154–156°. After one recrystallization from 15 ml. of ethanol, the melting point was 155–156°.

Anal. Calcd. for $C_6H_{12}O_2N_4$: N, 32.54. Found: N, 32.36.

Benzalaminoguanidonium Salt of Methylnitrosonitroguanidine.—A solution of 1.62 g. (0.01 mole) of benzalaminoguanidine in 10 ml. of water and 5 ml. of ethanol was mixed with 1.47 g. (0.01 mole) of methylnitrosonitroguanidine. The mixture was allowed to stand for twenty-four hours at room temperature. There was some gas evolution. After chilling the solution at 0° for one hour, the white solid was removed by filtration and washed with a small volume of cold water; yield 2.6 g. (84.1%); m. p. 123–124°. A rapid recrystallization from 110 ml. of absolute ethanol gave small, flat, white needles; m. p. 124–125° with decomposition. A mixed melting point with methylnitrosonitroguanidine was 110°.

Anal. Calcd. for $C_8H_{10}N_4 \cdot C_2H_5O_3N_5$: C, 38.83; H, 4.89; N, 40.76. Found: C, 39.01; H, 4.94; N, 41.14.

An absolute ethanol solution of this compound gave a picrate decomposing at 255°; a mixed melting point with an authentic sample of benzalaminoguanidine was 254–255°.

A slurry of 1.0 g. of the addition compound, 0.8 g. of aniline and 5 ml. of water evolved gas for two days at room temperature. The resulting paste was chilled to 0°, and the *p*H adjusted to about 4.5 with concentrated hydrochloric acid. The solid material was removed by filtration and washed with two 5-ml. portions of cold ethanol. The yield of dried product was 0.2 g.; m. p. 151–152°. A mixed melting point with a sample of phenylnitroguanidine was 153°.

This salt decomposed with gas evolution when boiled for a few minutes with 95% ethanol. Both benzalaminoguanidine picrate (m. p. 254–255°) and an unknown picrate, melting at 208–209° (dec.) after recrystallization, were recovered by treating the resulting solution with picric acid.

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3-Chloro-1,1,1-trifluoro-2-propanone

BY HUBERT M. HILL, E. B. TOWNE AND J. B. DICKEY

The only reference in the literature to 3-chloro-1,1,1-trifluoro-2-propanone is that included in a patent.[1] The method of preparation, which was not given, consisted in the acid hydrolysis of ethyl α-chloro-γ,γ,γ-trifluoroacetoacetate. This compound was prepared by the chlorination of ethyl γ,γ,γ-trifluoroacetoacetate.

Both of these compounds are powerful nasal irritants and should be handled only under a hood.

Ethyl α-Chloro-γ,γ,γ-trifluoroacetoacetate.—Chlorine was passed through 120 g. of ethyl γ,γ,γ-trifluoroacetoacetate at 20° until a gain in weight of 26 g. was obtained. The dissolved hydrogen chloride was removed by blowing air through the solution. Rectification yielded 25 g. of prerun to 67° (23 mm.) and 112 g. of product, b.p. 67–69° (23 mm.), $n^{19.5}\mathrm{D}$ 1.3890.

Anal. Calcd. for $C_6H_6ClF_3O_3$: Cl, 16.2. Found: Cl, 16.1.

3-Chloro-1,1,1-trifluoro-2-propanone.—A mixture of 86.5 g. of ethyl α-chloro-γ,γ,γ-trifluoroacetoacetate and 200 ml. of 30% sulfuric acid was refluxed, with stirring, for eight hours. The resultant solution was extracted with six 50-ml. portions of ether, and the extract was dried by treatment with phosphorus pentoxide and rectified from fresh phosphorus pentoxide. There was obtained 23.7 g. of product, b.p. 71–72°, $n^{20}\mathrm{D}$ 1.3440.

Anal. Calcd. for $C_3H_2ClF_3O$: Cl, 24.2. Found: Cl, 23.6.

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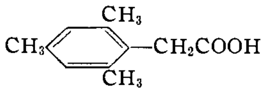
[1] Dickey and McNally, U. S. Patent 2,442,345, June 1, 1948.

Coupling of Certain Benzyl Halides in the Formation of Grignard Reagents

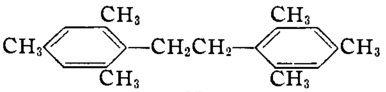
BY WILBERT J. HUMPHLETT AND CHARLES R. HAUSER

The tendency of certain substituted benzyl halides to undergo coupling in the preparation of their Grignard reagents is well known. Some new observations of this sort are reported below.

α^2-Chloroisodurene (2,4,6-trimethylbenzyl chloride), on treatment with magnesium under the usual conditions, followed by carbonation, gave only a 13% yield of the corresponding acid (I) and a 59% yield of the coupled product (II). Pentamethylbenzyl chloride,[1] on similar treatment, gave only a trace of the corresponding acid and a 70% yield of the coupled product (III). Under similar conditions benzyl chloride produced an 82% yield of phenylacetic acid. Under conditions which produce a good yield of allylmagnesium chloride, α^2-chloroisodurene gave, on carbonation of the Grignard reagent, a 29% yield of the acid (I) and a 40% yield of the coupled product (II). 2,4,6-Tribromobenzyl bromide failed to react with magnesium in refluxing ether even in the presence of added iodine. However, when treated with methylmagnesium iodide this halide underwent coupling to form (IV) in 62% yield.



I



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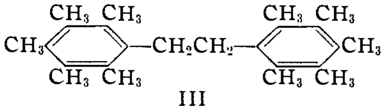
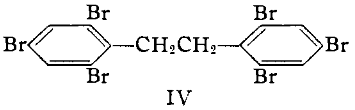


III



IV

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[1] In connection with another study, an attempt was made to treat this chloride with sodium cyanide in ethanol and with cuprous cyanide by the von Braun method, but no appreciable amounts of the corresponding nitrile were obtained. This seems rather surprising in view of the good yield of nitrile produced in the corresponding reaction between α^2-chloroisodurene and sodium cyanide; see Fuson and Rabjohn, "Organic Syntheses," Vol. 25, John Wiley and Sons, Inc., New York, N. Y., 1945, p. 65.