

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

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

(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).

as determined by melting and mixed melting points, optical rotation and crystal form with oleanene III, obtained by Winterstein and Stein² from oleanolic acid. Inasmuch as the preparation of both hydrocarbons involves a Clemmensen reduction which Winterstein and Stein² have shown results in a molecular rearrangement in the case of oleanene III, and both hydrocarbons are decarboxylated derivatives, it is not possible to state that echinocystic acid and oleanolic acid have exactly the same skeletons but the possibility that such is the case is very likely.

Experimental

A solution of 0.132 g. of norechinocystenone in 250 cc. of 95% ethyl alcohol was added to 5 g. of amalgamated zinc. The mixture was boiled under a reflux condenser and a slow stream (2-3 bubbles per second) of dry hydrogen chloride was passed in for thirty-six hours. The solution was poured into an equal volume of water and evaporated to 50 cc. After dilution with water to 100 cc. the mixture was extracted with ether. The ether layer was washed with dilute hydrochloric acid, sodium hydroxide and water and dried over anhydrous sodium sulfate. After removal of the ether the residue was crystallized from methyl alcohol in which it is only slightly soluble, and then from acetone to a constant melting point of 224-225°; $[\alpha]^{25}_D +31.3 \pm 3^\circ$; $c = 1.408$ in toluene, $l = 0.5$ dm.

Anal. Calcd. for $C_{29}H_{48}$: C, 87.80; H, 12.20. Found: C, 87.79; H, 12.12.

The same product as determined by melting and mixed melting points was obtained on reducing norechinocystendione by the above procedure.

Oleanylene II and oleanene III were prepared from oleanolic acid³ according to the procedures of Winterstein and Stein.² The oleanene III was crystallized twice from glacial acetic acid and then from acetone until its melting point was 216.5-220.5°; $[\alpha]^{25}_D +30.7 \pm 3^\circ$; $c = 2.082$ in toluene, $l = 0.5$ dm.

A mixture with an equal part of the hydrocarbon obtained from norechinocystenone, m. p. 218-221.5°⁴, melted at 216.5-221°. The melting points of the mixture and of the two pure products were taken simultaneously in the same bath. Slow evaporation of solutions of the hydrocarbons from both sources gave well formed hexagonal plates which were indistinguishable under a lens. The properties of oleanene III recorded by Winterstein and Stein² are m. p. 225-226°; $[\alpha]^{20}_D +30.1$, $c = 1.76$ in chloroform.

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(2) Winterstein and Stein, *Ann.*, **502**, 223 (1933).

(3) We are indebted to Dr. C. N. Anderson of Lever Brothers Company, Cambridge, Mass., for a supply of crude barium oleanolate derived from clove oil residues.

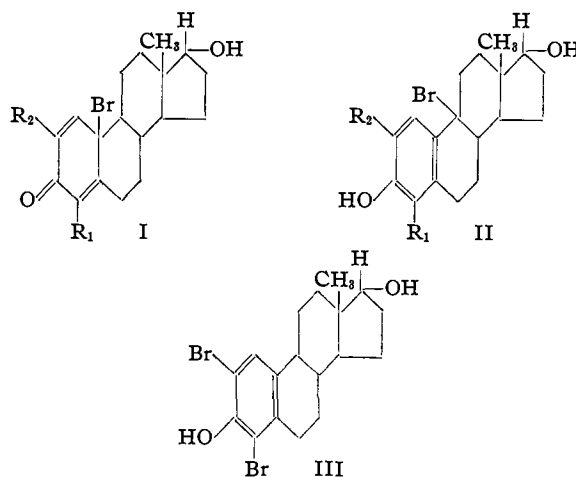
(4) The maximum melting point of 224-225° is obtained only with difficulty and large losses, so that the lower melting product was used for comparison purposes.

2,4-Dibromo- α -oestradiol

BY ROBERT BURNS WOODWARD

As evidenced by the investigations of Doisy,¹ Butenandt,² and Marrian,³ the phenolic sex hormones are extensively halogenated under the conditions obtaining in the determination of the iodine number with the Rosenmund-Kuhnmann reagent. The number of halogen atoms consumed by one mole of the hormone varied widely with the conditions. Although both Butenandt and Doisy isolated halogen-containing products, these were insufficiently characterized and until further investigation must be regarded as of equivocal nature. Only in the case of equilenin has a definitely pure halogen-substituted hormone been prepared, *viz.*, monobromoequilenin, prepared by Girard, *et al.*,⁴ likewise by the action of the Rosenmund-Kuhnmann reagent. On the other hand, Marrian and Haslewood³ found that the methyl ethers of the hormones consumed approximately one mole of halogen quite smoothly in the iodine number determinations, and this result was confirmed by the isolation of monobromoestrone methyl ether and monobromoestriol methyl ether.

In the course of a related investigation, we have found that α -oestradiol is converted smoothly and almost quantitatively into a dibromoestradiol on standing overnight in alcohol solution with the theoretical quantity of N-bromoacetamide. Since no halogen was removed on treatment with alcoholic silver nitrate or potassium hydroxide, the product was not 2-(or 4)-10-dibromo- $\Delta^{1,4}$ -oestra-



(1) Thayer, Levin and Doisy, *J. Biol. Chem.*, **91**, 791 (1931).

(2) Butenandt, Störmer and Westphal, *Z. physiol. Chem.*, **208**, 149 (1932).

(3) Marrian and Haslewood, *J. Soc. Chem. Ind.*, **51**, 277T (1932).

(4) Girard, Sandulesco, Fridenson and Rutgers, *Compt. rend.*, **195**, 981 (1932).