TABLE I

Ester	Grignard reagent	Product I	B.p., °C.	Yield, %	Product II	B.p., °C.	Yield, %
CF_3COOCH_3	Methyl + isopropyl	$CF_3CHOHCH_3$[a]	76–77	49			
$CF_3COOC_2H_5$	Methyl + isopropyl	$CF_3CHOHCH_3$[a]	76–77	60			
$C_2F_5COOCH_3$	Methyl + isopropyl	$C_2F_5CHOHCH_3$[b]	86–87.5	55	C_2F_5—$CHOHCH(CH_3)_2$[b]	108–109	10
$C_2F_5COOC_2H_5$	Methyl + isopropyl	$C_2F_5CHOHCH_3$[b]	86–87.5	55			
$C_3F_7COOCH_3$	Methyl + isopropyl	$C_3F_7CHOHCH_3$[c]	101–102	68	$C_3F_7CHOHCH(CH_3)_2$[g]	124–125	11
$C_3F_7COOC_2H_5$	Methyl + isopropyl	$C_3F_7CHOHCH_3$[c]	101–102	63			
CF_3COOCH_3	Ethyl + isopropyl	$CF_3CHOHC_2H_5$[d]	91–92	54	$CF_3CHOHCH(CH_3)_2$[h]	99–100	14
$C_2F_5COOCH_3$	Ethyl + isopropyl	$C_2F_5CHOHC_2H_5$[b]	99–100	48	$C_2F_5CHOHCH(CH_3)_2$[b]	108–109	17
$C_3F_7COOCH_3$	Ethyl + isopropyl	$C_3F_7CH(OH)C_2H_5$[e]	113–115	59	$C_3F_7CHOHCH(CH_3)_2$[g]	124–125	14
$C_3F_7COOCH_3$	Phenyl + isopropyl	$C_3F_7CHOHC_6H_5$[f]	94–95[i]	49	C_3F_7—$COH(C_6H_5)_2$[i]	147–148[i]	2

[a] F. Swarts, *Bull. soc. chim.*, **38**, 99 (1929). [b] E. T. McBee, J. F. Higgins and O. R. Pierce, THIS JOURNAL, **74**, 1387 (1952). [c] Calcd. for $C_5H_5F_7O$: C, 28.00; H, 2.34. Found: C, 28.02; H, 2.41. A small amount of $C_3F_7COH(CH_3)_2$ was formed. [d] See ref. 2. [e] E. T. McBee, O. R. Pierce and W. F. Marzluff, THIS JOURNAL, **75**, 1609 (1953). [f] Calcd. for $C_{10}H_7F_7O$: C, 43.50; H, 2.53. Found: C, 43.55; H, 2.58. [g] E. T. McBee, O. R. Pierce and M. C. Chen, THIS JOURNAL, **75**, 2324 (1953). [h] Calcd. for $C_5H_9F_3O$: C, 42.20; H, 6.32. Found: C, 42.11; H, 6.32. [i] Calcd. for $C_{16}H_{11}F_7O$: C, 55.00; H, 3.09. Found: C, 54.82; H, 3.14. [j] 10 mm.

were conducted with the individual Grignard reagent and may be attributed to the more bulky nature of the isopropyl group.

Experimental

A typical experiment is described as follows: A 2-liter, 3-necked flask was equipped with a mercury-sealed stirrer, an addition funnel, a reflux condenser and a calcium chloride drying tube. Six hundred ml. of anhydrous ether and 30.35 g. (1.25 moles) of magnesium turnings were placed in the reaction flask. A solution of 71 g. (0.5 mole) of methyl iodide, 92 g. (0.75 mole) of isopropyl bromide and an equal volume of ether was added slowly. After the addition was complete, the mixture was stirred for an additional hour. The Grignard reagent was cooled in an ice-bath and then a solution of 0.5 mole of the ester and an equal volume of anhydrous ether was added slowly. After the addition, the mixture was stirred overnight. The mixture was poured onto ice and then acidified with dilute hydrochloric acid. The ether was separated and the aqueous layer extracted several times with ether. The combined ether extracts were washed with several portions of a saturated sodium sulfite solution and then dried with anhydrous sodium sulfate. The ether solution was then rectified in a glass helix packed Todd distillation assembly.

The reaction products were identified by comparison of their physical properties to known compounds or, in the case of new materials, by analysis and infrared spectra determinations.

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Steroidal Sapogenins. X.[1] Qualitative Color Test for Pseudosapogenins

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The key step in transformation of steroidal sapogenins to pregnane derivatives is conversion to the so-called "pseudosapogenin" acetates,[2] *i.e.*, 20(22)-furostenol acetates. Because of the difficulty of crystallization of the products and the lack of significant detail in their infrared spectra, the extent of completion of the pseudomerization reaction may be followed, in a general way, by disappearance of the characteristic spiroketal absorption bands of the starting material,[3] rather than by the appearance of any properties characteristic of the product.

We have discovered that when the Tortelli–Jaffé color reaction[4,5] is applied to pseudosapogenins, a blue color is formed differing from the typical green color produced by ditertiary bridgehead ethylenic bonds or by olefins isomerizable to this type. The development of the blue color is apparently specific for the pseudosapogenin structure and does not occur with unsaturated steroids having double bonds at C_5–C_6, C_9–C_{11}, C_3–C_4, C_{16}–C_{17}, with dihydropseudosapogenins or with dihydrosapogenins. We have not tested pseudosapogenins with ditertiary, bridgehead ethylenic bonds.

The ultraviolet spectrum of the blue-colored material produced in the test shows maxima at 307 and 607 mμ (Beckman spectrophotometer). Bromine is transparent at 607 mμ at the concentrations used. Attempts to adapt the reaction for quantitative measurements were unsuccessful because the intensity of color developed reaches a maximum with about 1 mg. of steroid (in 10 ml. total volume) and is lower with quantities below and above this concentration. Color development does not follow the Beer–Lambert law. We have found the test to be particularly useful as an indication of completeness of reaction in pseudosapogenin transformations, *e.g.*, hydrogenation, oxidation, and the like.

Experimental

The color test was carried out in several ways. In the most sensitive method, the sample, 1 mg. of pseudosapogenin in 1 ml. of commercial C.P. chloroform, was diluted with 5 ml. of glacial acetic acid and mixed with 1 ml. of 0.1% bromine in chloroform. The mixture was underlayered with 0.1 ml. of 1% bromine in chloroform and after 30 minutes was diluted to 10 ml. with acetic acid and mixed.

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(2) R. E. Marker, *et al.*, see for example, THIS JOURNAL, **63**, 774 (1941); **69**, 2167 (1947).

(3) M. E. Wall, M. M. Krider, E. S. Rothman and C. R. Eddy, *J. Biol. Chem.*, **198**, 538 (1952).

(4) M. Tortelli and E. Jaffé, *Chem. Z.*, **39**, 14 (1915).

(5) I. M. Heilbron and F. S. Spring, *Biochem. J.*, **24**, 133 (1930).

For a rapid but less sensitive procedure, the Tortelli-Jaffé test as modified by Heilbron and Spring[5] gave a blue zone at a position intermediate between the liquid–liquid interface and the surface. The color developed within 5 minutes using amounts of pseudosapogenins over 0.3 mg. in the volume recommended. The compounds tested are listed below.

Positive color reaction:

20(22)-Furosten-26-ol
(3-desoxy-pseudosarsasapogenin)
(3-desoxy-pseudosmilagenin)
5α-20(22)-Furostene-3β,26-diol-12-one
(pseudohecogenin)
5,20(22)-Furostadiene-3β, 26-diol
(pseudodiosgenin)
20(22)-Furostene-2,3β,26-triol
(pseudomarkogenin)
(pseudosamogenin)
5α-20(22)-furostene-3β, 26-diol
(pseudotigogenin)

Negative color reaction:

16,22-Epoxy-20ξ-cholestane-3β,26-diol
(dihydropseudotigogenin)
16,22-Epoxy-20ξ, 22ξ-coprostane-3β,26-diol
(dihydropseudosarsasapogenin)
16,22-Epoxy-22b-coprostan-26-ol
(dihydro-3-desoxysarsasapogenin)
3β,16-Dihydroxy-allopregnan-20-one 16-(5-acetoxy-4-methyl valerate) (tigone)
22a-Spirosta-3,5-diene
5-Spirostenes and acetates
5α,22a-Spirost-9-(11)-en-3β-ol
(9-dehydrohecogenin)
Saturated sapogenins
Saturated 3-desoxysapogenins
3β,26-Dihydroxy-cholest-5-ene-16,22-dione
(kryptogenin)
3β,26-Dihydroxy-furost-16(23)-en-21-one
(fesogenin)
16-Pregnene-3,20-dione
16-Allopregnene-2α,3β-diol-20-one diacetate
16-Allopregnen-3β-ol-20-one acetate
Cholestan-3β-ol
Cholesterol
Stigmasterol
Progesterone

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Aromatic Alkylation. I. Intact Alkylation of Benzene and Toluene with Diisobutene

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Although Huston[1] and co-workers have reported a 22% yield of 2,2,4-trimethyl-4-phenylpentane (I) by alkylation of benzene with 2,4,4-trimethyl-2-pentanol in the presence of aluminum chloride, no one, as far as we know, has reported the synthesis of I from the corresponding olefin, diisobutene.

In the alkylation of benzene with di- and triisobutene in the presence of sulfuric acid at 0°, the polymers were reported[2] to undergo depolymerization resulting in the production of mono- and di-*t*-butylbenzene and hydrocarbons corresponding to tributylbenzenes.

Reaction of toluene with diisobutene in the presence of hydrogen fluoride at 0 to 6° produced mono- and di-*t*-butyltoluene.[3] Others have reported similar results with catalysts such as alkane sulfonic acid,[4] aluminum chloride[5] and aluminum chloride–nitropropane.[6]

Pines, *et al.*,[7] recently reported the synthesis of compound I from the corresponding *t*-octylphenol. After testing the stability of compound I in the presence of several alkylating catalysts, they concluded that in the alkylation of benzene with diisobutene, fragmentation products must result from depolymerization occurring prior to alkylation.

In the course of our study of the reaction of aromatics with scission-susceptible olefins we have found that the intact alkylation of toluene with diisobutene may be accomplished by using aluminum chloride–nitrobenzene as catalyst. Of the olefin charged, 84.7% was converted to *t*-octyltoluene (II). Products of fragmentation such as *t*-butyltoluene and di-*t*-butyltoluene were substantially absent. Higher isobutene polymers were not detected. Therefore the ultimate yield of II might well approach theoretical.

Comparison of the infrared spectrogram of II with the spectrogram which Dr. Pines very kindly supplied us for the corresponding *t*-octylbenzene, compound I, indicates that the octyl side chains of both compounds have the same configuration. Also by infrared analysis the ratio of para to meta substitution is 95/5. We have therefore assigned to the main portion of II the structure 2,2,4-trimethyl-4-(*p*-tolyl)-pentane.

With aluminum chloride–nitromethane the yield was slightly lower, but the product was contaminated either with polymer or with isomeric octyltoluenes showing evidence of rearrangements in the octyl side chain.

As expected, benzene was more difficult to octylate. Both of the above catalyst complexes effected some octylation. This was accompanied, however, by considerable fragmentation and polymerization. By infrared analysis it was estimated that not more than about 50% of the octylbenzene was compound I, the balance being other isomers resulting from skeletal isomerization.

Experimental

Alkylation Procedure.—The catalyst complex was prepared by dissolving the $AlCl_3$ (0.08–0.09 mole) in nitromethane or nitrobenzene. A mixture of 1 mole of diisobutene and 1 mole of aromatic was added at 25° with stirring to a solution of the catalyst complex in 4 moles of aromatic. The addition usually required 70 to 80 minutes, after which the reactants were stirred at 25° for an additional 10 to 15 minutes. Finally, the mixture was poured on ice and the organic layer separated, washed, dried and distilled. Select fractions were analyzed by infrared absorption. Results of typical experiments are given in Table I.

***p*-*t*-Octyltoluene, 2,2,4-Trimethyl-4-(*p*-tolyl)-pentane.**—The cut boiling 249° (760 mm.) from expt. 45 consisted of about 95% para and 5% meta isomers, m.p. −10°, $n^{25}D$ 1.4939, d^{20}_4 0.8736.

Anal. Calcd. for $C_{15}H_{24}$: C, 88.1; H, 11.9; mol. wt., 204.3. Found: C, 88.1; H, 11.8; mol. wt., 200.

(1) R. C. Huston, R. L. Guile, J. J. Sculati and W. N. Wasson, *J. Org. Chem.*, **6**, 252 (1941).

(2) V. N. Ipatieff and H. Pines, THIS JOURNAL, **58**, 1056 (1936).

(3) W. S. Calcott, J. M. Tinker and V. Weinmayr, *ibid.*, **61**, 1010 (1939).

(4) W. A. Proell and C. E. Adams, *Ind. Eng. Chem.*, **41**, 2217 (1949).

(5) E. Noelting, *Chim. et Ind.*, **6**, 719 (1921).

(6) L. Schmerling, *Ind. Eng. Chem.*, **40**, 2072 (1948).

(7) H. Pines, R. Myerholtz, Jr., and V. N. Ipatieff, THIS JOURNAL, **75**, 937 (1953).