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
RECEIVED AUGUST 14, 1950

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
RECEIVED JUNE 22, 1950

---

[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-

---

[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).

ways were recovered unchanged. No olefins or condensation products of the haloethanes could be found, either in the reaction mixture, or as gaseous products of the reaction.

1,2-Dichloro-1,1,2-trifluoro-2-iodoethane.—Chlorotrifluoroethylene (88 g.) was bubbled through a mixture of 162 g. of iodine monochloride and 500 ml. of 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113) during the course of 5 hours. As the reaction proceeded the iodine chloride passed into solution, and the temperature of the reaction mixture rose to 35°. After the absorption of the olefin had ceased, the reaction mixture was washed with sodium thiosulfate solution, and then with sodium carbonate solution until colorless, and was dried over sodium carbonate. Fractional distillation of the solution gave 119 g., 57% of theory, of 1,2-dichloro-1,1,2-trifluoro-2-iodoethane boiling 43–44° at 100 mm., n^{25}_D 1.4474, d^{25}_{20} 2.1959. *Anal.* Calcd. for $C_2Cl_2F_3I$: C, 9.29; mol. wt., 279; MR_D 34.3. Found: C, 8.87; mol. wt., 271, determined in n-C_7F_{16}; MR_D 34.0. This material was stored in the dark at room temperature for several months without excessive decomposition. The above structure was assigned by analogy to other addition reactions with this olefin.[4]

A much less stable compound, thought to be 1-chloro-1,2,2-trifluoro-1,2-diiodoethane, was obtained in 30–35% yield by the distillation of a mixture of equal weights of chlorotrifluoroethylene and iodine which had stood at room temperature for several days sealed in a Pyrex reactor. This material, boiling 54–55° at 20 mm., with slight decomposition, and having a density of greater than 2.5, decomposed readily upon standing to yield crystals of iodine, but no other residue. A reliable analysis or refractive index could not be obtained because of this instability.

---

[4] W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274, issued October, 1946; C. W. Huskins and P. Tarrant, "Preparation and Reactions of Certain Chlorofluoroethylenes," Report of Office of Naval Research under Contract N8onr503, June 15, 1946; J. A. Young and P. Tarrant, THIS JOURNAL, **71**, 2432 (1949); K. E. Rapp, *et al.*, *ibid.*, **72**, 3642 (1950); R. L. Pruett, *et al.*, *ibid.*, **72**, 3646 (1950); J. T. Barr, *et al.*, *ibid.*, **72**, 4480 (1950).

RESEARCH LABORATORIES, K-25 PLANT
CARBIDE AND CARBON CHEMICALS DIVISION
UNION CARBIDE AND CARBON CORPORATION
OAK RIDGE, TENNESSEE
RECEIVED JUNE 22, 1950

An Improved Synthesis of Mescaline

BY FRED BENINGTON AND RICHARD D. MORIN

In connection with certain studies of the synthesis of phenethylamines, we have had the occasion to prepare mescaline, β-(3,4,5-trimethoxyphenyl)-ethylamine, an alkaloid which occurs naturally in the cacti *Anhalonium*. The literature cites the synthesis of this alkaloid by two methods, neither of which gives a satisfactory yield.

Slotta and Heller[1] synthesized mescaline in four steps from 3,4,5-trimethoxybenzaldehyde in an over-all yield of 28%. A more direct method *via* the condensation of 3,4,5-trimethoxybenzaldehyde with nitromethane, followed by the reduction of the resulting nitrostyrene, was employed by Späth.[2] The nitrostyrene was first reduced to the corresponding aldoxime, which on further reduction gave mescaline. The two-stage reduction gave a 24.9% yield, and the over-all yield of mescaline from the aldehyde was only 20.8%.

An elegant method for reduction of β-nitrostyrenes to phenethylamines with lithium aluminum hydride has been reported.[3] Reduction of 3,4,5-trimethoxy-β-nitrostyrene by this method resulted in an 89% yield of mescaline hydrochloride. The over-all yield from 3,4,5-trimethoxybenzaldehyde has been increased to 65%.

Experimental[4]

3,4,5-Trimethoxybenzaldehyde.—Gallic acid was converted to trimethylgallic acid in 80% yield by methylation with methyl sulfate.[5] Trimethylgalloyl chloride was prepared in 81% yield by the action of phosphorus pentachloride on trimethylgallic acid.[1] The acid chloride was purified by distillation and redistillation under reduced pressure; b.p. 131–133° (2 mm.); m.p. 83–84°. Rosenmund reduction of 3,4,5-trimethoxybenzaldehyde was carried out as described[1] using 52 g. of 3% Pd–$BaSO_4$ catalyst per mole of acid chloride. Dry xylene was the solvent. The product was recovered by removal of the catalyst by filtration, stripping off the xylene and fractional distillation of the residue under reduced pressure. A forerun of pyrogallol trimethyl ether, b.p. 82–100° (0.1 mm.), was obtained, and 3,4,5-trimethoxybenzaldehyde was collected as the fraction boiling at 106–112° (0.1 mm.). After crystallization from alcohol the aldehyde melted at 73–74°; yield 59%.

3,4,5-Trimethoxy-β-nitrostyrene.—This compound was prepared by the procedure of Späth[2] in 82.7% yield; m.p. 121–122° after recrystallization from alcohol.

Mescaline Hydrochloride.—Reduction of 7.2 g. (0.03 mole) of 3,4,5-trimethoxy-β-nitrostyrene with 5.7 g. of lithium aluminum hydride was carried out as described[3a] for 4-hydroxy-3-methoxy-β-nitrostyrene. The yield of mescaline picrate, m.p. 210–212°, was 11.4 g. (86%). After recrystallization from alcohol, the picrate melted at 214–216°; reported[2] 216–218°. The mescaline picrate was converted to mescaline hydrochloride as described[3a] in 92% yield; m.p. 180–181° (after recrystallization from alcohol); reported[1] 181°.

---

[1] K. H. Slotta and H. Heller, *Ber.*, **63**, 3029 (1930).

[2] E. Späth, *Monatsh.*, **40**, 144 (1919).

[3] (a) F. A. Ramirez and A. Burger, THIS JOURNAL, **72**, 2781 (1950); (b) R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948); (c) K. E. Hamlin and A. W. Weston, *ibid.*, **71**, 2210 (1949).

[4] All melting and boiling points uncorrected.

[5] H. Gilman and A. H. Blatt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1941, Coll. Vol. I, 2nd Ed., p. 537.

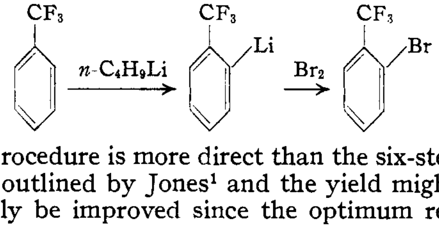
BATTELLE MEMORIAL INSTITUTE
COLUMBUS 1, OHIO
RECEIVED NOVEMBER 3, 1950

Preparation of *o*-Bromobenzotrifluoride

BY ROBERT A. BENKESER AND ROLAND G. SEVERSON

In view of the recent interest in ortho and para derivatives of benzotrifluoride,[1,2] we are hereby reporting a two-step synthesis of *o*-bromobenzotrifluoride.

Metallation of benzotrifluoride with *n*-butyllithium has been shown to yield largely the ortho isomer.[3] Treatment of the metallated product with bromine vapor forms *o*-bromobenzotrifluoride in a 28% over-all yield.



This procedure is more direct than the six-step synthesis outlined by Jones[1] and the yield might conceivably be improved since the optimum reaction conditions were not investigated. As a proof of structure, *o*-bromobenzotrifluoride was found to undergo halogen–metal interconversion with *n*-butyllithium. The product upon carbonation was *o*-trifluoromethylbenzoic acid. It is of interest that

---

[1] R. Jones, THIS JOURNAL, **69**, 2346 (1947).

[2] M. Lilyquist, J. G. Wisler and P. Tarrant, Abstracts of 118th Meeting of the American Chemical Society, Chicago, Illinois, 1950.

[3] J. D. Roberts and D. Y. Curtin, THIS JOURNAL, **68**, 1658 (1946).