of specificity attendant with this rearrangement; XIII is the favored ion pair with some contributions from XIV and or XV. It is interesting to compare these results with those found in the rearrangements of *trans*-9-decalyl perbenzoate and *p*-methoxy-*p'*-nitrobenzoyl peroxide.<sup>9</sup> In the case of the *trans*-9-decalyl perbenzoate an ion pair similar to XIII was formed exclusively, whereas with the *p*-methoxy-*p'*-nitrobenzoyl peroxide an ion pair similar to XIII was favored; however, equilibrating paths were also utilized.

In order to further investigate reactions of this general type, labeled VIII was prepared and allowed to rearrange in acetic acid to give X. X was cleaved as before to give XII. Combustion of the  $\alpha$ -naphthylurethans of XII, XIIa and b led to erratic values. Finally the *p*-nitrobenzoate esters were prepared and analyzed. Unfortunately, this derivative with its extra oxygens causes a loss in precision in the analysis. The data on the *p*-nitrobenzoate of XII indicate quite strongly that complete equilibration has taken place during the solvolysis.

In order to investigate the stability of X, labeled samples of Xa and Xb were prepared from XIIa and XIIb and solvolyzed until 25% of the starting material was destroyed. The results of these experiments are listed in Table I as the XIIa and XIIb series. It can be seen that X undergoes a rather rapid equilibration of the label much more so than VII. These findings are in agreement with the idea that VIII gives rise to an "external ion pair." Since the X which was isolated from VIII is evidently completely equilibrated, it is impossible to know whether the rearrangement proceeded with partial equilibration or complete equilibration. In other words, one cannot make the same sort of calculation that was made with VII. In general these findings are in accord with the idea that the carbonium ion from VIII will be more stable than that from VII and therefore also

give rise to an ion pair which is considerably more stable than that from VII.

**Acknowledgment.**—We wish to thank the Research Corporation for a Frederick Gardner Cottrell Grant. We are also indebted to the Esso Research and Engineering Corp. and the Colgate Palmolive Co. for the mass-spectral analyses.

#### Experimental<sup>10</sup>

**Hydratropaldehyde-carbonyl-O<sup>18</sup> (III).**—A mixture of 40.2 g. (0.30 mole) of hydratropaldehyde and 50.0 g. of H<sub>2</sub>O<sup>18</sup>, *ca.* 1.5 atom % O<sup>18</sup>, to which there had been added 0.1 ml. of concentrated sulfuric acid, was stirred at room temperature for 14 hr. The aldehyde was taken up in petroleum ether and then dried over potassium carbonate. Distillation afforded 34.9 g. of aldehyde, b.p. 96–98° (25 mm.), *n*<sub>D</sub><sup>20</sup>, *n*<sub>D</sub><sup>25</sup> 1.5146.

**Hydratropic Alcohol-hydroxyl-O<sup>18</sup> (V).**—To a stirred solution of 6.0 g. (0.158 mole) of lithium aluminum hydride in 250 ml. of dry ether was added 34.5 g. (0.308 mole) of III in 25 ml. of dry ether. The mixture was stirred for 3 hr., and then ice and 120 ml. of 20% sulfuric acid were added. The ether layer was washed with 50 ml. of water and then dried over magnesium sulfate. The ether was removed and the residue was distilled to afford 28.7 g. (82%) of V, b.p. 114–117° (25 mm.), *n*<sub>D</sub><sup>20</sup> 1.5258.

The  $\alpha$ -naphthylurethan of V was prepared by allowing 0.51 g. (0.0030 mole) of  $\alpha$ -naphthyl isocyanate and 0.41 g. (0.0030 mole) of V to react in 3 ml. of hexane at room temperature. The urethan was crystallized from hexane, m.p. 103–104°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>19</sub>O<sub>2</sub>N: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.68; H, 6.40; N, 4.53.

***p*-Bromobenzenesulfonate of V (VII).**—To an ice-cold solution of 27.2 g. (0.20 mole) of V in 125 ml. of pyridine was added 53.6 g. (0.21 mole) of *p*-bromobenzenesulfonyl chloride in 60 ml. of dry pyridine. The mixture was kept in a refrigerator for 30 hr. and was then poured onto a mixture of ice and dilute sulfuric acid. The precipitated ester was filtered and dried to give 61.4 g. of material, m.p. 72–75°. The crude ester was crystallized from benzene-hexane to afford 51.4 g. of VII, m.p. 81–82° (lit.<sup>4</sup> 81.5–82.5°).

**Rearrangement of VII to IX.**—A solution of 48.0 g. of VII in 2 l. of glacial acetic acid, to which had been added 20 ml. of acetic anhydride, was heated at 100.4° for 95 minutes. The solution was poured onto ice and extracted with three one-liter portions of a 1:1 mixture of ether-petroleum ether (30–60°). The organic extracts were washed with 10% potassium carbonate solution and dried over magnesium sulfate. The organic solution was concentrated to 400 ml.; a precipitate of 20.8 g. of VII was obtained. The mother liquors were concentrated to 100 ml. to give 1.52 g. of material, m.p. 69–77°. The remaining solvent was removed and a third crop of material, m.p. 78–79.5°, 1.50 g., was obtained.

The first two fractions were dissolved in fresh acetic acid and solvolyzed in the same manner. Following the same isolation procedure, 9.0 g. of VII was recovered and 0.60 g. of impure IX was obtained. The two third fractions from these runs were combined and recrystallized from hexane to yield 1.85 g. of IX, m.p. 77–78° (lit.<sup>6</sup> 80–81°). The infrared spectrum of this material was identical to that of an authentic sample prepared from benzylmethylcarbinol.

**Cleavage of Recovered VII.**—To a stirred solution of 0.65 g. (0.0283 mole) of sodium in liquid ammonia was added 1.78 g. (0.0050 mole) of finely divided VII. The mixture was stirred for five minutes and then solid ammonium chloride was added. Water was then added and the ammonia was allowed to evaporate. The aqueous solution was extracted with two 30-ml. portions of ether, and the ether extracts were dried over magnesium sulfate. The ether was distilled and the residue was evaporatively distilled at 17 mm., block temperature 120°, to give 0.49 g. of material whose infrared spectrum was identical to that of a known sample of V.

The  $\alpha$ -naphthylurethan was prepared as described earlier, m.p. 103–103.5°.

**Cleavage of IX.**—In the same manner as used with VII, 1.72 g. of IX was cleaved to yield 0.35 g. of XI, b.p. 120°.

(9) D. B. Denney and D. G. Denney, *THIS JOURNAL*, in press.

(10) Analyses by G. Robertson, Florham Park, N. J.

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.<sup>11</sup> 93°) after crystallization from hexane.

**Preparation of Benzyl Methyl Ketone-carbonyl-O<sup>18</sup>.**—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<sub>2</sub>O<sup>18</sup>. The ketone was distilled, b.p. 87–89° (12 mm.), yield 22.3 g.

**Preparation of Benzylmethylcarbinol-hydroxyl-O<sup>18</sup>.**—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.**— $\alpha$ -Methylhomoisaldehyde,<sup>12</sup> 50.0 g. (0.31 mole), was stirred with 37.0 g. of acidified H<sub>2</sub>O<sup>18</sup>, ca. 1.5 atom % O<sup>18</sup>. 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*<sub>D</sub><sup>20</sup> 1.5319.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>: 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.

(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).

*Anal.* Calcd. for C<sub>17</sub>H<sub>19</sub>O<sub>3</sub>N: 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.<sup>6</sup> 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*<sub>D</sub><sup>20</sup> 1.5240 (lit. b.p. 119° (4 mm.), *n*<sub>D</sub><sup>20</sup> 1.5261).

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

*Anal.* Calcd. for C<sub>21</sub>H<sub>21</sub>O<sub>3</sub>N: 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<sub>17</sub>H<sub>17</sub>O<sub>3</sub>N: C, 64.75; H, 5.43. Found: C, 64.49; H, 5.73.

**Preparation of *p*-Methoxybenzylmethylcarbinol-hydroxyl-O<sup>18</sup>.**—*p*-Methoxybenzyl methyl ketone was allowed to exchange with H<sub>2</sub>O<sup>18</sup> 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*<sub>D</sub><sup>20</sup> 1.5308; and XIIb, b.p. 106–110° (4 mm.), *n*<sub>D</sub><sup>20</sup> 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*<sub>D</sub><sup>20</sup> 1.5258.

The  $\alpha$ -naphthylurethan had m.p. 99–101°.

Xb was reduced to give recovered XIIb, b.p. 62–64° (0.7 mm.), *n*<sub>D</sub><sup>20</sup> 1.5258. The *p*-nitrobenzoate had m.p. 76–78°.

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM RESEARCH LABORATORIES, EASTMAN KODAK CO.]

## A New Method for the Preparation of Ethylene Sulfide<sup>1</sup>

BY DELBERT D. REYNOLDS

RECEIVED MAY 7, 1957

A new method for the preparation of ethylene sulfide is described. It involves pyrolysis of monothioethylene carbonate. The yields range from 80–88% and the ethylene sulfide is very pure, since the only by-product is carbon dioxide. The monothioethylene 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<sup>2</sup> and is an intermediate for numerous syntheses.<sup>3</sup> Several methods of synthesis have been reported in the literature. One of these involves the reaction of

2-chloroethylmercaptan with sodium bicarbonate.<sup>4</sup> 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<sup>3</sup> involves the reaction of ethylene oxide with potassium thiocyanate. The

(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.