The Reaction of Methanesulfenyl Chloride with Ethylene Oxide[1]

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In studying the reaction between methanesulfenyl chloride and ethylene oxide Brintzinger and Langheck[2] found that 2-chloroethyl methanesulfinate, $CH_3SO_2CH_2CH_2Cl$, was formed instead of the expected sulfenate ester. Their implied explanation was that the 2-chloroethyl methanesulfenate, $CH_3SOCH_2CH_2Cl$, originally formed, underwent rapid oxidation to the sulfinate ester.

We have examined this reaction and have found that it produces 2-chloroethyl methanesulfinate, methyl disulfide, and ethylene dichloride in equimolar amounts. The equation for the overall reaction is

$$3\ CH_3SCl + 2\ CH_2CH_2 \longrightarrow \underset{\diagdown O \diagup}{} \qquad CH_3SSCH_3 + ClCH_2CH_2Cl + CH_3\overset{\overset{O}{|}}{S}OCH_2CH_2Cl.$$

These results are readily explained in terms of the electrophilic character of methanesulfenyl chloride discussed in a recent publication from this laboratory.[3] It is believed that methanesulfenyl chloride (I) first reacts with ethylene oxide to form 2-chloroethyl methanesulfenate (II). A second mole of I then reacts with II by electrophilic attack on sulfur with elimination of ethylene dichloride and the formation of methyl methanethiolsulfinate (III). A third mole of I then reacts with III by electrophilic attack on the thiol sulfur with elimination of methanesulfinyl chloride (IV) and the formation of methyl disulfide. Finally, a second mole of ethylene oxide reacts with IV to form 2-chloroethyl methanesulfinate (V).

$$\underset{\text{I}}{CH_3SCl} + CH_2{-}CH_2 \longrightarrow \underset{\text{II}}{[CH_3SOCH_2CH_2Cl]}$$
$$\diagdown O \diagup$$

$$\underset{\text{II}}{[CH_3SOCH_2CH_2Cl]} + \underset{\text{I}}{CH_3SCl} \longrightarrow \left[\begin{matrix} O \\ | \\ CH_3SSCH_3 \end{matrix}\right]_{\text{III}} + ClCH_2CH_2Cl$$

$$\left[\begin{matrix} O \\ | \\ CH_3SSCH_3 \end{matrix}\right]_{\text{III}} + \underset{\text{I}}{CH_3SCl} \longrightarrow \left[\begin{matrix} O \\ | \\ CH_3SCl \end{matrix}\right]_{\text{IV}} + CH_3SSCH_3$$

$$\underset{\text{IV}}{CH_3\overset{\overset{O}{|}}{S}Cl} + CH_2CH_2 \longrightarrow CH_3\overset{\overset{O}{|}}{S}OCH_2CH_2Cl$$
$$\diagdown O \diagup$$

The first step in this sequence of reactions represents what one would expect to happen, as it would be consistent with the behavior of epoxides. It is further supported by the fact that Langford and Kharasch[4] have shown that trichloromethanesulfenyl chloride reacts with ethylene oxide to form 2-chloroethyl trichloromethanesulfenate, $Cl_3C{-}S{-}O{-}CH_2CH_2Cl$. Sosnovsky[5] prepared a number of alkyl trichloromethanesulfenate esters from trichloromethanesulfenyl chloride but all efforts in this laboratory to prepare similar compounds from I have failed. Although methanesulfenyl chloride is admittedly more reactive than trichloromethanesulfenyl chloride, the isolation of trichloromethanesulfenate esters may be a consequence of their lesser reactivity as compared to methanesulfenate esters.

No proof can be advanced at this time that the second and third steps take place as shown. Another study now in progress will, it is hoped, support our belief that the postulated reactions represent the most reasonable explanation for the products observed.

The proposed fourth step is supported by the fact that methanesulfinyl chloride (IV) has been found to react readily with ethylene oxide to form V in excellent yield.

EXPERIMENTAL

Preparation of methanesulfenyl chloride, (I). Liquid chlorine (32 g., 0.45 mole), after being condensed in a carefully tared test tube at the temperature of solid carbon dioxide, was allowed to evaporate into the space above 44.2 g. (0.47 mole) of methyl disulfide contained in a 32 × 200 mm. culture tube cooled in an acetone–Dry Ice bath. The methyl disulfide was occasionally shaken gently to bring about reaction between the solid methylsulfur trichloride which formed above the liquid surface and methyl disulfide. When the last of the chlorine had evaporated the tube was again shaken to complete the reaction between methylsulfur trichloride and methyl disulfide and when all solid had disappeared the methanesulfenyl chloride was ready for use.

The reaction of I *with ethylene oxide.* Compound I prepared above was transferred to a 500-ml. three neck flask fitted with mechanical stirrer and held at −20° while 29.5 g. (0.67 mole) of ethylene oxide was passed in. The reaction proceeded smoothly and when the last of the ethylene oxide had been added the reaction mixture had faded to a pale yellow color. After warming the mixture to room temperature it was distilled at reduced pressure through a system fitted with a trap cooled to the temperature of solid carbon dioxide.

The low-boiling fractions, including the condensate from the cold trap, were redistilled at atmospheric pressure through a 4-foot packed column and yielded 25 g. (0.25 mole, 84% yield) of ethylene chloride and 26.6 g. (0.28 mole, 94% yield) of methyl disulfide. Both products were identified by boiling points, density, and refractive index.

The higher boiling fraction weighed 38.2 g. and consisted of a faintly yellow liquid boiling at 108–110° (22 mm.).

(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research.

(2) H. Brintzinger and M. Langheck, *Chem. Ber.*, **86**, 557 (1953).

(3) I. B. Douglass, *J. Org. Chem.*, **24**, 2004 (1959).

(4) R. B. Langford and N. Kharasch, *J. Org. Chem.*, **23**, 1694 (1958).

(5) G. Sosnovsky, *J. Chem. Soc.*, 3139 (1956).

Redistillation yielded a colorless fraction identical in boiling point, refractive index, density and infrared absorption spectrum with the 2-chloroethyl methanesulfinate prepared by the reaction of pure methanesulfinyl chloride with ethylene oxide.

The reaction between I and ethylene oxide was repeated with the order of addition reversed. Ethylene oxide (0.66 mole) was placed in the flask fitted with stirrer and held at −20°, while 0.66 mole of I was added dropwise. On distilling the mixture there was obtained 16.4 g. (0.166 mole, 76%) of ethylene dichloride, 19.0 g. (0.202 mole, 92%) of methyl disulfide and 26.3 g. (0.184 mole, 84%) of 2-chloroethyl methanesulfinate.

The preparation of 2-chloroethyl methanesulfinate. Ethylene oxide (10 g., 0.23 mole) was passed into 19.7 g. (0.2 mole) of well stirred methanesulfinyl chloride[6] cooled to −20°. When all had been added the mixture was allowed to warm to room temperature and was distilled at reduced pressure. The colorless product weighed 23.4 g. (82%) and boiled at 108–110° (22 mm.). A middle fraction boiled unchanged at 110° (22 mm.), n_D^{25} 1.4760, d_4^0 1.3276 and d_4^{25} 1.2998.

Anal. Calcd. for $C_3H_7ClO_2S$: C, 25.27; H, 4.95; Cl, 24.86; S, 22.48. Found: C, 25.84; H, 6.02; Cl, 24.65; S, 22.2.

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(6) I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **23**, 330 (1958).

Bromination of Dihydroxanthotoxin. Synthesis of Furocoumarans

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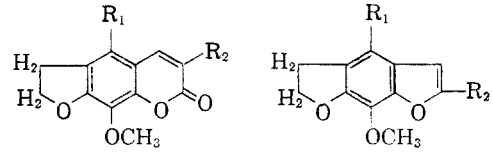
Recently, there was reported[2] the isolation of a monobromo substituted derivative of 2,3-dihydroxanthotoxin (I. $R_1 = R_2 = H$), which was not the 4-bromo isomer (I. $R_1 = Br$; $R_2 = H$), but which gave a compound $C_{12}H_{10}O_5$ on treatment with 6*N* sodium hydroxide. While the present work was in progress, Horton and Paul[3] suggested II ($R_1 = H$, $R_2 = CO_2H$) as the structure of $C_{12}H_{10}O_5$, which could be expected from the action of sodium hydroxide on 6-bromo-2,3-dihydroxanthotoxin (I. $R_1 = H$; $R_2 = Br$). Our results confirm the latter suggestion, because a sample of $C_{12}H_{10}O_5$, obtained by the procedure of Brokke and Christensen,[2] was easily converted to an acid chloride (II. $R_1 = H$; $R_2 = COCl$), an anilide (II. $R_1 = H$; $R_2 = CONHC_6H_5$), and a methyl ester (II. $R_1 = H$; $R_2 = CO_2CH_3$). Its infrared spectrum showed absorption at 2690, 2580, 2520, 2490, and 2350 cm.$^{-1}$ (OH, bonded, acid) and at 1670, 1680 (sh) cm.$^{-1}$ (C=O, acid). On heating under reduced pressure, the compound lost a molecule of carbon dioxide, as would be expected for structure II ($R_1 = H$; $R_2 = COOH$). The resultant furocoumaran (II. $R_1 = R_2 = H$) gave a deep blue color on warming with concentrated sulfuric acid, which is analogous to the behavior reported[4] for other similarly constituted benzofurans. These results establish 6-bromo-2,3-dihydroxanthotoxin (I. $R_1 = H$; $R_2 = Br$) as the product of reaction between 2,3-dihydroxanthotoxin and one equivalent of bromine.



I II

Treatment of 2,3-dihydroxanthotoxin with two equivalents of bromine produced a dibromo derivative. It has been assigned structure I ($R_1 = R_2 = Br$) because it was also obtained by bromination of 4-bromo-2,3-dihydroxanthotoxin[2] (I. $R_1 = Br$; $R_2 = H$) and because treatment with sodium hydroxide converted it to $C_{12}H_9O_5Br$, which must have structure II ($R_1 = Br$; $R_2 = COOH$). While repeating some of the earlier work, a sample of 4-amino-2,3-dihydroxanthotoxin (I. $R_1 = NH_2$; $R_2 = H$) was obtained, which melted at 243–245° instead of the reported[2] 214–216°. A mixture of this compound and 4-aminoxanthotoxin melted at 214–216°. The aminodihydro compound was also converted to the corresponding ethyl carbamate (I. $R_1 = NHCO_2C_2H_5$; $R_2 = H$).

EXPERIMENTAL[5]

2,3-Dihydroxanthotoxin (I. $R_1 = R_2 = H$). Xanthotoxin (28.50 g.) dissolved in 355 ml. of glacial acetic acid at 45° and the solution, plus 2.5 g. of 5% palladium on charcoal, was shaken under 60 pounds hydrogen pressure until 1 equivalent of hydrogen had been absorbed (*ca.* 20 min.). After removing the catalyst and concentrating the solution, the product crystallized and was finally obtained as colorless needles (20.85 g.; 69%), m.p. 159.3–159.5°, after recrystallization from acetic acid; reported[2]: 31% yield, m.p. 160–161°.

6-Bromo-2,3-dihydroxanthotoxin (I. $R_1 = H$; $R_2 = Br$). This compound was prepared according to the method of Brokke and Christensen[2] who report m.p. 202–203°. A sample, m.p. 207.5°, was obtained.

6-Carboxy-2,3-dihydro-8-methoxybenzo[1,2-b,5,4-b']difuran (II, $R_1 = H$; $R_2 = CO_2H$) was prepared according to Brokke and Christensen,[2] who report m.p. 264–268°. A sample, m.p. 267.5° dec., was obtained from ethanol.

The *acid chloride* (II. $R_1 = H$; $R_2 = COCl$) was obtained by adding small portions of phosphorus pentachloride to a suspension of 46.8 g. of II($R_1 = H$; $R_2 = CO_2H$) in 2 l. of chloroform until a clear solution was obtained. Concentration under reduced pressure left a residue which was obtained as 19.8 g. (40% yield) of yellow needles, m.p. 133.5–134.5°, after two recrystallizations from dry xylene.

Anal. Calcd. for $C_{12}H_9O_4Cl$: C, 57.0; H, 3.59; Cl, 14.0. Found: C, 57.6; H, 3.32; Cl, 13.85.

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(3) W. J. Horton and E. G. Paul, *J. Org. Chem.* **24**, 2000 (1959).

(4) Hantzch, *Ber.*, **19**, 2933 (1886).

(5) All melting points are corrected.