

with a type K potentiometer and a copper-constantan thermocouple calibrated against a thermometer which had been calibrated by the Bureau of Standards. The molecular weights were determined by the vapor density method.

The measured vapor pressures could all be represented by an equation of the conventional form: $\log p = A/T + B$. The values of the constants, the average deviation of the observed from the calculated vapor pressures and the values of certain derived quantities and of the molecular weights are given in the table.

Compd.....	P(CH ₃) ₃	As(CH ₃) ₃	Sb(CH ₃) ₃
A.....	-1518	-1456	-1697
B.....	7.7627	7.3936	7.7068
Av. dev., %.....	1	1.5	<1
B. p., °C.....	37.8 ^a	49.5 ^b	78.5 ^c
ΔH_{vap} , cal.....	6943	6660	7760
Trouton's constant, cal./T	22.3	20.6	22.1
Mol. wt. { Obsd.....	75.5	119.0
{ Calcd.....	76.10	120.03

^a Previous recorded value, 40-42° (Cahours and Hofmann, *Ann.*, 104, 29 (1857)). ^b Previous recorded values, 51.9° (Renshaw and Holm, *THIS JOURNAL*, 42, 1468 (1920)); 51-53° (Dyke and Jones, *J. Chem. Soc.*, 2426 (1930)); 68-73° (G. Natta, *Chem. Zentr.*, 98, I, 416 (1927)); 74° (Paneth and Loleit, *J. Chem. Soc.*, 366 (1935)). ^c Previous recorded values, 82° (Paneth and Loleit, *ibid.*, 366 (1935)); 80.6° (Landolt, *J. prakt. Chem.*, 84, 329 (1861)).

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Hydrogen Fluoride as a Condensing Agent. XI. The Reaction of Alcohols and Ethers with Benzene¹

BY J. H. SIMONS AND S. ARCHER

Hydrogen fluoride has been found² to be an effective catalyst for alkylations in which aliphatic alcohols and ethers are used. We have now made additional studies of this reaction using primary, secondary, and tertiary alcohols and their ethers. Good yields were obtained with secondary and tertiary compounds at room temperature; but with primary compounds except benzyl alcohol and ether, 100° was necessary to obtain appreciable yields. *n*-Butyl alcohol and *n*-butyl ether both gave *s*-butylbenzene in about 20% yield. Benzyl alcohol and benzyl ether

(1) For the previous paper see Simons, Archer and Randall, *THIS JOURNAL*, 62, 485 (1940).

(2) (a) Calcott, Tinker and Weigmayr, *ibid.*, 61, 1010 (1939); (b) Simons, Archer and Passino, *ibid.*, 60, 2956 (1938).

both gave a 65-70% yield of diphenylmethane at room temperature. From the reaction of isopropyl alcohol with benzene in a mole ratio of about one to seven, four compounds were isolated: isopropylbenzene, 1,4-diisopropylbenzene, 1,2,4-triisopropylbenzene, and 1,2,4,5-tetraisopropylbenzene, in yields of 22.4, 14, 26, and 28%, respectively. The ether gave the same products in yields of 26, 24, 25, and 8%. *t*-Butyl alcohol and *t*-amyl alcohol reacted with benzene, when the mole ratios were about one to seven, to give about 40% monoalkylated and 50% dialkylated products.

Several items of interest are noted from the above experimental results. Alcohols react more readily, *i. e.*, give a good yield at lower temperature, than the corresponding chlorides. For example, secondary chlorides reacted very slowly to give low yields in a twenty-four hour reaction time at room temperature, whereas secondary alcohols or ethers gave high yields at the same temperature. Although the mechanism of the reaction is unknown, one fact is obvious and may be a contributing factor when it is known. When the chlorides are used, hydrogen chloride is evolved; and for reactions at atmospheric pressure its thermodynamic activity in the reaction mixture must equal that for the gas at one atmosphere. When alcohols or ethers are used, water is a product of the reaction; and it remains in solution in the hydrogen fluoride. Its activity in this solution is very much lower than liquid water at the same temperature. For certain mechanisms this difference would contribute to the driving force of the reaction.

The other point of interest lies in the fact that when aluminum chloride is used as the condensing agent, the chlorides react more readily than the alcohols. Reasoning from this and also from the fact that chlorides can be made from the alcohols by treatment with aluminum chloride, the formation of the chloride may be postulated as the first step in the reaction. As the ease of reaction is in the opposite order when hydrogen fluoride is used, the reaction in this case may proceed through a different mechanism.

The ease of reaction of benzyl alcohol is a strong argument against the hypothesis that an olefin is an intermediate in the reaction. Such a mechanism has been postulated by McKenna and Sowa³ for reactions between alcohols and benzene

(3) McKenna and Sowa, *ibid.*, 59, 470 (1937).

in which boron trifluoride was employed. The formation of mesitylene from toluene and methanol in the presence of aluminum chloride reported by Norris and Ingraham⁴ also supports this argument.

Calcott, Tinker, and Weinmayr^{2a} reporting condensation reactions catalyzed by hydrogen fluoride state, "Dibenzyl ether gave benzyl isocyclic compounds while benzyl alcohol polymerized to 1,2,3,4,5,6-hexaphenylcyclohexane." In our hands, both the alcohol and the ether reacted to give diphenylmethane when treated with benzene and hydrogen fluoride. At room temperature and at 100° alkylation rather than polymerization was the only reaction.

(4) Norris and Ingraham, *THIS JOURNAL*, **60**, 1421 (1938).

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Hydrogen Fluoride as a Condensing Agent. XII. Reactions of Methyl, Ethyl and Phenyl Compounds with Benzene and its Derivatives¹

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The use of hydrogen fluoride to promote alkylations has been shown in recent publications from this Laboratory. We are now reporting a study of its use in conjunction with a variety of reagents of potential value for methylation, ethylation, and phenylation. An alcohol, ester and halide were used in investigating each alkylation, and other reagents were used in some cases. Ethylation proceeded with a variety of substances, namely: ethyl alcohol, ethyl iodide, ethyl chlorocarbonate, ethyl acetate, and ethyl ether. Ethyl alcohol and benzene at 200° gave very high yields of ethyl- and diethylbenzenes, while the other reagents gave varying yields with benzene and toluene. Ethylene was tried at 0°, but although indications of the formation of ethylbenzene were observed no product was isolated; and the reaction was not attempted at higher temperatures. Methyl alcohol, methyl acetate, and methyl iodide failed, however, to react with benzene, toluene, or phenol to give methylated products at temperatures up to 200°. The reaction between phenol and methyl alcohol resulted in the formation of anisole, instead of alkylated phenol. Phenol, phenyl acetate, chlorobenzene, and diphenyl ether

(1) For the previous paper of this series see Simons and Archer, *THIS JOURNAL*, **62**, 1623 (1940).

all failed to give phenylated products, when treated with hydrogen fluoride and an aromatic compound at temperatures up to 200°. Acylation occurred when phenyl acetate was caused to react with benzene at 200° and some acetophenone and phenol were formed.

The formation of anisole led to the attempt at similar reactions. From a reaction between ethyl alcohol and phenol no phenetole was isolated although ethylation occurred, and phenol heated alone at 200° with hydrogen fluoride failed to give diphenyl ether. When diphenyl ether was heated alone with hydrogen fluoride at 210°, some splitting did occur as a small amount of phenol was isolated. The stability of the phenyl ethers is in marked contrast to the ease of reaction of the aliphatic ethers. Anisole has previously been made by the condensation of phenol and methyl alcohol using boron fluoride as the condensing agent.²

The failure of hydrogen fluoride to effect methylations is in contrast to the use of aluminum chloride for these reactions. Investigators³ have recently been able to methylate using methyl alcohol and aluminum chloride. Methylations by means of methyl chloride in the presence of aluminum chloride are well known.

Very little tar formation was experienced with reactions at 200° with the exception of a few experiments in which phenol was used as a reagent.

(2) Sowa, Hennion and Nieuwland, *ibid.*, **57**, 709 (1935).

(3) Norris and Ingraham, *ibid.*, **60**, 1421 (1938); Tsukervanik and Vikhrova, *J. Gen. Chem. (U. S. S. R.)*, **7**, 632-636 (1937).

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Saponins and Sapogenins. XV. The Interrelationship of Echinocystic Acid and Oleanolic Acid

BY DAVID TODD, G. H. HARRIS AND C. R. NOLLER

Previous work¹ has indicated that echinocystic acid is closely related to other triterpenoid sapogenins but no derived products identical with those from other triterpenoids have been obtained in which the carbon skeleton remained intact. It has now been found that Clemmensen reduction of norechinocystenone or norechinocystendione gives a hydrocarbon which is identical

(1) Bergsteinsson and Noller, *THIS JOURNAL*, **56**, 1403 (1934); Noller, *ibid.*, **56**, 1582 (1934); White and Noller, *ibid.*, **61**, 983 (1939).