in which boron trifluoride was employed. The formation of mesitylene from toluene and methanol in the presence of aluminum chloride reported by Norris and Ingraham[4] 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.

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[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 Derivatives[1]

BY J. H. SIMONS AND H. J. PASSINO

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 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. Investigators[3] 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.

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

[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 work[1] 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

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