

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CANISIUS COLLEGE]

### Trimethylene Oxides. I. Reaction of 2-Chloro-4-hexanol and 1-Phenyl-3-chloro-1-butanol with Alkali<sup>1</sup>

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The reaction of 2-chloro-4-hexanol with potassium hydroxide gave 2-hexen-4-ol, propylene, propionic acid as well as the expected 1-methyl-3-ethyltrimethylene oxide. The reaction of 1-phenyl-3-chloro-1-butanol with base gave propylene, benzyl alcohol, benzoic acid, biphenyl and the dimer of phenylbutadiene. No trimethylene oxide was isolated in the latter reaction.

The intramolecular Williamson reaction has been utilized in the synthesis of substituted trimethylene oxides by heating the appropriate 1,3-halohydrin or the acetate thereof with powdered, aqueous or alcoholic potassium hydroxide. This method has been successfully applied to the preparation of 1-,<sup>2,3</sup> 1,1-<sup>4</sup> and 2,2-disubstituted trimethylene oxides.<sup>5</sup>

Lespieau<sup>2</sup> reported an unsuccessful attempt to prepare 1-methyl-3-ethyltrimethylene oxide by the reaction of 2-chloro-4-hexanol (I) and powdered potassium hydroxide. The product of this reaction, in low yield, was an unsaturated alcohol postulated as 2-hexen-4-ol on the basis of its molar refraction and the absence of chlorine.

The reaction of I with finely powdered potassium hydroxide gave a mixture of propylene (21%), identified as the dibromo derivative, 1-methyl-3-ethyltrimethylene oxide (II) (25%), 2-hexen-4-ol (III) (25%), propionic acid (18%), identified as the *p*-bromophenacyl ester and amide, water and 21% of unreacted I.

Treatment of II with a dilute solution of ferric chloride gave an orange precipitate. This was reported by Lespieau<sup>2</sup> as a characteristic reaction of trimethylene oxides. It did not decolorize a 2% solution of bromine in carbon tetrachloride in the cold, but evolved hydrogen bromide upon heating. The infrared absorption spectrum of II was characterized by a very strong band at 10.2  $\mu$  and a strong band at 8.2  $\mu$ . The spectrum of 1-methyltrimethylene oxide showed corresponding bands and agreed with the published spectrum in all details.<sup>6</sup> Barrow and Searles<sup>6</sup> have reported that the infrared spectra of trimethylene oxides are characterized by strong bands at 10.2 to 10.3 and 8 $\mu$ , the exact value of the latter depending upon the substituents on the oxide ring. The molar refraction of II agreed satisfactorily with the postulated 1-methyl-3-ethyltrimethylene oxide structure.

Compound III decolorized a bromine-carbon tetrachloride solution and was identified as 2-hexen-4-ol by its physical constants, molar refraction and the identity of its phenylurethan with that of authentic material prepared by the reaction of ethylmagnesium bromide and crotonaldehyde.

Dehydrohalogenation of 2-chloro-4-hexanol (I)

(1) Abstracted from the M.S. Theses of W. A. Himmler and H. J. Pepe, Canisius College, June, 1953.

(2) R. Lespieau, *Bull. soc. chim.*, [5] **7**, 254 (1940).

(3) Celanese Corporation of America, British Patent 585,245 (February 3, 1947).

(4) (a) C. Moureu and G. Barrett, *Bull. soc. chim.*, [4] **29**, 993 (1921);

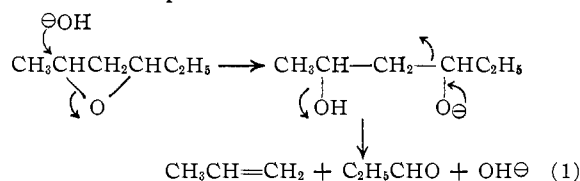
(b) G. M. Bennett and W. G. Philip, *J. Chem. Soc.*, 1937 (1928).

(5) (a) R. Fonteyne and M. Tacket, *Natuurw. Tijdschr.*, **25**, 49 (1943); (b) S. Searles and M. J. Gortatowski, *THIS JOURNAL*, **75**, 3030 (1953).

(6) G. M. Barrow and S. Searles, *ibid.*, **75**, 1175 (1953).

would be expected to yield the unsaturated alcohol III and/or the trimethylene oxide (II). Both of these products were obtained in this investigation. The formation of propylene and propionic acid are indicative of the operation of a cleavage reaction.

Barbot<sup>7</sup> has postulated an unstable intermediate with a trimethylene oxide structure to account for the formation of olefinic and carbonyl compounds in the alkaline pyrolysis of 1,3-chlorohydrins. In addition, this mechanism is applied to the alkaline pyrolysis of 1,3-glycols and  $\beta,\gamma$ -unsaturated carbonyls. All three of these intermediates are compatible with our reaction conditions. The cleavage reaction can be postulated as



The propionic acid isolated in this investigation may have been formed from propionaldehyde by direct oxidation or a Cannizzaro reaction. However, the propanol which should accompany the acid as a result of the latter reaction was not detected. The usual alkali condensation product of propionaldehyde is propionaldol. However, Barbot has shown that aldols are pyrolyzed to two moles of aldehyde.<sup>7</sup>

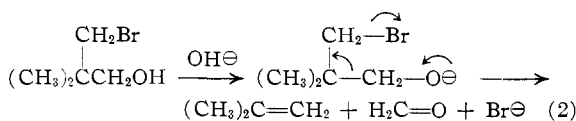
The reaction of 1-phenyl-3-chloro-1-butanol (IV) with finely powdered potassium hydroxide gave a mixture of propylene (20%), benzyl alcohol (14%), identified by its physical constants and the identity of its  $\alpha$ -naphthylurethan and 3,5-dinitrobenzoates with authentic material, benzoic acid (12%), identified by mixed melting point and the preparation of the amide and *p*-bromophenacyl ester, biphenyl (10%), identified by mixed melting point, the dimer of phenylbutadiene (33%), identified by its physical constants, molecular weight and chemical behavior, and a large resinous residue.

The reaction of 1-phenyl-3-chlorobutanol (IV) with base failed to yield any isolatable trimethylene oxide. The dehydrohalogenation reaction was accompanied by dehydration to yield phenylbutadiene. Since the dimer is readily formed under the influence of heat<sup>8</sup> failure to isolate the monomeric diene is not unexpected. The cleavage reaction in this case gave propylene and the Cannizzaro products of benzaldehyde, benzyl alcohol and benzoic acid.

(7) A. Barbot, *Bull. soc. chim.*, [5] **2**, 1438 (1935).

(8) I. E. Muskat and M. Herrman, *THIS JOURNAL*, **53**, 252 (1931).

Searles and Gortatowski<sup>5b</sup> reported that the reaction of 3-bromo-2,2-dimethyl-1-propanol with potassium hydroxide gave 10–25% yields of 2,2-dimethyltrimethylene oxide accompanied by the cleavage products isobutylene and formaldehyde as well as the Cannizzaro products of the aldehyde, methanol and formic acid. The cleavage products were postulated as arising from a rearrangement of the same alkoxide ion which is the intermediate for the cyclization reaction



The failure to isolate the trimethylene oxide from the alkyl aryl disubstituted chlorohydrin may be due to the operation of the reaction in equation 2 or to the cleavage of initially formed oxide as in equation 1.

The formation of biphenyl in our investigation could be accounted for by a free radical mechanism although the operation of such a mechanism would not be anticipated in a reaction of this nature. The origin of the biphenyl is therefore obscure.

### Experimental

**$\beta$ -Chlorobutyraldehyde.**—Anhydrous gaseous hydrogen chloride was passed into a solution of 350 g. (5 moles) of crotonaldehyde in an equal volume of ether. The temperature was maintained below  $-10^\circ$  by means of a Dry Ice-acetone freezing mixture during the course of the addition of 182.5 g. (5 moles) of gas. The cold solution was shaken for ten minutes with 30 g. of anhydrous sodium carbonate, decanted and shaken again with 30 g. of anhydrous calcium chloride. The ethereal solution of the  $\beta$ -chlorobutyraldehyde was utilized in the reaction with the Grignard reagent without further treatment due to the rapid trimerization of the monomeric aldehyde.<sup>9</sup>

**2-Chloro-4-hexanol.**—The ether solution of  $\beta$ -chlorobutyraldehyde, held below  $-10^\circ$  by means of a jacketed dropping funnel containing a freezing mixture, was added dropwise to the ethyl Grignard reagent prepared from 145.9 g. (6 moles) of magnesium turnings and 654 g. (6 moles) of ethyl bromide in 1400 cc. of ether. The temperature of the reaction was held below  $0^\circ$  during the course of the two-hour addition. Stirring was continued at room temperature for one hour. The reaction mixture was poured on cracked ice and acidified with cold 5% sulfuric acid. The ether layer was dried over anhydrous sodium carbonate and distilled to yield 290.5 g. (42.6%) of 2-chloro-4-hexanol, b.p.  $51-53^\circ$  (1.6 mm.),  $d^{25}_4$  0.9734,  $n^{25}_D$  1.4419 (lit.<sup>10</sup> b.p.  $78-79^\circ$  (13 mm.),  $d^{10}_4$  1.0012,  $n^{10}_D$  1.4433).

**2-Chloro-4-acetoxyhexane.**—Acetyl chloride (180.5 g., 2.3 moles) was rapidly added over 30 minutes to 290.5 g. (2.13 moles) of 2-chloro-4-hexanol. Upon completion of the addition the reaction mixture was refluxed for 15 minutes. After the addition of 100 ml. of water, the ether layer was washed with a saturated sodium carbonate solution and dried over anhydrous sodium carbonate. Distillation gave 260.3 g. (68.5% yield) of 2-chloro-4-acetoxyhexane, b.p.  $56^\circ$  (1.8 mm.),  $d^{25}_4$  1.0102,  $n^{25}_D$  1.4300,  $MR$  45.68 (obs.), 45.66 (calcd.) (lit.<sup>11</sup> b.p.  $83.4^\circ$  (11 mm.),  $d^{24}_4$  1.0151,  $n^{24}_D$  1.435).

**1-Phenyl-3-chloro-1-butanol.**—The reaction of  $\beta$ -chlorobutyraldehyde and the phenyl Grignard reagent prepared from 97.2 g. (4 moles) of magnesium turnings and 785 g. (5 moles) of bromobenzene in 1.5 l. of ether was carried out as described above for the preparation of 2-chloro-4-hexanol. Distillation gave 404 g. (55%) of 1-phenyl-3-chloro-1-butanol, b.p.  $106-107^\circ$  (1 mm.),  $d^{30}_4$  1.1007,  $n^{25}_D$  1.5315,  $n^{30}_D$  1.5293,  $MR$  50.78 (obs.), 51.16 (calcd.). The  $\alpha$ -naphthylurethan had m.p.  $141-142^\circ$ .

(9) (a) Kekule, *Ann.*, **162**, 100 (1872); (b) B. Helferich and E. Besler, *Ber.*, **57B**, 1276 (1924).

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{19}\text{NO}_2\text{Cl}$ : N, 3.93; Cl, 10.06. Found: N, 3.97; Cl, 9.97.

**1-Phenyl-3-chlorobutyl Acetate.**—The reaction of 180.5 g. (2.3 moles) of acetyl chloride and 369 g. (2 moles) of 1-phenyl-3-chloro-1-butanol, as above, gave 445 g. (74% yield) of haloacetate, b.p.  $107-108^\circ$  (1.2 mm.),  $d^{25}_4$  1.1027,  $n^{25}_D$  1.5042.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{Cl}$ : C, 63.57; H, 6.66;  $MR$ , 60.54. Found: C, 63.73; H, 6.59;  $MR$ , 60.89.

**Reaction of 2-Chloro-4-hexanol (I) with Base.**—A mixture of 68.25 g. (0.50 mole) of I and 56 g. (1 mole) of finely powdered potassium hydroxide was stirred at room temperature until a vigorous exothermic reaction occurred in 15–30 minutes. The reaction temperature was maintained at  $75-100^\circ$  while gaseous propylene was evolved and collected in a cold trap and four consecutive bromine-carbon tetrachloride traps. After two hours, the reaction mixture was heated to  $130^\circ$  and held at this temperature for 1–2 hours while 1-methyl-3-ethyltrimethylene oxide was distilled from the reaction mixture and collected in the cold trap. The propylene was distilled from the oxide in the cold trap and collected in the bromine-carbon tetrachloride traps. Distillation of the residue in the cold trap gave 7.1 g. of 1-methyl-3-ethyltrimethylene oxide (II), b.p.  $98-99^\circ$ ,  $d^{25}_4$  0.8157,  $n^{25}_D$  1.3972.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{12}\text{O}$ : C, 71.95; H, 12.08;  $MR$ , 29.35. Found<sup>10</sup>: C, 70.46, 70.65; H, 12.65, 12.37;  $MR$ , 29.58.

Two hundred milliliters of water and an equal volume of ether were added to the cooled reaction mixture which was then stirred for 20 minutes. The ether layer, combined with an ether wash of the aqueous layer, was dried and distilled to give 5.48 g. of II (total yield 12.58 g., 25.2%) and 12.6 g. (25.2%) of 2-hexen-4-ol (III), b.p.  $134-135^\circ$ ,  $d^{25}_4$  0.8367,  $n^{25}_D$  1.4300 (lit.<sup>11</sup> b.p.  $135-135.5^\circ$ ,  $d^{25}_4$  0.8346,  $n^{25}_D$  1.4325),  $MR$ , 30.96 (obs.), 30.97 (calcd.), as well as 14.2 g. (20.8%) of unreacted I.

The aqueous layer was acidified with 6 *N* hydrochloric acid and continuously extracted with ether for seven days to yield 6.8 g. (18.4%) of propionic acid, b.p.  $141^\circ$ ,  $n^{20}_D$  1.3879 (lit. b.p.  $141.4^\circ$ ,  $n^{17}_D$  1.3874<sup>12b</sup>).

The material in the bromine traps was distilled, after the decomposition of excess bromine with sodium thiosulfate, to yield 21.3 g. (21.08%) of 1,2-dibromopropane, b.p.  $53-54^\circ$  (36 mm.)  $141^\circ$  (756 mm.),  $n^{20}_D$  1.5198 (lit.<sup>13</sup> b.p.  $139-142^\circ$ ,  $n^{20}_D$  1.5192).

The phenylurethan of III was prepared in the usual way, catalyzed by the addition of one drop of triethylamine, recrystallized from petroleum ether, and had m.p.  $79-80^\circ$  which was not depressed by the urethan of authentic 2-hexen-4-ol.<sup>11</sup>

*Anal.* Calcd. for  $\text{C}_{13}\text{H}_{17}\text{NO}_2$ : N, 6.39. Found: N, 6.23.

The *p*-bromophenacyl ester, m.p.  $62-64^\circ$ , and the amide, m.p.  $78-79^\circ$ , of propionic acid were not depressed by the corresponding derivatives of authentic material.

**Reaction of 1-Phenyl-3-chloro-1-butanol (IV) with Base.**—A mixture of 185.5 g. (1 mole) of IV and 112 g. (2 moles) of powdered potassium hydroxide was stirred at room temperature until, after 15 minutes, a vigorous exothermic reaction occurred. The reaction temperature was held below  $80^\circ$  by means of a cooling bath while the evolved propylene was collected in bromine-carbon tetrachloride traps. In preliminary experiments the temperature was observed to rise to  $225^\circ$  in less than one minute at the onset of the exothermic reaction. After two hours, the reaction mixture was heated to  $125^\circ$  and held at this temperature for one hour.

The reaction mixture was diluted with 200 ml. of water and 200 ml. of ether and stirred for ten minutes. The ether layer, combined with an ether wash of the aqueous

(10) Bennett and Philip, ref. 4b, reported great difficulty in analyzing disubstituted trimethylene oxides. Searles (private communication) has made the same observation.

(11) R. S. Airs, M. P. Balfe and J. Kenyon, *J. Chem. Soc.*, **18** (1942).

(12) (a) N. D. Cheronis and J. B. Entrikin, "Semi-Micro Qualitative Organic Analysis," T. Y. Crowell Co., New York, 1947, p. 358; (b) G. S. Whitby, *J. Chem. Soc.*, 1458 (1926).

(13) M. S. Kharasch, J. G. McNab and M. C. McNab, *This Journal*, **57**, 2463 (1935).

layer, was dried and distilled to give 16 g. (14%) of benzyl alcohol, b.p. 92° (9 mm.),  $n_D^{20}$  1.5388, 11 g. of biphenyl, b.p. 75–85° (1 mm.) and 43 g. (33%) of a viscous oil, b.p. 158–163° (1 mm.),  $n_D^{20}$  1.5990, and a large resinous residue.

The aqueous layer was acidified with 6 *N* hydrochloric acid to yield, after recrystallization from water, 14 g. (12%) of benzoic acid, m.p. 121°.

The propylene was identified as the dibromo compound, 40 g. (20%), b.p. 141°, m.p. –55°,  $n_D^{20}$  1.5199 (lit.<sup>13</sup> b.p. 141°, m.p. –55.6°,  $n_D^{20}$  1.5203). The  $\alpha$ -naphthylurethane, m.p. 133–134° (lit.<sup>14</sup> m.p. 134.5°) and 3,5-dinitrobenzoate, m.p. 112–113° (lit.<sup>15</sup> m.p. 112°) of benzyl alcohol were not depressed on admixture with authentic material. The biphenyl, m.p. 69°, did not depress the melting point of authentic biphenyl. The *p*-bromophenacyl ester, m.p. 117–118° (lit.<sup>16</sup> 119°) and the amide, m.p. 129° (lit.<sup>17</sup> m.p. 130°) of benzoic acid were not depressed by the derivatives of authentic material.

The viscous oil was found to readily decolorize bromine solutions and on oxidation with potassium permanganate in acetone<sup>18</sup> gave benzoic acid. A molecular weight of 263 by the Rast method indicated that the compound was probably the dimer of phenylbutadiene, molecular weight 260 (lit.<sup>3</sup> b.p. 160° (1 mm.),  $n_D^{20}$  1.5988).

Permanganate oxidation of 15 g. of the resinous residue gave 5 g. of benzoic acid.

Preliminary attempts to prepare the oxides by treatment of the chlorohydrins or the acetates thereof with a molten mixture of potassium and sodium hydroxides<sup>19</sup> gave large quantities of gaseous olefin and, in the case of IV, no product was obtained in the anticipated boiling range of the oxide.

$\beta$ -Chloropropionaldehyde was prepared by the passage of three moles of hydrogen chloride into an ethereal solution of three moles of acrolein while maintaining the temperature below –10°. The ethereal solution was shaken with anhydrous potassium carbonate and calcium chloride and utilized in the Grignard reaction without further purification.

(14) V. T. Bickel and H. E. French, *THIS JOURNAL*, **48**, 747 (1926).

(15) O. Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., p. 166.

(16) W. L. Judefind and E. E. Reid, *THIS JOURNAL*, **42**, 1043 (1920).

(17) Reference 12a, p. 363.

(18) C. N. Riiber, *Ber.*, **37**, 2275 (1904).

(19) S. Searles, *THIS JOURNAL*, **73**, 124 (1951).

**4-Chloro-2-butanol.**—The reaction of  $\beta$ -chloropropionaldehyde and the Grignard reagent prepared from 72.9 g. (3 moles) of magnesium and 426 g. (3 moles) of methyl iodide gave a 33% yield of 4-chloro-2-butanol, b.p. 48–50° (2 mm.). In order to obtain pure product the bath temperature was maintained below 80° during the distillation.

**4-Chloro-2-acetoxybutane.**—A mixture of 132 g. (1.2 moles) of 4-chloro-2-butanol and 150 ml. (1.45 moles) of acetic anhydride in the presence of a few drops of concentrated sulfuric acid was shaken intermittently for 30 minutes while an exothermic reaction took place. The reaction mixture was then refluxed for 1.5 hours and decomposed with water. The organic layer was separated, washed with water and dried over anhydrous sodium carbonate. The crude product obtained by atmospheric distillation was redistilled *in vacuo* to yield 149 g. (83%) of ester, b.p. 68–70° (11 mm.).

**1-Methyltrimethylene Oxide.**—A mixture of 196 g. (4.9 moles) of sodium hydroxide, 196 g. (3.5 moles) of potassium hydroxide and 15 ml. of water was heated in a 1-l. flask equipped with a dropping funnel, thermometer, stirrer and a 15-in. Vigreux column connected to a water-cooled condenser with an ice-cooled receiver. The temperature was raised to 160° and 200 g. (1.33 moles) of 4-chloro-2-acetoxybutane was rapidly added dropwise with efficient stirring over a period of 45 minutes. The temperature was maintained between 150–160° during the addition while the vigorous reaction produced white fumes which were collected in the cooled receiver. The vapor temperature of the distillate was 60–70°. Distillation ceased on the completion of the addition and the reaction temperature was slowly raised to 220° over a period of one hour while additional distillate was collected. The crude distillate, 83 g., was fractionated through a 1.5-ft. helices-packed column to yield 65 g. (68%) of oxide, b.p. 59–60°,  $n_D^{20}$  1.3886 (lit.<sup>3b</sup> b.p. 59.4–59.7° (736 mm.),  $n_D^{20}$  1.3889).

Infrared absorption spectra of the trimethylene oxides were obtained in a 0.025-mm. cell with a Perkin-Elmer spectrophotometer.

**Acknowledgments.**—We wish to acknowledge the assistance of Robert C. Petry and Paul F. Forsyth who prepared 1-methyltrimethylene oxide and its precursors.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

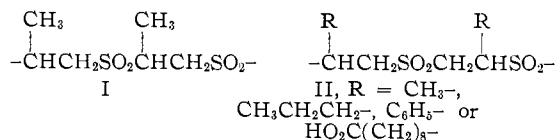
## The Structure of Propylene Polysulfone

BY C. S. MARVEL AND E. D. WEIL<sup>1</sup>

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Evidence originally presented in support of the postulated "head-to-head" structure of olefin-sulfur dioxide copolymers has been re-examined and found to have been misleading because of certain previously-unrecognized rearrangements which occurred during the synthesis of reference compounds. Evidence has been found for a "head-to-tail" structure in the propylene-sulfur dioxide copolymer. The oxidation product of polymerized propylene sulfide has been found to be similar in structure to the propylene-sulfur dioxide copolymer.

The earliest publications describing the copolymer of propylene and sulfur dioxide presented conflicting opinions on the structure of this polymer. Staudinger and Ritzenthaler<sup>2</sup> proposed a "head-to-tail" structure I but presented no experimental evidence for this proposal. Marvel and co-workers<sup>3–6</sup> investigated the structure of the copolymers of sulfur dioxide with propylene, pentene-1, styrene, and 10-hendecenoic acid, and proposed a "head-to-head, tail-to-tail" structure (II)



for these substances on the basis of degradation reactions and syntheses of the degradation products by reactions believed at that time to be unequivocal.

Subsequent to these investigations, an increasingly large body of evidence has accumulated showing that in polymers formed by the free-radical mechanism the monomer units comprising the polymer chain are arranged predominantly in the head-to-tail manner; no vinyl homopolymer is now

(1) National Science Foundation Fellow 1952–1953.

(2) H. Staudinger and B. Ritzenthaler, *Ber.*, **68**, 455 (1935).

(3) M. Hunt and C. S. Marvel, *THIS JOURNAL*, **57**, 1691 (1935).

(4) F. J. Glavis, L. L. Ryden and C. S. Marvel, *ibid.*, **59**, 707 (1937).

(5) C. S. Marvel, S. J. Davis and F. J. Glavis, *ibid.*, **60**, 1450 (1938).

(6) C. S. Marvel and W. H. Sharkey, *ibid.*, **61**, 1603 (1939).