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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CHINA LAKE, CALIFORNIA RECEIVED SEPTEMBER 13, 1949

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.), $n^{19.5}D$ 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°, $n^{20}D$ 1.3440.

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

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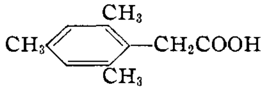
[1] Dickey and McNally, U. S. Patent 2,442,345, June 1, 1948.

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.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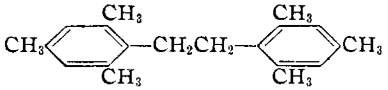
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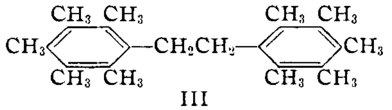
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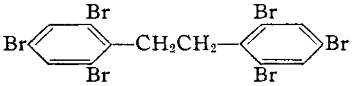
IV

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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.

Experimental

Reactions of α^2-Chloroisodurene.—A solution of 16.9 g. (0.1 mole) of α^2-chloroisodurene[2] (b. p. 126–130° at 21 mm.) in 75 ml. of ether was added to 2.7 g. (0.11 atom) of magnesium foil (Merck, reagent grade) covered by 25 ml. of ether in the manner usually employed in the preparation of Grignard reagents. After refluxing one hour, the mixture (consisting of a suspension of white solid and much unreacted magnesium) was poured onto excess powdered Dry Ice. After coming to room temperature the resulting mixture was stirred with dilute hydrochloric acid with external cooling. The ether phase was combined with an ether extraction of the aqueous phase. The combined ether solution was extracted with excess sodium hydroxide solution. After drying over Drierite, the ether solution was fractionated yielding 7.9 g. (59%) of crude 1,2-dimesitylethane. Recrystallization from ethanol resulted in little loss; m. p. 116–117°; reported m. p. 117–118°.[3] This hydrocarbon yielded the tetrabromo derivative, 1,2-di-(3,5-dibromomesityl)-ethane, m. p. 177–179° after recrystallization from xylene; reported m. p. 178–180°.[3]

The sodium hydroxide extract, containing added ice, was acidified with hydrochloric acid and extracted several times with ether. The combined ether extractions were washed with water and dried over Drierite. An aliquot titrated with standard base indicated a yield of 13% of mesitylacetic acid. A blank indicated that no titratable hydrochloric acid was extracted in this manner. From a portion of the ether extract, there was obtained a sample of mesitylacetic acid, m. p. 166–168°; reported m. p. 167–168°.[1] Calcd. for $C_{11}H_{14}O_2$: neut. equiv., 178. Found: neut. equiv., 179.

When α^2-chloroisodurene was added to magnesium in ether during ten hours according to the procedure for preparing allylmagnesium chloride[4] and the reaction mixture worked up as described above, there were obtained a 40% yield of 1,2-dimesitylethane, m. p. 116–117°, and a 29% yield (determined by titration) of mesitylacetic acid, m. p. 167–168° (isolated sample).

Pentamethylbenzyl Chloride.—This compound was prepared by the chloromethylation of pentamethylbenzene (b. p. 118–120° at 30 mm.) by the general method of Vavon[5] except that a 20% excess of chloromethyl ether was employed. The chloride was isolated in 91% yield as a white solid, m. p. 80°[6] and b. p. 180–182° at 30 mm. Two recrystallizations from glacial acetic acid-water failed to raise the melting point.

Anal.[7] Calcd. for $C_{12}H_{17}Cl$: C, 73.27; H, 8.71; Cl, 18.03. Found: C, 73.26; H, 8.58; Cl, 18.17.

Reaction with Pentamethylbenzyl Chloride.—This halide (19.7 g., 0.1 mole) reacted with 2.7 g. (0.11 atom) of magnesium, followed by carbonation and treatment with acid. The ether phase on standing for half an hour precipitated 11.2 g. (70%) of 1,2-di-(pentamethylphenyl)-ethane, m. p. 241–243°. After three recrystallizations from dioxane, the product melted at 241.5–242°.

Anal.[7] Calcd. for $C_{24}H_{34}$: C, 89.37; H, 10.63. Found: C, 89.27; H, 10.57.

The sodium hydroxide extract of the ether phase yielded only a trace of white solid acid, presumably pentamethylphenylacetic acid.

Coupling of 2,4,6-Tribromobenzyl Bromide.—This halide[2] (5 g., 0.012 mole) was treated with methylmagnesium iodide by the method of Fuson[8] for coupling di-*o*-methylbenzyl chlorides. Crude 1,2-di-(2,4,6-tribromophenyl)-ethane, m. p. 216–220°, precipitated from the ether phase of the acidified reaction mixture. A further small quantity of product was obtained by fractionation of the ether; combined yield, 2.7 g. (69%). After recrystallization from 1500 ml. of ethanol, the product melted at 221°.

Anal.[7] Calcd. for $C_{14}H_8Br_6$: C, 25.64; H, 1.23; Br, 73.11. *Found*: C, 26.04; H, 1.40; Br, 73.10.

DEPARTMENT OF CHEMISTRY
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[2] Hauser and Humphlett, *J. Org. Chem.*, **15**, 364 (1950).

[3] Wenzel, *Monatsh.*, **35**, 953 (1914).

[4] Kharasch and Fuchs, *J. Org. Chem.*, **9**, 364 (1944).

[5] Vavon, Bolle and Calin, *Bull. soc. chim.*, [5] **6**, 1025 (1939).

[6] Jacobsen [*Ber.*, **22**, 1217 (1889)] reported 99° as the melting point for this chloride prepared in unreported yield from hexamethylbenzene and phosphorus pentachloride.

[7] Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

[8] Fuson, Denton and Kneisley, THIS JOURNAL, **63**, 2652 (1941).

Pentaphenylacetone and Tetraphenylacetone[1]

BY SIMON W. KANTOR AND CHARLES R. HAUSER

In connection with another study, pure pentaphenylacetone[2] was synthesized conveniently in high yield by the acylation of potassium diphenylmethide with triphenylacetyl chloride.[3] The ketone was evidently converted to its potassium derivative in the reaction mixture and, in order to obtain maximum yield, two molecular equivalents of potassium diphenylmethide to one of the acid chloride were employed.

$$(C_6H_5)_3CCOCl + 2KCH(C_6H_5)_2 \longrightarrow K[(C_6H_5)_3CCOC(C_6H_5)_2] + KCl + CH_2(C_6H_5)_2$$

The two reactants were readily prepared. The potassium diphenylmethide was obtained from diphenylmethane by metalation with potassium amide[4] and the triphenylacetyl chloride, from the corresponding carboxylic acid[5] which was prepared by the carbonation of potassium triphenylmethide.[6]

In a similar manner, *sym*-tetraphenylacetone was synthesized conveniently in good yield by the acylation of potassium diphenylmethide with diphenylacetyl chloride.

$$(C_6H_5)_2CHCOCl + 2KCH(C_6H_5)_2 \longrightarrow K[(C_6H_5)_2CHCOC(C_6H_5)_2] + KCl + CH_2(C_6H_5)_2$$

In this case, there was also formed apparently a little of the O-acyl derivative of the ketone which was hydrolyzed with alkali, regenerating the ketone.

Both of these ketones are relatively unreactive. Vorländer and Rack[7] reported that tetraphenylacetone fails to undergo any carbonyl reactions and that it does not exhibit the properties of the

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[1] This work was carried out under contract N7 onr-455 with the Office of Naval Research.

[2] Wieland, Hintermaier and Dennstedt (*Ann.*, **452**, 23 (1927)) prepared this ketone by the thermal decomposition of diphenylacetylazotriphenylmethane but the method was tedious and the yield was low.

[3] An attempt to effect this acylation with methyl triphenylacetate failed to produce pentaphenylacetone. Instead, there was obtained triphenylacetic acid (56%), recovered diphenylmethane (63%) and considerable residual oil. The displacement of the triphenylacetate anion by the diphenylmethide anion might appear to have occurred but the diphenylethane, which would then have been formed, was not found.

[4] Yost and Hauser, THIS JOURNAL, **69**, 2325 (1947).

[5] Bistrzycki and Landtwing, *Ber.*, **41**, 687 (1908).

[6] Levine, Baumgarten and Hauser, THIS JOURNAL, **66**, 1230 (1944).

[7] Vorländer and Rack, *Ber.*, **56B**, 1125 (1923).