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

Hydrogen Fluoride as a Condensing Agent. XVIII. Aralkyl Ketones

BY J. H. SIMONS AND EDWARD O. RAMLER[1]

In previous papers of this series hydrogen fluoride has been studied as a condensing agent for a number of organic chemical reactions. Herein is described its effect on acetophenone and related aralkyl ketones. In a number of experiments in which acetophenone was treated with hydrogen fluoride at approximately 100° benzoic acid and a resin were isolated from the reaction products. The resinous polymer was found to contain α-methylstyrene units. This interesting result prompted the present study. Incidentally in the course of this work, alkylation of acetophenone with hydrogen fluoride as the catalyst was attempted at about 100° unsuccessfully.

In the presence of hydrogen chloride and hydrogen bromide acetophenone, propiophenone, and other partially substituted ketones undergo intermolecular condensations with themselves.[2] Acetophenone forms both dypnone and *sym*-triphenylbenzene. Propiophenone was found by Grignard and Colonge,[3] to form 1,3-diphenyl-2-methylpentene-2-one-1 with both hydrogen iodide and hydrogen bromide. The yield was greater with hydrogen iodide and the reaction did not occur with hydrogen chloride. Fredenhagen and Fredenhagen[4] dissolved acetophenone in hydrogen fluoride at room temperature and below and recovered the acetophenone unchanged.

Acetophenone could yield benzoic acid in the presence of hydrogen fluoride in three ways: (1) a direct splitting with hydrogen fluoride to give benzoyl fluoride and methane, (2) a catalytic autoöxidation, and (3) a condensation of two or more molecules followed by a splitting of the resultant to form benzoyl fluoride and another product. The first of these is immediately excluded as no methane was produced. Experiments were performed to decide between the second and third possibilities and the second was eliminated.

Propiophenone and isobutyrophenone also were studied to investigate the effect of the number of hydrogen atoms on the carbon atom adjacent to the carbonyl group. Benzoic acid was produced by the former but not by the latter. It, however, formed a resin. Benzophenone and α-trichloroacetophenone were tried, and both of these were recovered unchanged from a treatment with hydrogen fluoride at 100°. They have no α-hydrogen atom. This indicates that the formation of benzoic acid requires at least two hydrogen atoms on the carbon atom adjacent to the carbonyl group while the resin is formed if there is one or more.

The formation of benzoic acid by alternative three requires a reaction with hydrogen fluoride of unusual character. In order to investigate this, dypnone, which is a condensed product of acetophenone, was treated with hydrogen fluoride. It gave benzoic acid and the resin. As a further step in the correlation dypnone was obtained from acetophenone by a treatment with hydrogen fluoride at 50°, and an unsaturated ketone identified as 1,3-diphenyl-2-methylpentene-2-one-1 was obtained by a similar treatment of propiophenone at 55°. This does not follow the systematic effect of molecular weight of the halogen halide on the condensation of these ketones.

Procedures and Results

In Table I is given a summary of most of the experiments. The reactions were performed in a copper bomb for about sixteen to twenty hours. The reaction products were poured onto ice and ether extracted. A sodium carbonate treatment was used to remove hydrogen fluoride; and a subsequent sulfuric acid treatment drove the benzoic acid into the ether solution, which was then distilled. The carboxylic acids were recrystallized and identified by mixed melting points with known samples. The resins were left as residues.

The resins, when first obtained, were viscous liquids which subsequently formed shellac-like solids. They were found soluble in ether, benzene, acetone and alcohol. Sublimation and molecular distillation were tried without success. The polymers from acetophenone, propiophenone and isobutyrophenone had the same appearance. They

---

(1) Present address, E. I. du Pont de Nemours and Company, Plastics Department, Arlington, New Jersey.

(2) C. Engler and H. E. Bethold, *Ber.*, **7**, 1123 (1874); M. Delacre, *Bull. classe. sci., Acad. roy. Belg.* [3] **20**, 467 (1890); F. Henrich and A. Wirth, *Monatsh.*, **25**, 431 (1904); E. P. Kohler, *Am. Chem. J.*, **31**, 658 (1904); B. N. Dolgov and Y. N. Volnov, *J. Gen. Chem.* (U. S. S. R.), **1**, 340 (1931); *Abs.*, **26**, 2186 (1932).

(3) V. Grignard and J. Colonge, *Compt. rend.*, **190**, 1349 (1930).

(4) K. Fredenhagen and H. Fredenhagen, *Z. anorg. allgem. Chem.*, **243**, 39 (1939).

TABLE I

Ketone	Moles HF / Moles ketone	Temp., °C.	% Acid[b]	% Polymer[b]	Other products
Acetophenone	9	99	34	46	None
Propiophenone	15	99	34.4	60	None
Isobutyrophenone	11	99	None	75	None
Benzophenone	24	99	None	None	None
α-Trichloroacetophenone	14	169	None	None	None
Acetophenone	6	25	None	None	None
p-t-Butylacetophenone	10	99	33[a]	43	None
Dypnone	26	99	34	57	None[d]
Acetophenone	9	50	16.2	20	Dypnone (23.8%)[b]
Propiophenone	12	55	59	30	Unsat. ketone (3.5%)[b,c]

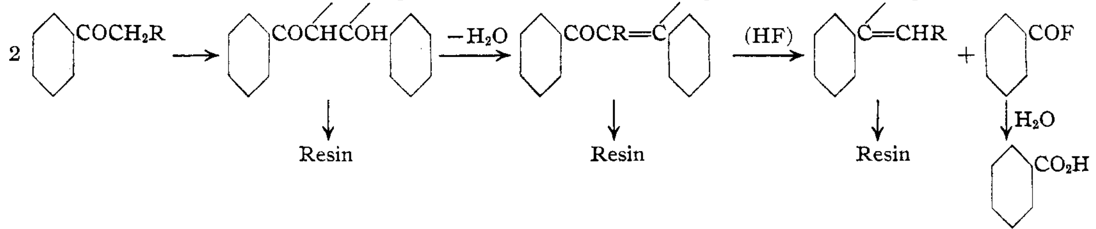
[a] *p-t*-Butylbenzoic acid. [b] Based on the amount of ketone not recovered and on the theory that one molecule of acid is produced from two molecules of the ketones except in the case of dypnone where one molecule of acid is produced from one molecule of ketone. [c] Product was 1,3-diphenyl-2-methylpentene-2-one-1. The dypnone was identified by the mixed melting point of the *syn*-oxime with a known sample; m. p. 129–131°. A sample of 1,3-diphenyl-2-methylpentene-2-one-1 was prepared by the action of hydrogen bromide on propiophenone and found to be identical with the unsaturated ketone obtained from propiophenone and HF by means of a mixed melting point of the 2,4-dinitrophenylhydrazones; m. p. 175°. [d] No dypnone was recovered.

were dark brown, glassy solids, which were apparently mixtures. The polymer from acetophenone, when heated to above 300° gave a small amount of an unsaturated liquid which distilled at about 164°. It yielded acetophenone on treatment with cold neutral permanganate. The 2,4-dinitrophenylhydrazone of this acetophenone was prepared, m. p. 228°. This indicates the unsaturated liquid to be α-methylstyrene and the resin to contain α-methylstyrene units. A similar treatment of the residue of the propiophenone condensation gave an unsaturated liquid which distilled at about 200° and was thought to be 3-phenylpentene-2. It gave propiophenone upon oxidation with cold potassium permanganate. The 2,4-dinitrophenylhydrazone melted at 182°.

In order to establish the fact that the formation of benzoic acid did not result from an autoöxidation, a number of experiments were performed. Oxygen was added to the acetophenone condensation mixtures under a variety of conditions, but this increase of oxidation environment reduced rather than increased the yield of benzoic acid. Benzophenone should give benzoic acid by oxidation, if this is the nature of the reaction. If acetophenone gives benzoic acid by oxidation, then it should be capable of supplying the oxygen to form benzoic acid from benzophenone. In order to test this, *p-t*-butylacetophenone was mixed with benzophenone and heated with hydrogen fluoride for seventeen hours at 100°. No benzoic acid was found. These experiments indicate that the formation of the benzoic acid did not proceed through an autoöxidation.

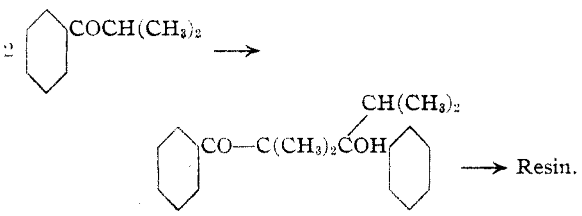
Discussion

The results of these experiments show that aralkyl ketones related to acetophenone undergo a condensation in the presence of hydrogen fluoride. There are apparently at least two different condensations possible. One of these requires at least one hydrogen atom on the carbon atom adjacent to the carbonyl group, and a resinous product is formed. In another one, two or three hydrogen atoms in the same position are necessary; and benzoic acid (by hydrolysis of the reaction mixture) is formed in addition to a resin, a portion of which may be a substituted styrene polymer. As the formation of the benzoic acid is shown not to result from either a splitting of the original ketone with hydrogen fluoride or an autoöxidation, the following postulation is made for the course of the reaction.



For acetophenone R is H and for propiophenone R is CH_3.

For isobutyrophenone



For benzophenone and α-trichloroacetophenone similar condensations cannot take place.

Summary

Aromatic ketones were found to condense with themselves in the presence of hydrogen fluoride. Those containing two or three hydrogen atoms on the carbon atom adjacent to the carbonyl group (propiophenone and acetophenone) gave benzoic acid and a resin as the products. At a lower temperature dypnone was formed from acetophenone and 1,3-diphenyl-2-methylpentene-2-one-1 from propiophenone. A similar treatment with dypnone gave benzoic acid and a resin. α-Methylstyrene and 3-phenylpentene-2 were obtained, respectively, from the resins from acetophenone and propiophenone. Isobutyrophenone gave a resin but no benzoic acid, and benzophenone and α-trichloroacetophenone gave no reaction.

It is postulated that the condensation proceeds to form first a tertiary alcohol. Only ketones with one or more alpha hydrogen atoms can do this. This tertiary alcohol can polymerize. It can also dehydrate to form an unsaturated ketone, if there are two or three alpha hydrogen atoms in the original ketone. This unsaturated ketone can either polymerize or react with hydrogen fluoride to form benzoyl fluoride and a substituted styrene polymer.

STATE COLLEGE, PA. RECEIVED APRIL 1, 1943

[CONTRIBUTION FROM SHAWINIGAN CHEMICALS LIMITED]

The Viscosity Function. IV. Non-ideal Systems

BY ERNEST P. IRANY

Measurements and interpretations of the viscosity of liquid mixtures have been and are being published in great scope and variety. While the reliability of the measurements cannot in general be questioned, the conclusions drawn from them are mostly based on postulates which are misleading.

Recognition of ideality or non-ideality[1,2] in a given system and the correct location of maximum and minimum deviations depend entirely on the use of significant and additive quantities. A survey of the literature shows viscosity and concentration expressed in units of various definitions, the choice and combination being more a matter of precedent or preference than of reasoned principle. In consequence, a large number of published statements on association and compound formation are uncertain if not definitely wrong. It is the purpose of this paper to emphasize the need of critical revision of the whole field based on a uniform and reliable method of evaluation.

As claimed in the preceding papers of this series[1] the existence of unique and generally valid solutions of the viscosity function of liquids has been established. These solutions have been expressed in the form of functional scales of viscosity which in the following are applied to a selection of typical non-ideal mixtures. The viscosity measurements are taken from the literature; where required they are supplemented by the author's own data.

In all methods of graphical analysis of viscosity–composition diagrams the investigator tacitly assumes from the start, a certain law of ideality. If, for example, he has decided on weight units for composition and on absolute viscosity units for viscosity, he bases all his observations on the understanding that the straight line connecting the pure components in his diagram represents that sequence of conditions which should obtain if the mixture were ideal. Any divergence from this straight line may then be credited with significance. Each combination of units thus defines its own regime of ideal additivity, but obviously only one can be true.

The errors incurred become most serious where the actual divergence from ideality is small and

---

[1] Irany, THIS JOURNAL, **60**, 2106 (1938); **63**, 2611 (1941).

[2] Parks and Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Co., New York, N. Y., 1932, p. 127.