V in 100 ml. of dry ether, chilled in a chloroform–Dry Ice bath, gave a pale yellow solution, which was added to a Grignard solution prepared from 10.2 g. (0.42 atom) of magnesium, 60 g. of *n*-butyl bromide and 125 ml. of dry ether. The procedure from this point was the same as that described for the preparation of IV. The amount of sodium used for the ring cleavage step was 8.6 g. The product was boiled at 84–88° (9 mm.) and weighed 14.7 g. (48.5% based on V). The properties of a sample purified by refractionation were: b.p. 62° (2 mm.), $n^{25}\text{D}$ 1.4440.

Anal. Calcd. for $C_9H_{18}O$: C, 76.02; H, 12.75. Found: C, 76.40; H, 12.76.

The allophanate of VII, crystallized out of dilute ethanol, melted at 141–142°.

Anal. Calcd. for $C_{11}H_{20}O_3N_2$: C, 57.86; H, 8.83. Found: C, 57.97; H, 8.83.

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The Chlorination of 2,3-Dimethylbutadiene: Configuration of the Solid Dichloride

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Interest in the stereochemistry of 1,4-addition[1] prompted us to investigate the nature of the 1,4-adduct of chlorine and 2,3-dimethylbutadiene. The diene, whose principal conformation has variously been reported as s-*cis*[2] and as s-*trans*[3] affords a mixture of *cis*- and *trans*-1,4-dibromo-2,3-dimethyl-2-butenes on bromination.[4]

We have prepared *trans*-1,4-dichloro-2,3-dimethyl-2-butene by the reaction of the *trans*-1,4-diol and phosphorus trichloride, and we have demonstrated that the same solid is one of the products formed from the direct chlorination of 2,3-dimethylbutadiene. Unfortunately we have been unable to prepare the *cis* isomer, and the question of the formation of this substance by direct 1,4-addition must therefore be left open for the present.

Experimental[5]

***trans*-2,3-Dimethyl-2-butene-1,4-diol.**—This compound was prepared by hydrolysis in 31% yield of the diacetate, m.p. 37–38°, according to the procedure of Sweeting and Johnson.[4] There was obtained a white crystalline solid, m.p. 81–82° from ether or ethanol (lit.[4] m.p. 57–58°). The bisphenylurethan melted at 156–157° (lit.[4] m.p. 157.0–157.5°). It is conceivable that the diol reported by Sweeting and Johnson is a crystalline modification of that obtained in this work.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.10; H, 10.41. Found: C, 62.09; H, 10.42.

***trans*-1,4-Dichloro-2,3-dimethyl-2-butene.**—(A) A solution of 11.0 g. (0.095 mole) of the *trans*-1,4-diol and 7.6 g. of anhydrous pyridine was added slowly to 8.8 g. (0.064 mole) of phosphorus trichloride while the temperature of the reaction mixture was kept below 10°. Water was added to the reaction mixture after completion of the addition. The product was extracted with ether, and the ether layer washed with sodium bicarbonate and dried over drierite. Distillation gave 5.0 g. (33%) of the desired compound, b.p. 65° (6.8 mm.), crystals from hexane, m.p. 30°.

Anal. Calcd. for $C_6H_{10}Cl_2$: C, 47.10; H, 6.58; Cl, 46.32. Found: C, 47.26; H, 6.78; Cl, 46.20.

The infrared spectrum[6] of a 5% solution of the compound in carbon tetrachloride exhibited pronounced absorption maxima at the following wave lengths (μ): 3.40, 6.88, 7.25, 7.95, 8.25, 8.59, 9.24, 10.73, 11.44, 14.20. It should be noted that the 7.95 maximum has been associated[7] with compounds of the type $RR'C{=}CR''CH_2Cl$.

(B) A saturated solution of chlorine in carbon tetrachloride (250 ml., 0.61 mole) was added to a solution of 50.0 g. (0.61 mole) of 2,3-dimethylbutadiene[8] in 200 ml. of purified[9] carbon tetrachloride. Throughout the addition, which took 3.5 hours, vigorous stirring was maintained, and the temperature of the reaction mixture was kept near −20°. The reaction mixture was distilled, but no clean-cut fractions could be obtained; at the same time some dehydrochlorination was evidently taking place. Five cuts were collected at fairly arbitrary intervals: 35–44° (42 mm.), 46–49° (31 mm.), 39–43° (20 mm.), 55–65° (5 to 6 mm.), 65–72° (5.3 mm.). The last two fractions were combined and chilled to 0°. The crystals which formed were separated from the supernatant liquid and after recrystallization from ligroin afforded 12.0 g. (13%), m.p. 32–34° (lit.[10] m.p. 35°, b.p. 80–84° (18 mm.)). The infrared spectrum was identical with that of the sample prepared by procedure (A), and the substance gave *trans*-1,4-acetoxy-2,3-dimethyl-2-butene, m.p. 37–38°, upon acetolysis according to the method described for the 1,4-dibromide.[4]

Attempted Preparation of *cis*-1,4-Dichloro-2,3-dimethyl-2-butene.—A solution of 14.0 g. (0.120 mole) of *cis*-2,3-dimethyl-2-butene-1,4-diol,[4] bisphenylurethan m.p. 147–148° (lit.[4] m.p. 147–148°), in 9.6 g. of anhydrous pyridine was added slowly to 17.1 g. (0.125 mole) of phosphorus trichloride while the temperature of the reaction mixture was kept below 10°. The product, worked up as described for the *trans* isomer, gave on distillation 3.1 g. of a material, b.p. 83–84° (13.5 mm.), $n^{25}\text{D}$ 1.4620, d^{25}_4 0.974.

Anal. Calcd. for $C_6H_{10}Cl_2$: C, 47.10; H, 6.58; Cl, 46.32. Found: C, 57.65; H, 9.13; Cl, 23.24.

Possibly, an explanation of the failure of the reaction to give the expected product may be found in a consideration of side reactions involving cyclization, which would be less likely to occur with the *trans* isomer. The analysis is suggestive of a mixture of products.

The *p*-bromobenzenesulfonate of the diol, prepared in the usual way, formed well defined tabular crystals from ether which rapidly turned brown and black on exposure to air. The instability of this derivative was deemed sufficient reason for discontinuing an alternate approach to the synthesis of the *cis*-dichloride, based on a displacement reaction by chloride on the brosylate.

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The Direction of Free Radical Addition to $CF_2{=}CFCl$

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In our preceding paper,[1] we have interpreted the free radical condensation of CF_3I with $CF_2{=}CFCl$ as directed to $CF_3{-}CFCl{-}CF_2I$, and that of CCl_3Br with $CF_2{=}CFCl$ as directed to $CCl_3{-}CFCl{-}CF_2Br$; this has been criticized by Miller,[2] with

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