tions of two amines. The addition of ammonium reineckate solution saturated at 0° to 0.015% aniline hydrochloride or to 0.005% ethylammonium chloride at 0° resulted in the formation of a definite precipitate of the amine reineckate. It would thus appear that the use of ammonium reineckate for the isolation of many amines from very dilute aqueous solutions may be of practical value.

Experimental

Formation of Reineckates.—Hydrochloric acid was added to an aqueous solution or suspension of the amine until the mixture became acidic to congo red. The resulting solution was cooled to room temperature and a filtered, saturated (about 5%) solution of ammonium reineckate was added. Precipitation of the salt began immediately, but the solution was cooled in an ice-bath to improve the yield. The use of an excess (50–100%) of either reagent leads to a significant increase in yield.

Recrystallization.—The reineckates were recrystallized by warming in 70–80% ethyl alcohol to about 60°, filtering, and refrigerating. A few reineckates were sufficiently soluble to make it necessary to use more dilute alcohol. Drying was accomplished over phosphorus pentoxide at room temperature in a vacuum desiccator. Two or three recrystallizations were sufficient to give constant decomposition point and satisfactory analyses.

Analysis.—A weighed sample of the reineckate was heated carefully in a porcelain crucible until the initial vigorous decomposition was complete. The crucible was then ignited with a Meker burner until constant weight was achieved; the residue was weighed as Cr_2O_3. Analyses were run in duplicate and agreed well with theoretical (Table I).

LABORATORY OF ORGANIC CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON 6, WISCONSIN
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Alkyl-Substituted Chlorofluoroethanes[1]

BY JOHN T. BARR, J. DONALD GIBSON AND R. H. LAFFERTY, JR.

The Prins reaction has recently been extended to include the addition of polyhalo alkanes to polyfluoro alkenes.[2–5] This note describes the aluminum chloride catalyzed condensation of monochloroalkanes with chlorotrifluoroethylene and *unsym*-dichlorodifluoroethylene. The expected products were obtained with poor conversions, and in addition materials were obtained in which the aluminum chloride had substituted chlorine for fluorine in the original addition products.

The Reaction of Isopropyl Chloride and Polyfluoro Olefins.—A mixture of 127 g. of isopropyl chloride, 221 g. of chlorotrifluoroethylene and 25 g. of aluminum chloride was heated to 44° for 18 hours with mechanical shaking. The unreacted olefin was recovered and the residue was washed with water several times, dried over anhydrous sodium carbonate and distilled. Following the removal of the isopropyl chloride there was obtained 10 ml. of material boiling 26–26.2° at 30 mm. (112–113° at 750 mm.) and 2 ml. of material boiling 66–68° at 30 mm. There remained in the still-pot about 3 g. of residues.

The lower boiling material was found to have $n^{25}{}_D$ 1.3870, $d^{25}{}_4$ 1.3004. *Anal.* Calcd. for $C_5H_7Cl_2F_3$: C, 30.77; H, 3.59; Cl, 36.41; MR_D 35.3. Found: C, 30.24; H, 3.65; Cl, 36.68; MR_D 35.3.

The higher boiling material had $n^{25}{}_D$ 1.4078. *Anal.* Calcd. for $C_5H_7Cl_3F_2$: C, 28.37; H, 3.31; Cl, 50.35. Found: C, 29.04; H, 3.55; Cl, 47.76.

A material identical with the higher boiling product was prepared by the aluminum chloride catalyzed condensation of isopropyl chloride with *unsym*-dichlorodifluoroethylene. Therefore it is proposed that the lower boiling material has the structure $(CH_3)_2CHCClFCClF_2$, and the higher boiling the structure $(CH_3)_2CHCCl_2CClF_2$.

Lower reaction temperatures and the use of the "tube" method of Schmerling[6] resulted in the production of a larger proportion of the lower boiling material and a smaller degree of conversion.

The Reaction of *t*-Butyl Chloride and Chlorotrifluoroethylene.—Under the conditions described for the isopropyl chloride reaction, *t*-butyl chloride and chlorotrifluoroethylene gave 5–10% yields of $(CH_3)_3CCClFCClF_2$, b.p. 55–57° at 50 mm., $n^{25}{}_D$ 1.4020, and $(CH_3)_3CCCl_2CClF_2$, b.p. 77–80° at 25 mm., $n^{25}{}_D$ 1.4405. *Anal.* Calcd. for $C_6H_9Cl_2F_3$: Cl, 33.93. Found: Cl, 34.10. Calcd. for $C_6H_9Cl_3F_2$: Cl, 47.17. Found: Cl, 46.68.

Other Prins Type Reactions Attempted.—Only a trace of reaction could be detected when *n*-butyl chloride was substituted for *t*-butyl chloride.

Allyl chloride could not be used as the alkyl halide because of immediate and extensive polymer formation in the presence of aluminum chloride.

When an attempt was made to use 1-chloro-1,1-difluoroethane as the alkyl halide with chlorotrifluoroethylene only methylchloroform was isolated as a reaction product.

1,2-Dichlorohexafluorocyclobutane and chlorotrifluoroethylene gave no product when heated together in the presence of aluminum chloride. This result was to be expected, since neither of these materials reacted separately with aluminum chloride.

Aluminum bromide could not be used as the catalyst in these reactions, because of its great tendency to substitute bromine for other halogens and because of extensive polymer formation by the alkyl halides in its presence. Stannic chloride and boron trifluoride–ethyl ether did not appear to have catalytic activity.

RESEARCH LABORATORIES, K-25 PLANT
CARBIDE AND CARBON CHEMICALS CORPORATION
OAK RIDGE, TENNESSEE
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[1] This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

[2] Harmon, U. S. Patent 2,404,706, issued July 1946.

[3] Imperial Chemical Industries, Ltd., British Patent 581,254, issued October 1946; *C. A.*, **41**, 2427 (1947).

[4] E. I. du Pont de Nemours and Company, British Patent 581,662, issued October 1946; *C. A.*, **41**, 2427 (1947).

[5] E. I. du Pont de Nemours and Company, British Patent 583,874, issued January 1947; *C. A.*, **41**, 5141 (1947).

[6] Schmerling, THIS JOURNAL, **68**, 1650 (1948).

Completely Halogenated Ethanes Containing Iodine[1]

BY JOHN T. BARR, J. DONALD GIBSON AND ROBERT H. LAFFERTY, JR.

The use of highly fluorinated materials in Grignard syntheses has been relatively unsuccessful, except to give the corresponding fluorohydrocarbon.[2,3] During the course of work here two completely halogenated ethanes containing iodine, 1,2-dichloro-1,1,2-trifluoro-2-iodoethane, and a material thought to be 1-chloro-1,2,2-trifluoro-1,2-diiodoethane, were prepared. Ethereal solutions of both compounds reacted readily with sodium or magnesium, but all attempts to perform a Grignard synthesis were unsuccessful. The Grignard reagent itself apparently was formed by the usual procedure, forming a lower layer in the reaction flask, although there was no evidence of reaction upon the addition of compounds such as benzaldehyde, methyl ethyl ketone or α-naphthyl isocyanate. These compounds al-

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[1] This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, at Oak Ridge, Tennessee.

[2] J. J. Brice, W. H. Pearlson and J. H. Simons, THIS JOURNAL, **68**, 968 (1946).

[3] E. T. McBee and A. Truchan, *ibid.*, **70**, 2910 (1948).