Conversion of Diisopropylcarbinol to Dimethylisobutylcarbinyl Chloride.—The carbinol was kindly supplied by the du Pont Ammonia Department. It was fractionated through a 2.2 × 90 cm. column; b. p. 137–8° (738 mm.), $n^{20}_{\rm D}$ 1.4246, d^{20}_4 0.831.[12] The carbinol (464 g.) absorbed hydrogen chloride gas more slowly than the other carbinols studied. At first a pale purple color was formed. This gradually changed to brownish yellow. Reaction was complete in ten weeks at 20° and the yield of chloride was quantitative. It was distilled at 3 mm. to give 272 g. of chloride, b. p. (Cottrell) 127–128° dec. (733 mm.), $n^{20}_{\rm D}$ 1.4180, d^{20}_4 0.861. These properties correspond to dimethylisobutylcarbinyl chloride.[11] The identity was confirmed by conversion of the chloride, in 32% yield,[13] to dimethylisobutylcarbinol, b. p. (Cottrell) 130–131° (738 mm.), $n^{20}_{\rm D}$ 1.4166, d^{20}_4 0.811.[14] Treatment of fraction 7 with hydrogen chloride at 0° gave the tertiary chloride. No color appeared.

Conversion of Methylisobutylcarbinol to its Chloride.[15]—The carbinol was made in 42% yield from isobutylmagnesium bromide and acetaldehyde: b. p. 129.5° (734 mm.), $n^{20}_{\rm D}$ 1.4111, d^{20}_4 0.807.[16] Treatment of 408 g. of the carbinol with dry hydrogen chloride in the usual way for eighteen weeks gave 398 g. of crude chloride, 82% yield. Fractionation and refractionation gave methylisobutylcarbinyl chloride, b. p. (Cottrell) 111–112° (733 mm.) $n^{20}_{\rm D}$ 1.4113, d^{20}_4 0.861. The identity was substantiated further by conversion to the carbinol in 62% yield through the Grignard reagent.[5] The methylisobutylcarbinol was identified by b. p. 68° (64 mm.), $n^{20}_{\rm D}$ 1.4112 and conversion to the α-naphthylurethan, m. p. and mixed m. p. 96–97°.

Conversion of Methylisoamylcarbinol to its Chloride.—The carbinol was prepared in 65% yield from acetaldehyde and isoamylmagnesium chloride; b. p. 150.5–151° (742 mm.), $n^{20}_{\rm D}$ 1.4180, d^{20}_4 0.814. In the usual way hydrogen chloride gas was passed into 464 g. of the carbinol. After six weeks the chloride was separated and treated as usual. The partial condenser was kept at 14–15° and the heating bath at 50–52°. Fractionation gave a 90% yield of chloride, b. p. 138° dec. (735 mm.), d^{20}_4 0.863. Conversion of the chloride through the Grignard reagent and oxygen gave methylisoamylcarbinol in 60% yield, b. p. 151–152° (736 mm.), $n^{20}_{\rm D}$ 1.4180, α-naphthylurethan, m. p. and mixed m. p. 84–85°.

Conversion of Methylneopentylcarbinol to its Chloride.—The carbinol was prepared in 64% yield by reduction of methyl neopentyl ketone,[17] b. p. 136.5° (738 mm.), $n^{20}_{\rm D}$ 1.4180. The carbinol (36 g.) saturated with hydrogen chloride and allowed to stand for eight weeks gave a 90% yield of chloride which was distilled through a 1.1 × 70 cm. column[5] to give mainly methylneopentylcarbinyl chloride, b. p. 93° (250 mm.), $n^{20}_{\rm D}$ 1.4180; d^{20}_4 0.855. Only 2 g. of low boiling material was obtained. The chloride was converted to the carbinol in the usual way and the latter was converted to the α-naphthylurethan, m. p. 83°, mixed m. p. 84°.

Summary

1. It has not been possible to convert methylisopropylcarbinol to the corresponding secondary chloride.

2. Four secondary carbinols having tertiary hydrogen atoms alpha to the carbinol group gave tertiary chlorides on treatment with hydrogen chloride at room temperature.

3. Three secondary carbinols having no branch in the alpha position reacted normally without rearrangement to give the secondary chlorides.

STATE COLLEGE, PENNA.

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[13] The yield of olefins was 30%, the higher boiling material only 2.5 g.

[14] *Cf.* deGraef, *Bull. soc. chim. Belg.*, **40**, 315 (1931).

[15] This chloride has been obtained by Levene and Mikeska, *J. Biol. Chem.*, **65**, 509 (1925), and by Maass and Sivertz, THIS JOURNAL, **47**, 2883 (1925). The iodide has been made by Umnova, *J. Russ. Phys.-Chem. Soc.*, **42**, 1530–1543.

[16] Vavon, *Compt. rend.*, **155**, 287 (1912).

[17] Whitmore and Homeyer, THIS JOURNAL, **55**, 4194 (1933).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Tertiary Butyl Chloride from Tertiary Amyl Chloride and Hydrogen Fluoride

BY J. H. SIMONS, G. H. FLEMING, FRANK C. WHITMORE AND W. E. BISSINGER

Bockemüller[1] states that alkyl chlorides, bromides and iodides are only slightly soluble in anhydrous hydrogen fluoride and that no reaction takes place when the alkyl halides are mixed with hydrogen fluoride. In the gaseous state at higher temperatures, and in the presence of a metallic fluoride catalyst, the alkyl halide will undergo double decomposition with hydrogen fluoride, yielding an alkyl fluoride. No investigations of the action of hydrogen fluoride on tertiary chlorides, bromides, or iodides, were found in the literature. The present study was started to fill this gap.

There have been obtained 10–17% yields of *t*-butyl chloride by treating *t*-amyl chloride with an equimolal quantity of anhydrous hydrogen fluoride at 0°. Besides the *t*-butyl chloride, there was also obtained a mixture probably containing hexyl, heptyl, decyl or undecyl (possibly both), and pentadecyl chlorides.

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[1] Bockemüller, Sammlung chemischer und chemisch-technischer Vortrage, 1936.

It is interesting to note the apparent ease of formation of the tertiary butyl group under the influence of certain catalysts. Gilman[2] found that *n*-amyl chloride, *n*-hexyl bromide, and *n*-octadecyl bromide, with the ethyl ester of 5-bromofuroic acid in the presence of aluminum chloride, form in each case the same product, ethyl 4-*t*-butyl-5-bromofuroate.

Experimental

The *t*-amyl chloride was prepared by stirring 20 moles (2120 g.) of commercial *t*-amyl alcohol with 6600 cc. of concentrated hydrochloric acid. The crude *t*-amyl chloride was washed with water, dried with anhydrous potassium carbonate, and distilled from potassium carbonate through a 123 × 2.5 cm. column (15 theoretical plates) packed with single turn glass helices,[3] boiling point 37–38° (150 mm.), n^{20}_{D} 1.4053.

In order to check the purity of this *t*-amyl chloride, 100 g. of it was redistilled through a 1.1 × 45 cm. column (8 theoretical plates). The first portion of distillate boiled at 84.5° (730 mm.), thus proving the absence of *t*-butyl chloride, boiling point 51°. The literature gives the boiling point of *t*-amyl chloride as 86° (760 mm.) and n^{20}_{D} 1.4054.

The anhydrous hydrogen fluoride was a commercial product received in steel cylinders.

The procedure in a typical run was as follows: 6 moles (120 g.) of hydrogen fluoride was distilled into a dry 1-liter copper flask which was packed in a salt–ice mixture; a copper tube served as the inner tube of the Liebig condenser used in this distillation. When the required amount of hydrogen fluoride had been introduced into the flask, 6 moles (636 g.) of *t*-amyl chloride was poured into the hydrogen fluoride. The copper flask was connected immediately to a 2-hole rubber stopper which was fitted with a mercury-seal copper stirrer and a reflux condenser of copper tubing. Stirring at 0° was continued for three days. A constant evolution of hydrogen chloride occurred. When this evolution ceased the reaction was considered complete. The mixture was poured on 200 g. of ice in a 2-liter separatory funnel and washed with cold 5% sodium bicarbonate solution until the lower water layer was basic to litmus. The oil was separated, washed with ice water and dried with three 15-g. portions of potassium carbonate. Finally it was distilled from 12 g. of carbonate through a 1.1 × 45 cm. column packed with glass helices, giving 70 g. of material boiling between 40 to 60°. Redistillation of this low boiling material yielded 60 g. of *t*-butyl chloride, boiling point 49–50° (735 mm.), n^{20}_{D} 1.3855. This was further identified by conversion to trimethylacetanilide and trimethylacetic acid and its anilide.

Identification of *t*-Butyl Chloride

A. Preparation of Trimethylacetanilide.—A sample (1.5 cc.) of the material of b. p. 49–50°, n^{20}_{D} 1.3855, was dissolved in 6 cc. of ethyl ether and converted to the Grignard compound in the usual manner; an ether solution of phenyl isocyanate was added until no further reaction was observed and the complex was then decomposed on ice and hydrochloric acid. The ether layer was separated, the ether removed on the steam-bath, and the solid anilide recrystallized once from petroleum ether; melting point 131°. After a second recrystallization from petroleum ether it melted at 132.5–133°; melting point of known trimethylacetanilide 132.5–133°; mixed melting point 132°.

B. Preparation of Trimethylacetic Acid and its Anilide.—In a similar manner 23 g. of the material boiling at 49–50°, n^{20}_{D} 1.3855, was dissolved in ether and converted to the Grignard compound; dry carbon dioxide gas was then bubbled into the cold mixture. The complex was decomposed on ice and hydrochloric acid and after separation of the ether layer and evaporation of the ether, the residual oil was distilled from a 25-cc. distilling flask. There was obtained 10.8 g. of trimethylacetic acid, boiling point 162–163°; melting point 28–33°.

A portion (1.5 g.) of this acid was converted to the acid chloride by refluxing with thionyl chloride. A benzene–aniline solution was added and the mixture heated on the steam-bath. Finally the benzene solution was washed with dilute acid, dilute alkali, and water, filtered, and evaporated to dryness. Recrystallized once from petroleum ether, the anilide melted at 132.5°; mixed melting point with known trimethylacetanilide 133–133.5°.

After the material boiling below 60° had been removed the pressure was reduced and the residue fractionated. The following table presents the summarized results of the distillation.

Fractions	B. p. °C.	Mm.	Index	Gm.	Exptl. mol. wt.	% Cl Found	Remarks
1	40–60	735	1.3760–1.3865	70			*t*-Butyl chloride
2	37–41	146	1.4060	55			Unreacted *t*-amyl chloride
3–5	32–49	92	1.4062–1.4140	23			
6–9	49–53	92	1.4152–1.4175	42	123	28.1	
11–13	19–30	5.5	1.4222–1.4257	20			Hexyl and heptyl chlorides
14–16	30–32	5.0	1.4275–1.4282	25			
19–22	49–54	5.0	1.4328–1.4372	26			
23–25	54–57	5.0	1.4382–1.4400	18			Decyl or undecyl chlorides
26–28	57–63	5.0	1.4409–1.4420	25	188	17.7	
30–31	67–71	4.0	1.4440–1.4445	12			
33–35	78–91	4.0	1.4471–1.4479	16	236	11.2	Pentadecyl chloride

There was no fluorine in the fractions corresponding to the hexyl and heptyl chlorides. No tests for fluorine were made on the higher fractions.

Some preliminary investigation of this reaction had been carried out by D. E. Badertscher in 1933 in this Laboratory. A further study of this type of reaction is in progress.

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[2] Gilman, Burtner and Turck, THIS JOURNAL, **57**, 909 (1935).

[3] Wilson, Parker and Laughlin, *ibid*, **55**, 2795 (1933).

Summary

t-Butyl chloride in 10–17% yields has been obtained by treating *t*-amyl chloride with anhydrous hydrogen fluoride at 0°.

In addition to the *t*-butyl chloride, there was obtained a mixture probably containing hexyl, heptyl, decyl or undecyl, and pentadecyl chlorides.

STATE COLLEGE, PENNSYLVANIA RECEIVED JULY 1, 1938

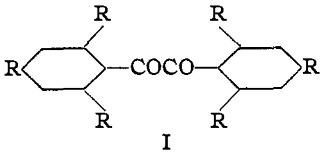
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Action of Methylmagnesium Halides on 2,4,6-Trisubstituted Benzoyl Chlorides

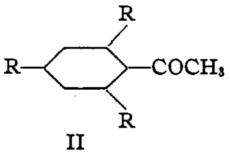
BY REYNOLD C. FUSON, J. H. VAN CAMPEN AND D. E. WOLF

The reaction of 2,4,6-trisubstituted benzoyl chlorides with methylmagnesium halides has been shown to give rise to three different types of products, depending on the nature of the substituents. In order to determine the influence of the substituents on the course of the reaction we have studied the action of methylmagnesium halides on certain benzoyl chlorides carrying alkyl groups or halogen atoms in the *ortho* positions.

In all cases the initial reaction is evidently either (1) coupling of the acid chloride to yield a benzil or (2) methylation to give the corresponding methyl ketone. For example, with 2,4,6-trimethylbenzoyl chloride and 2,4,6-triethylbenzoyl chloride both types of reactions are observed. The corresponding hexaalkylbenzils (I) and 2,4,6-trialkylacetophenones (II) are formed in nearly equal amounts.[1]

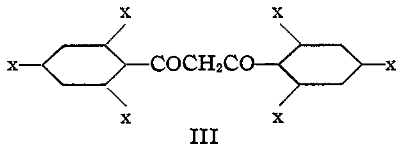


I



II

However, halogen atoms in the *ortho* positions suppress the coupling reaction entirely. 2,4,6-Trichlorobenzoyl chloride gives none of the benzil. The methyl ketone appears to be the primary product. It is of interest that this ketone is acylated readily, and under the conditions used is isolated chiefly as the corresponding 1,3-diketone (III, x = Cl).[2]

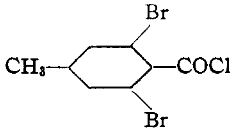


III

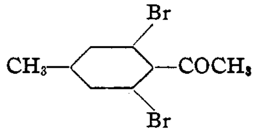
2,4,6-Tribromobenzoyl chloride reacted very sluggishly with methylmagnesium bromide or iodide, and the chief product was the 1,3-diketone, di-(2,4,6-tribromobenzoyl)-methane. The methyl ketone also was isolated in small amounts. Bromination of the diketone gave a heptabromo derivative, which could be reduced to the parent diketone by treatment with hydrogen iodide. The heptabromo compound, like the original diketone, gave a red color with an alcoholic ferric chloride solution. These facts serve to confirm the structures of the compounds in question.

Some evidence also is available to indicate that the 1,3-diketone is the result of a secondary reaction involving the methyl ketone. When the iodomagnesium enolate of the latter was treated with 2,4,6-tribromobenzoyl chloride the 1,3-diketone (III, x = Br) was formed.

One condensation was carried out with 2,6-dibromo-4-methylbenzoyl chloride (IV) and methylmagnesium iodide.



IV



V

The chloride was added slowly to a concentrated solution containing a great excess of the Grignard reagent. In this case also the reaction was exclusively of the second type; however, it stopped at the first stage giving only the methyl ketone (V). The identity of the latter was confirmed by converting it into the benzal derivative.

Experimental

A. Preparation of the Acid Chlorides

2,4,6-Trichlorobenzoyl Chloride.—This compound was prepared from 2,4,6-trichloroaniline by way of the nitrile and acid. For the synthesis of the nitrile a modification of Montagne's method[3] was employed. The nitrile was isolated by extraction and used without further purification.

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[1] Fuson and Corse, THIS JOURNAL, **60**, 2063 (1938).

[2] Ross and Fuson, *ibid.*, **59**, 1508 (1937).

[3] Montagne, *Rec. trav. chim.*, **21**, 376 (1902).