*iso*butyl alcohol and the subsequent rehydration of the *iso*butylene thus formed. The method can be adapted to any laboratory scale.

BURLINGTON, VERMONT

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

TRIPHENYLFLUOROMETHANE

BY F. F. BLICKE

RECEIVED MARCH 20, 1924

Triphenylhalomethanes have been in continual demand for the preparation of substances containing a triphenylmethyl group; consequently, triphenylchloro-, bromo- and iodomethane are well-known compounds. In connection with certain work, however, it was found that the abovementioned halides were not entirely suitable for our purpose.

The halogen in triphenylchloromethane is less reactive than the halogen in triphenylbromomethane and, normally, it might be expected that the fluorine compound would be even less reactive than the chloride. Still, considering the extreme chemical reactivity of fluorine itself and the abnormal behavior of so many inorganic fluorides it seemed not improbable that triphenylfluoromethane might prove to be an unusually reactive substance. Moreover, A. F. Holleman has shown that fluorine in certain substituted benzene compounds shows a remarkable reactivity.[1]

We were able to prepare triphenylfluoromethane by the action of acetyl fluoride on a benzene solution of triphenylcarbinol.[2] $(C_6H_5)_3C\text{-}OH + CH_3CO\text{-}F = (C_6H_5)_3C\text{-}F + CH_3CO\text{-}OH$.

Judging from the reactions studied, it can be said that the fluoride is unquestionably a less reactive substance than the corresponding chloride. The fluoride, unlike the chloride, is unacted upon by molecular silver, mercury or zinc. Even at 80° silver does not remove the fluorine.

The chloro compound reacts almost immediately and quantitatively with absolute ethyl alcohol with the formation of triphenylmethyl ethyl ether.[3] The fluoride can be recrystallized unchanged from alcohol.

Suspended in water for 12 hours, the fluoride shows no signs of hydrolysis and can be recovered unchanged. When boiled with aqueous sodium hydroxide, aqueous silver nitrate or with acetic acid the fluoride is converted into the carbinol.

The fluoro compound, dissolved in absolute ether, is reduced quanti-

---

[1] Holleman, *Rec. trav. chim.*, **23**, 256 (1904); **24**, 28 (1905).

[2] Gomberg and Davis [THIS JOURNAL, **25**, 1271 (1903)] were the first to show that acetyl chloride reacts with triphenylcarbinol with the formation of triphenylchloromethane, and not triphenylmethyl acetate as might be expected. Later L. Henry [*Bull. acad. roy. Belg.*, **1905**, 537; **1906**, 261) showed that tertiary alcohols in general react with acetyl chloride with the formation of the corresponding carbinol chloride.

[3] Gomberg and Kamm, THIS JOURNAL, **39**, 2011 (1917).

tatively to triphenylmethane by zinc chloride, similarly to the chloride.[4]

The fluoride condenses slowly with amines such as *p*-toluidine with the formation of triphenylmethyl-*p*-toluidine.[5]

Triphenylfluoromethane does not condense with benzene in the presence of aluminum chloride to form tetraphenylmethane.

Triphenylchloromethane reacts with phenylmagnesium bromide with the formation of tetraphenylmethane;[6] the yield of the latter substance, however, is poor and varies from 0.5 to 12%. This is due to the fact that the chloromethane is simultaneously converted into other products such as triphenylmethyl, triphenylmethane and triphenylcarbinol. It was found that triphenylfluoromethane reacts instantly with a cold ether solution of phenylmagnesium bromide with the production of an orange solution, the color being due to the presence of triphenylmethyl which was isolated in the form of its peroxide. No tetraphenylmethane was obtained; the only other reaction products found were carbinol and a red oil.

The fluoro compound, like the chloride, instantly reduces potassium permanganate dissolved in acetone; triphenylcarbinol is produced in quantitative yield.

All of the other triphenylhalomethanes instantly yield colored addition products with certain inorganic salts. The fluoride forms a red oil with aluminum chloride, an orange compound with stannous chloride and with ferric chloride, and a yellow substance with zinc chloride or fluoride.

Experimental Part

Acetyl Fluoride.—To zinc carbonate in a Bakelite beaker was added slightly more than the calculated amount of 48% hydrofluoric acid necessary to convert it into the fluoride. After the water had evaporated from the mixture the material was air-dried and pulverized. The zinc fluoride prepared in this manner contains four molecules of water of crystallization, and in order to render it anhydrous it was heated to 150° in a round-bottom flask, in a bath, and the water driven off under reduced pressure. When the fluoride is heated in air it is converted to a considerable extent into zinc oxide.

For the preparation of acetyl fluoride[7] a copper flask embedded in solder was used.[8] In it was placed 312 g. of pure acetyl chloride and it was then securely closed by means of a screw clamp and a rubber gasket, cooled in ice and 206 g. of zinc fluoride was added, in small portions, during the course of several hours. The mixture was then allowed to remain at room temperature for three days. The flask was immersed in a bath, heated to 35–40°, and the acetyl fluoride distilled through a long fractionating column which

---

[4] Gomberg, THIS JOURNAL, **35**, 204 (1913).

[5] Elbs, *Ber.*, **17**, 706 (1884). Gomberg, THIS JOURNAL, **24**, 611 (1902).

[6] Gomberg and Cone, *Ber.*, **39**, 1463 (1906). Gomberg and Kamm, THIS JOURNAL, **39**, 2010 (1917).

[7] Meslans [*Ann. chim. phys.*, [7] **1**, 411 (1894)] prepared acetyl fluoride by the action of acetyl chloride on zinc fluoride, but we have modified his method.

[8] Considerable pressure is developed during the preparation of this substance; the walls of a lead flask which was originally used were blown out.

contained a quantity of coarsely powdered zinc fluoride. This crude acetyl fluoride was then poured into a small copper flask which contained zinc fluoride and again distilled through a column of zinc fluoride. The purified acetyl fluoride, which boiled at 20–25°, was used at once. The yield based on acetyl chloride was about 40%.

Triphenylfluoromethane.—Thirty g. of dry triphenylcarbinol was suspended in 150 cc. of benzene and 30 cc. of acetyl fluoride added. The mixture became yellow at once, and after 24 hours all of the carbinol had dissolved. The reaction should be carried out in a thick-walled flask and the stopper securely fastened in place since pressure is developed, due to the excess of low-boiling acetyl fluoride. The mixture was shaken frequently and allowed to stand for four days protected from light. Most of the benzene was then removed by distillation, the concentrated solution was quickly filtered and dry petroleum ether added to the filtrate. Large, slightly yellow crystals began to form immediately. After some time the liquid was decanted from the crystals and the latter were recrystallized twice from petroleum ether. The fluoride melts at 102–104°. The yield of pure, colorless fluoride, based on carbinol, was about 85%.

The fluoride is very soluble in benzene, ether and carbon disulfide.

The material was analyzed in the following way. A solution of 0.5000 g. of substance in 5 cc. of benzene was refluxed for 12 hours with 0.82 g. of silver nitrate dissolved in 15 cc. of water. Upon removal of the benzene on a steam-bath pure triphenylcarbinol was obtained; m. p., 159–160°; yield, 0.487 g. (calc. 0.496). To the aqueous solution, which contained silver fluoride and the excess of silver nitrate, just enough sodium chloride was added to convert all of the silver into silver chloride. The latter was removed by filtration and the neutralized solution of sodium fluoride was treated with an excess of a saturated solution of lead chloride, which precipitated the fluorine as PbFCl.[9]

Analysis. Calc. for $C_{19}H_{15}F$: F, 7.25. Found: 7.10.

Behavior toward Metals.—Three tubes were prepared, each of which contained a solution of 0.5 g. of the fluoride dissolved in 10 cc. of benzene. To one tube were added 10 molecular equivalents of molecular silver, to another a corresponding amount of mercury and to a third zinc. The tubes were sealed, oxygen being excluded, and shaken for 24 hours at room temperature. No color developed in any of the tubes and the fluoride was recovered unchanged. Triphenylchloromethane, under exactly the same conditions, reacts instantly with the above-mentioned metals with the formation of an intensely colored solution of triphenylmethyl. Copper, bronze and magnesium, using absolute ether as a solvent, were likewise not acted upon. One g. of the fluoride, dissolved in benzene, was boiled with 3 g. of molecular silver in an atmosphere of nitrogen for six hours. The solution remained colorless and the fluoride was recovered unchanged.

Reduction of the Fluoride.—One g. of the material, 4 g. of zinc chloride and 15 cc. of absolute ether were shaken in a sealed tube for 12 hours. As soon as these substances were mixed the ether was colored a deep yellow. After 12 hours the ether was black. The mixture was poured into an evaporating dish and the solvent allowed to evaporate. The triphenylmethane formed was extracted with benzene. Upon evaporation of the latter solvent the characteristic transparent crystals of the compound which triphenylmethane forms with benzene resulted. The methane was purified by distillation; m. p., 92–93°; yield, 0.9 g.

Reaction with Amines.—A mixture of 2.6 g. of the fluoride dissolved in 10 cc. of benzene, and 2.2 g. of *p*-toluidine dissolved in 5 cc. of the same solvent, was refluxed in a bath for eight hours. The *p*-toluidine hydrofluoride was removed by filtration and the reaction product separated from the unchanged material by fractional crystallization from benzene. The triphenylmethyl-*p*-toluidine was recrystallized from a mixture of chloroform and alcohol; m. p., 177–178°; yield, 2.2 g.

---

[9] Starck, *Z. anorg. Chem.*, **70**, 173 (1911).

Reaction with Potassium Permanganate.—To a solution of 2.1 g. of triphenylchloromethane in 30 cc. of alcohol-free acetone was added 0.8 g. of potassium permanganate, dissolved in the same solvent. The permanganate was reduced instantly and the chloride was converted quantitatively into the carbinol. Identical results were obtained with the fluoride.

It is our intention to study the lability of fluorine in tertiary aliphatic carbinol fluorides; these we hope to prepare by the action of acetyl fluoride on the carbinols.

Summary

Triphenylfluoromethane has been synthesized and described.

The ordinary method for the preparation of triphenylmethyl—action of silver, mercury or zinc on a solution of a triphenylhalomethane—fails in the case of the fluoride; no trace of fluorine is removed by these metals. In certain other reactions the fluoride behaves similarily to the chloride.

In general it may be stated that the fluorine in triphenylfluoromethane is much less labile than the chlorine in triphenylchloromethane.

ANN ARBOR, MICHIGAN

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

SIMPLIFICATION OF THE GATTERMANN SYNTHESIS OF AROMATIC ALDEHYDES. II

BY ROGER ADAMS AND EDNA MONTGOMERY[1]

RECEIVED MARCH 21, 1924

In a recent communication from this Laboratory,[2] a convenient simplification of the Gattermann reaction for the synthesis of certain hydroxyaldehydes was described. Various phenols were treated in dry ether with zinc cyanide, and then dry hydrogen chloride was passed in. By this procedure, anhydrous hydrogen cyanide was formed in the reaction mixture and condensed with the hydrogen chloride and phenol to give a condensation product which was hydrolyzed to an hydroxyaldehyde. The zinc chloride which was produced at the same time acted as an effective condensing agent. Thus the most disagreeable feature of the Gattermann reaction, the handling of anhydrous hydrogen cyanide, was avoided. An easy method for the preparation of zinc cyanide was also described.

Gattermann[3] found that, in order to prepare aldehydes from certain phenols or phenol ethers, it was necessary to use anhydrous aluminum chloride as a condensing agent with the phenol or phenol ether, hydrogen cyanide and hydrogen chloride, zinc chloride being unsatisfactory. A study has been made of the synthesis of the aldehydes from various phen-

---

[1] This communication is an abstract of a thesis submitted by Edna Montgomery in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Illinois.

[2] Adams and Levine, THIS JOURNAL, **45**, 2373 (1923).

[3] Gattermann, *Ann.*, **357**, 313 (1907).