[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

Hydrogen Fluoride as a Condensing Agent. VIII.[1] The Alkylation of Benzene by Esters

BY J. H. SIMONS, S. ARCHER AND D. I. RANDALL

The alkylation of aromatic compounds by esters recently has been reported by Kane and Lowy,[2] by Bowden,[3] who used aluminum chloride, and by McKenna and Sowa,[4] who employed boron trifluoride as the condensing agent.

In this communication it is shown that in the presence of hydrogen fluoride esters react with benzene to produce mainly alkylbenzenes. The reaction may be represented by the equation

$$RCOOR' + C_6H_6 = RCOOH + C_6H_5R''$$

where R″ may be the same as R′ or a rearranged form thereof. As it has been found[1] that acids can acylate aromatic compounds in the presence of hydrogen fluoride, the presence of ketones in the reaction products would be expected from a reaction of the liberated acid with either benzene or the alkylbenzene present. This actually proved to be the case, as in a number of experiments ketones were isolated in sufficient quantities to permit characterization. Bowden[3] in his study of this type of reaction using aluminum chloride, did not isolate any carbonyl compounds although he made a special effort to do so.

McKenna and Sowa[4] postulated that this type of alkylation proceeded through two stages, first, the formation of an olefin and an acid from the ester and second, the reaction of the olefin with benzene to give the alkylated benzene. An alternative mechanism, which they rejected, involved a metathesis between the ester and the aromatic compound. Rejection was based on the fact that esters of straight chain alcohols do not give normal alkylbenzenes. There is, however, another mechanism by which this reaction can occur. Hydrogen fluoride is an extremely powerful ionizing solvent. The ester may ionize to produce a positive alkyl ion and a negative acyl ion. This reaction would be assisted by the strong acid properties of the solvent, which would neutralize the acyl ion to form the carboxylic acid which in turn would further react with the solvent.[5] As the charge on the alkyl ion probably would not be localized, reaction would occur with the carbon atom which would result in the greatest reduction of free energy. A rearranged product could be formed.

$$RCO_2R' + HF = RCO_2H_2^+ + R'^+ + 2F^-$$

The fact that benzyl acetate will react with benzene to give, in the presence of hydrogen fluoride, diphenylmethane in yields of 75% of the theoretical seems to be strong evidence supporting the ionic rather than the olefin mechanism.

In accordance with the observations of previous investigators it was found that *n*-butyl acetate and *s*-butyl isobutyrate gave *s*-butylbenzene, isopropyl acetate gave isopropylbenzene, and *t*-butyl and benzyl acetates gave the corresponding alkylbenzenes.

Experimental

TABLE I

In every case one-third mole of ester and 400 cc. benzene were used. All boiling points are at 742 mm. unless otherwise noted.

Ester	G. HF	Time, hrs.	Product[6] % yield	Name	B. p., °C.	n^{20}
t-Butyl acetate	89	16	71	*t*-Butylbenzene	170–171	1.4921
t-Butyl acetate	169	16	73	*t*-Butylbenzene	72 at 32 mm.	1.4923
Isopropyl acetate	165	17	53	Isopropylbenzene	149–150	1.4911
n-Butyl acetate	180	17	60	*s*-Butylbenzene	170.5–171	1.4902
s-Butyl isobutyrate	90	17	56	*s*-Butylbenzene	170–171	1.4901
Benzyl acetate	70	15	75	Diphenylmethane	259–261	

The reactions were carried out in a copper bomb at steam-bath temperature in a manner reported previously.[1] All the acetates except *t*-butyl were made from the alcohol, acetic anhydride, and sodium acetate. *t*-Butyl acetate

(1) For previous paper in this series see THIS JOURNAL, **61**, 1795 (1939).

(2) Kane and Lowy, *ibid.*, **58**, 2605 (1936).

(3) Bowden, *ibid.*, **60**, 645 (1938).

(4) McKenna and Sowa, *ibid.*, **59**, 1204 (1937).

(5) Simons, *Chem. Rev.*, **8**, 213 (1931).

(6) The physical constants checked closely those reported in the summary by Ward and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 559 (1938).

was prepared according to the method of Norris and Rigby.[7] *s*-Butyl isobutyrate was made from the proper alcohol and acid using sulfuric acid as catalyst. The boiling points of the esters were *t*-butyl acetate 109–110°, isopropyl acetate 86–87°, *n*-butyl acetate 123.5–124°, *s*-butyl isobutyrate 141–142°, all at 734 mm., and benzyl acetate 105–105.5° (18 mm.).

The reaction of *t*-butyl acetate in which 169 g. of HF was used gave 3 g. of acetophenone, identified by means of its semicarbazone. The melting point was 198–199°, and when mixed with a known sample gave a melting point of 197–199°. Isopropyl acetate gave 4 g. of acetophenone, m. p. and mixed m. p. of the semicarbazone was 197–199°. A higher boiling ketonic fraction weighing 5 g. was also obtained. Its oxime melted at 68–69.5°. Widman[8] reports the melting point of *p*-isopropyl acetophenone oxime as 70–71°. When treated with semicarbazide in the usual manner a crystalline solid, m. p. 197°, was obtained. When mixed with acetophenone semicarbazone the m. p. was 169–175°.

Some higher boiling fractions were obtained in other experiments, but in quantities too small to permit positive identification.

To prove that the alkylbenzene obtained from *n*-butyl acetate and *s*-butyl isobutyrate was in both cases *s*-butylbenzene a diacetamino derivative was prepared. That of the *n*-butyl acetate melted at 188–189° and when mixed with the same derivative of the latter compound did not depress in melting point.

(7) Norris and Rigby, THIS JOURNAL, **54**, 2088 (1932).
(8) Widman, *Ber.*, **21**, 2226 (1888).

Summary

Hydrogen fluoride has been found to be an effective agent to alkylate benzene by means of esters. Reactions were carried out in a copper bomb at 80 to 100°. *t*-Butylbenzene, isopropylbenzene, and diphenylmethane were made from benzene and the acetates. *n*-Butyl acetate and *s*-butyl isobutyrate both gave secondary butylbenzene. Ketones also were formed in the reactions. Acetophenone was identified from those reactions in which acetates were used.

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The Isolation of Keturonic Acids as Crystalline Alkaloidal Salts[1]

BY J. P. HART AND M. R. EVERETT

In studies of the bromine oxidation of dilute solutions of more than 50 carbohydrates, Everett and Sheppard[2] have demonstrated the accumulation of keturonic acids. They found the yields of these substances to be related to the *cis–trans* structures of the original carbohydrates. Structural studies of the keturonic acids required their isolation in pure form. We are now reporting the isolation of alkaloidal salts of several keturonic acids, and the structures indicated by the properties of these salts. In order to avoid confusion the authors have named the keturonic acids as ketose derivatives.[3] Individual acids are differentiated by numbering the carboxyl carbon, the terminal carbon nearest the potential carbonyl being called one.[4]

Calcium *l*-sorbo-6-uronate has been isolated previously from *d*-glucose and *d*-gluconic lactone solutions oxidized by bromine,[5,6] and has been shown to be identical in properties with the calcium salts of Boutroux[7] and Kiliani.[8]

(1) Aided by a grant from the Research Appropriation of the University of Oklahoma Medical School.

(2) M. R. Everett and Fay Sheppard, University of Oklahoma Medical School Monograph, "Oxidation of Carbohydrates in Acid Solution," 1936.

(3) J. P. Hart and M. R. Everett, "A Suggested Nomenclature for Keturonic Acids," Abs. of Papers, 96th meeting of Am. Chem. Soc.

(4) The principal group of keturonic acids described in this paper are named as follows:

Keturonic acid	Parent aldohexoses
d-Sorbo-6-uronic	*l*-Glucose, *d*-Idose
l-Sorbo-6-uronic	*d*-Glucose, *l*-Idose
d-Fructo-6-uronic	*l*-Gulose, *d*-Mannose
l-Fructo-6-uronic	*d*-Gulose, *l*-Mannose
d-Tagato-6-uronic	*d*-Altrose, *l*-Galactose
l-Tagato-6-uronic	*l*-Altrose, *d*-Galactose
d-Psico-6-uronic	*l*-Allose, *d*-Talose
l-Psico-6-uronic	*d*-Allose, *l*-Talose

(5) E. W. Cook and R. T. Major, THIS JOURNAL, **57**, 773 (1935).
(6) J. P. Hart, Fay Sheppard, M. R. Everett, *J. Biol. Chem.*, **123**, lii (1938).
(7) L. Boutroux, *Compt. rend.*, **127**, 1225 (1907).
(8) H. Kiliani, *Ber.*, **55**, 2817 (1923).