Summary

Cyclopropane has been found to react with benzene catalyzed by hydrogen fluoride to give normal propylbenzenes in good yield. A possible mechanism for the reaction is postulated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Fluoride as a Condensing Agent. V. Reactions of Compounds Containing Oxygen and Reactions of Tertiary Halides with Olefins

BY J. H. SIMONS, S. ARCHER, AND H. J. PASSINO

In the preceding papers of this series[1] the usefulness of hydrogen fluoride has been shown as a condensing agent for reactions between aromatic compounds and either unsaturated compounds or halides. That this reagent will promote many other reactions can now be shown. It appears that it catalyzes the same reactions that acidic reagents such as sulfuric acid catalyze and also the reactions that metallic halides such as aluminum chloride or boron trifluoride catalyze. For some reactions it is not only more convenient technically but also produces higher yields. There are reactions that hydrogen fluoride promotes that have not been reported using other reagents. One of these is a reaction between an aliphatic halide and an olefin. Two examples of this reaction are reported here in preliminary form. These are the reactions of tertiary butyl chloride with trimethylethylene and with cyclohexene.

The reactions of compounds containing oxygen are somewhat different from reactions of compounds that do not. Due to the peculiar properties of hydrogen fluoride, one cannot predict its effect in these reactions. To show the usefulness of hydrogen fluoride for them an account of the following reactions is included. Tertiary butyl alcohol has been caused to react with benzene to form tertiary butyl benzene, tertiary butyl chloride has reacted with phenol to form tertiary butyl phenol, and tertiary butyl chloride has been made to react with ethyl furoate. For these reactions larger quantities of hydrogen fluoride are required.

Many other types of reactions undoubtedly can be performed by means of hydrogen fluoride but the variety that has now been accomplished shows the general usefulness of this reagent in organic reactions. The reasons for its apparent uniqueness probably can be found in its physical and chemical properties. These have been summarized by Simons.[2] Despite its apparent weakness in aqueous solutions, it is a very powerful acidic substance. This property of donating protons makes it a useful reagent for organic reactions such as polymerizations and rearrangements in which a positive organic ion is the intermediate. The fact that the other halogen halides are insoluble in it accounts for the reactions in which a halogen halide is eliminated. Its unusual ability to form addition compounds, which is so evident in its numerous complex inorganic compounds, probably accounts for its usefulness in reactions involving aromatic compounds. A complex intermediate similar to those postulated for reactions using aluminum chloride may be the active agent. It is certainly much more soluble in benzene than would be expected from its high dielectric constant. It is readily eliminated during the course of many organic reactions in which not more than one fluorine atom is attached to the same carbon atom, not because the carbon fluoride bond is weak but because the energy of formation of hydrogen fluoride is so very high.

Experimental

The same techniques were used as previously described[1] with the following exceptions. Tertiary butyl alcohol was added at one time as it clogged the delivery tube if added slowly. Ethyl furoate was used in solution in carbon tetrachloride. Much larger quantities of hydrogen fluoride were required in reactions involving oxygen containing compounds, and the reactions required a longer time. The reaction of ethyl furoate required about one hundred and fifty hours.

Tertiary Butyl Chloride and Trimethylethylene.—Distillation of the reaction products gave a constant boiling fraction of refractive index 1.4279–1.4315. It boiled 63–65° at 19 mm. This product was definitely an olefin with physical properties corresponding to the expected nonenes. The remainder of the material boiled over a continuous range of temperatures both above and below the constant boiling fraction. Apparently many products

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[1] Simons and Archer, THIS JOURNAL, **60**, 2952 and 2953 (1938); Simons, Archer and Adams, *ibid.*, **60**, 2955 (1938).

[2] Simons, *Chem. Rev.*, **8**, 213 (1931).

TABLE I

CONDENSATION REACTIONS USING HYDROGEN FLUORIDE INVOLVING OXYGEN CONTAINING COMPOUNDS

Alkyl compounds	Aromatic compound	Product	Yield, %	B. p., °C.
t-Butyl alcohol	Benzene	Mono-*t*-butylbenzene	3	165
		Di-*t*-butylbenzene	8	78–78.5[a]
t-Butyl chloride	Phenol	*p*-*t*-Butylphenol	85	234–238[b]
t-Butyl chloride	Ethyl furoate	Ethyl 5-*t*-butylfuroate	54	116–117 (16 mm.)[c]

[a] Melting point. A mixed melting point with known *p*-di-*t*-butylbenzene was 77–78°. [b] The *p*-*t*-butylphenol melted at 97–98°, *p*-toluenesulfonate of it melted at 108–109°. [c] n^{20} 1.4749, the ester on saponification gave 5-*t*-butylfuroic acid which melted at 105–105.5°.

are formed, and this reaction requires further study. The constant boiling fraction represents about 18% yield.

Tertiary Butyl Chloride and Cyclohexene.—Distillation of the reaction products gave a fraction boiling 40–42° under a pressure of 18 mm. and at 141.5–142° at 739 mm. The refractive index of this fraction was 1.4578. It decolorized bromine water and gave only a very weak chloride ion test. Since neither boiling point nor refractive index checks whatsoever with di- or triisobutylene, and since it appears to be an olefin, it is very probable that polymerization has occurred between the tertiary butyl chloride and the cyclohexene to give either a tertiary butyl cyclohexene or a substituted cyclohexyl ethylene.

The yield of this fraction was 31% of the theoretical. A triisobutylene fraction of less than 10% was also obtained.

Conclusions.—The general usefulness of hydrogen fluoride as a reagent in organic reactions has now been well established. The technique of its use is somewhat different than that of other similar reagents but its utility seems to be much greater than any of them. There are reactions such as that between an olefin and a tertiary chloride which it promotes that have not been previously reported.

Summary

Hydrogen fluoride has been found useful to catalyze reactions between tertiary butyl chloride and both trimethylethylene and cyclohexene. It also has been found to catalyze reactions involving oxygen containing compounds. Tertiary butyl alcohol has been caused to react with benzene, tertiary butyl chloride formed tertiary butylphenol upon reaction with phenol, and ethyl 5-*t*-butylfuroate was formed from tertiary butyl chloride and ethyl furoate.

An explanation for the general utility of hydrogen fluoride in organic reactions is sought in its chemical and physical properties.

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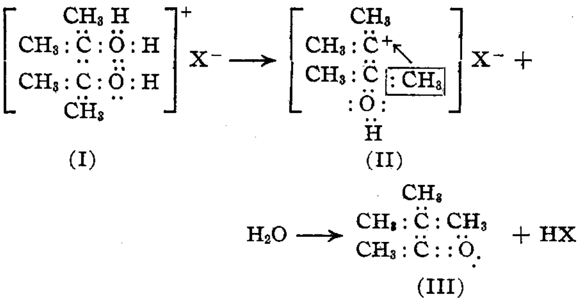
[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Pinacol–Pinacolone Rearrangement: the Preparation and Rearrangement of Tetramethylethylene Bromohydrin

BY GEORGE W. AYERS, JR.[1]

The Stieglitz mechanism[2] of the pinacol–pinacolone rearrangement assumes that an intermediate oxonium salt (I) loses water to leave a nucleus[3] (II) in which one of the carbon atoms possesses only three pairs of electrons. This "fault" in the molecule is then repaired by the migration of a negative methyl group, with its full complement of electrons, from the adjacent carbon atom to the electron deficient carbon atom



$$\left[\begin{array}{l}\quad\mathrm{CH_3}\ \mathrm{H}\\ \mathrm{CH_3:\ddot{C}:\ddot{O}:H}\\ \mathrm{CH_3:\ddot{C}:\ddot{O}:H}\\ \quad\mathrm{\ddot{C}H_3}\end{array}\right]^+ \mathrm{X}^- \longrightarrow \left[\begin{array}{l}\quad\mathrm{CH_3}\\ \mathrm{CH_3:\ddot{C}^+}\\ \mathrm{CH_3:\ddot{C}}\boxed{\mathrm{:CH_3}}\\ \quad\mathrm{:\ddot{O}:}\\ \quad\ \mathrm{H}\end{array}\right]\mathrm{X}^- + \mathrm{H_2O} \longrightarrow \begin{array}{l}\quad\mathrm{CH_3}\\ \mathrm{CH_3:\ddot{C}:CH_3}\\ \mathrm{CH_3:\ddot{C}::\ddot{O}}\end{array} + \mathrm{HX}$$

(I) (II) (III)

This rearrangement, in which one carbon atom is completely reduced and another completely oxi-

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[1] Under the supervision of the late Dr. Julius Stieglitz. This paper is a portion of the thesis presented by the author to the Graduate School of the University of Chicago for the degree of Doctor of Philosophy in December, 1931.

[2] (a) Stieglitz, *Am. Chem. J.*, **39**, 29, 166 (1908); (b) Derby, *ibid.*, **39**, 437 (1908); (c) McCracken, *ibid.*, **39**, 437, 586 (1908); (d) Migita, *Bull. Chem. Soc. Japan*, **3**, 308 (1928); (e) R. B. Cooper, Doctor's Dissertation, University of Chicago, 1930; (f) K. H. Adams, Doctor's Dissertation, University of Chicago, 1932; (g) Stieglitz, Cooper and Ayers, *Trans. Ill. State Acad. Sci.*, **25**, 173 (1933); for a review of previous work see Gilman, "Organic Chemistry, An Advanced Treatise," Vol. I, 1938, p. 720, and Porter, "Molecular Rearrangements," 1928, p. 85.

[3] See Whitmore, THIS JOURNAL, **54**, 3274 (1932).