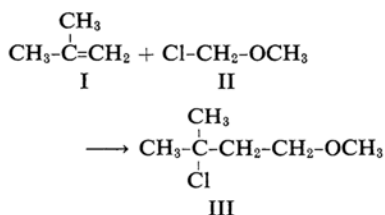


*The Reaction of Isobutene with Chloromethyl Methyl Ether in  
Liquid Sulfur Dioxide*

By NIICHIRO TOKURA, ISOO SHIRAI and KATSUO SHIINA

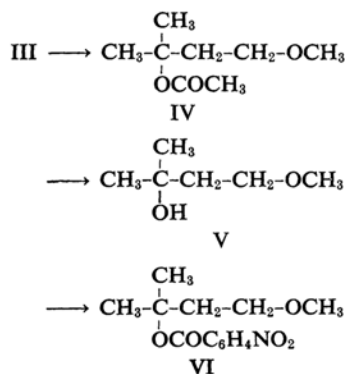
(Received August 7, 1961)

Isobutene (I) reacts with chloromethyl methylether (II) in liquid sulfur dioxide to give 2-chloro-4-methyl-2-methylbutane (III). Straus and Thiel<sup>1)</sup> have reported that the formation of III from I and II requires a catalyst such as mercuric chloride, while the present reaction in liquid sulfur dioxide is very rapid and is practically accomplished in a few minutes without any catalyst and at room temperature.



Structure III was confirmed by preparing some derivatives as follows:

1) F. Straus and W. Thiel, *Ann.*, **525**, 151 (1936).



III was treated with sodium acetate to afford 2-acetoxy-4-methoxy-2-methylbutane (IV). IV was hydrolyzed with alkali to 4-methoxy-2-methyl-2-butanol (V), which gave a *p*-nitrobenzoate (VI), m. p. 74.0°C.

Such cross-linking or jointing by the methylene group as has been seen elsewhere<sup>2)</sup> was not observed in the present experiment. The yield of III was depressed by the use of a catalyst such as stannic chloride owing to the predominating self-polymerization of isobutene.

#### Experimental

**Reaction of Isobutene (I) with Chloromethyl Methyl Ether (II) in Liquid Sulfur Dioxide.**—To 110 ml. of liquid sulfur dioxide was added 21.5 g. (0.38 mol.) of I, and 38.6 g. (0.48 mol.) of II was

then dropped into the mixture. The mixture was allowed to stand at room temperature for ten minutes and then mixed with ice water, and the liquid sulfur dioxide was evaporated. The residue was washed with sodium sulfate and distilled in vacuo. The transparent oil, b. p. 60~66°C/100 mmHg, was redistilled under ordinary pressure to yield 7.8 g. of pure 2-chloro-4-methoxy-2-methylbutane (III), b. p. 141~145°C (lit.<sup>1)</sup>, b. p. 136°C/751 mmHg. Found: C, 52.74; H, 9.51, Calcd. for C<sub>6</sub>H<sub>13</sub>OCl: C, 52.71; H, 9.57%, mol. wt., Found: 143 (benzene), Calcd.: 136.5. IR  $\nu_{\text{max}}^{\text{liq}}$  1295 cm<sup>-1</sup> (methoxy), no absorption at 1600 cm<sup>-1</sup> (C=C).

**2-Acetoxy-4-methoxy-2-methylbutane (IV).**—III was treated with anhydrous sodium acetate by a general procedure to give IV, b. p. 34.8~40.0°C/14 mmHg.

**4-Methoxy-2-methyl-2-butanol (V).**—IV was hydrolyzed with a 1 N potassium hydroxide solution to 4-methoxy-2-methyl-2-butanol (V), b. p. 54~55.5°C/20 mmHg. V gave a *p*-nitrobenzoate (VI), m. p. 74.0°C. Found: C, 58.38; H, 6.24; N, 5.36. Calcd. for C<sub>13</sub>H<sub>17</sub>O<sub>4</sub>N: C, 58.18; H, 6.63; N, 5.21%.

The present investigation was supported by a grant from the Ministry of Education. The liquid sulfur dioxide was supplied by the Befu Chemical Industries, Ltd. The authors are grateful to all of them.

The Chemical Research Institute  
of Non-Aqueous Solutions  
Tohoku University  
Katahira-cho, Sendai

2) R. Asami, T. Shiohata and N. Tokura, *Bull. Chem. Res. Inst. Non-Aqu. Soln. (Hisuiken-Hokoku)*, **10**, 99 (1961).