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.), $n^{25}D$ 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.), $n^{25}D$ 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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(5) Microanalyses are by W. Manser, Zurich.

(6) A Baird model B instrument with 0.1-mm. cells was employed. In this connection, the assistance afforded by correspondence with Dr. Ralph Nusbaum and his staff, Spectroscopy Section, Atomic Energy Project, U. C. L. A., Los Angeles, Calif., is gratefully acknowledged.

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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

(1) A. L. Henne and D. W. Kraus, THIS JOURNAL, **73**, 5303 (1951)

(2) W. T. Miller and J. Howald, 122d A.C.S. Meeting, 12K, Sept., 1952.

further elaboration by Haszeldine.[3] We find their criticism well founded and accept it. We also offer new experimental evidence confirming their view that the condensation places the CF_2, rather than the CFCl group in the middle.

On the experimental preparation of C_3F_6ClI or $C_3F_3Cl_4Br$ we all agree. As to the direction of addition, *i.e.*, the distinction between CF_3–$CFCl$–CF_2I or CF_3–CF_2–$CFClI$, and between CCl_3–$CFCl$–CF_2Br or CCl_3–CF_2–$CFClBr$, we based our original interpretation on the assumption that a conventional zinc in alcohol reaction would create an olefin without loss of organic fluorine in the first alternative, but would remove some fluorine in the second alternative if it reacted at all. Since, experimentally, no organic fluorine was lost, the first alternative was adopted. However, as soon as Miller showed that the zinc reaction was not restricted to the creation of a double bond, and could cause the formation of an organo-zinc compound, our assumption became inadequate, and our conclusion unsupported.

The action of zinc on $C_3F_3Cl_4Br$ was reinvestigated by a new procedure.[4] In solution in acetic anhydride, $C_3F_3Cl_4Br$ reacts very rapidly with zinc, and if the reaction is moderated by means of methylene chloride as an internal cooling agent (reflux at 40°), most of the reagent is transformed into crystalline $C_6F_6Cl_8$, m.p. 40° [*Anal.* F, 24.1; Cl, 59.6. Calcd.: F, 24.2; Cl, 60.4], and the balance of the reagent recovered intact. The zinc consumed is accounted for as zinc bromide only; there is no fluorine ion to be detected.

The C_6-compound can be either (CCl_3–$CFCl$–CF_2–)$_2$ or else (CCl_3–CF_2–$CFCl$–)$_2$ and therefore it does not solve the problem of the original direction of condensation between CCl_3Br and CF_2=$CFCl$. However, the first alternative should react quite easily with zinc and alcohol in a conventional reaction, to give a diene, CCl_2=CF—CF_2—CF_2—CF=CCl_2, while the second alternative should react much more sluggishly to give the monoölefin, CCl_3—CF_2—CF=CF—CF_2—CCl_3. Actually, the conventional zinc dehalogenation did not proceed noticeably below 110°, and it gave, quantitatively, a single product $C_6F_6Cl_6$. [*Anal.* F, 28.0; Cl, 52.2; F/Cl, 0.536. Calcd.: F, 28.6; Cl, 53.4; F/Cl, 0.536.] A diene $C_6F_6Cl_4$ would have required 34.8, 43.2 and 0.806, respectively.

The C_6-paraffin was therefore written CCl_3-$CF_2CFClCFClCF_2CCl_3$, obtained from two moles of CCl_3–CF_2–$CFClBr$. We are thus accepting and experimentally confirming the direction of free radical addition to CF_2=$CFCl$ proposed by our critics.

Experimental

One volume of $C_3F_3Cl_4Br$ (86 g. or 0.27 mole), zinc (17.7 g. or 0.27 atom), 3 volumes of CH_2Cl_2 and 2 volumes of acetic anhydride were stirred for six hours. The unused zinc amounted to 2.9 g. (0.044 atom), indicating a consumption of 14.8 g. (0.227 atom). Redistillation recovered 8.1 g. of $C_3F_3Cl_4Br$ (0.026 mole). Solid $C_6F_6Cl_6$ melting about 40° amounted to 60 g. (0.11 mole), which accounted for 0.22 mole of original $C_3F_3Cl_4Br$; this is an 81.5% yield and a 91% recovery of organic material.

$C_6F_6Cl_6$ did not react noticeably with zinc in boiling ethanol. A metal container was then loaded with $C_6F_6Cl_8$ (43 g. or 0.092 mole), zinc (6 g. or 0.092 atom) and 200 cc. of ethanol, and it was rocked at 110° for six hours. The working up gave 19 g. (0.049 mole) of $C_6F_6Cl_8$, d^{28}_4 1.8126, $n^{28}D$ 1.4501, *MR* 59.1, AR_F 1.2, and 16.5 g. (0.035 mole) of recovered $C_6F_6Cl_8$; this is a 52% yield and 90% recovery of organic material. In confirmation 2.7 g. (0.041 atom) of zinc was recovered, showing a consumption of 3.3 g. (0.051 atom).

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Preparation and Properties of Some New Chelating Agents[1]

BY E. G. KOVACH AND D. E. BARNES

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In conjunction with work being carried out in these laboratories on the mode of action of fungicides we wish to report the synthesis of two new compounds with chelating properties prepared as potential fungistatic agents. As an analog of the well-known 8-hydroxyquinoline we have prepared 7-indiazolol (VI), and as an analog of Cupferron we have prepared ammonium N-2-pyridyl-N-nitrosohydroxylamine (Pyridine Cupferron), replacing the phenyl group by a 2-pyridyl radical.

TABLE I

PRECIPITATING PROPERTIES AND FUNGITOXICITY OF 7-INDIAZOLOL AND AMMONIUM N-2-PYRIDYL-N-NITROSOHYDROXYLAMINE

	7-Indiazolol	Pyridine Cupferron
Maley–Mellor metals		
Cu^{++}	+ (purple)	+ (green)
Pb^{++}	+ (white)	+ (white)
Cd^{++}	+ (white)	+ (white)
Fe^{++}	+ (black)	+ (red)
Co^{++}	+ (rose)	− (intense red color)
Zn^{++}	+ (white)	−
Ni^{++}	+ (blue-gray)	−
Mn^{++}	−	−
Mg^{++}	−	−
Monovalent metals		
Ag^{+}	+ (white)	+ (white)
Divalent metals		
Hg^{++}	−	+ (yellow-white)
Sn^{++}	−	+ (white)
Ca^{++}	−	+ (white)
Ba^{++}	−	−
Sr^{++}	−	−
Trivalent metals		
Cr^{+++}	−	−
Bi^{+++}	−	−
Al^{+++}	−	−
Percentage inhibition of *growth* of *A. niger* at concn. of		
10^{-3} *M*	27	16
10^{-4} *M*	8	3
10^{-5} *M*	4	1

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