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 $C_{16}H_{24}$: 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).

TABLE I

Expt. no.	41	24	25	40	45
Solvent, mole		Nitromethane		Nitrobenzene	
	0.21	0.92	0.08	0.29	0.31
Aromatic	Benzene	Toluene	Toluene	Benzene	Toluene
Products[a]					
t-Butyl-	6.7	15.5	24.9	4.3	..
p-*t*-Octyl	..	62.6	44.6	..	80.5
m-*t*-Octyl	..	...	4.9	..	4.2
Octyl-	28.2	8.4	18.3	0.6	..
Di-*t*-butyl	13.0	...	...	0.4	..
Dodecyl	..	...	9.2	..	..
C_{12}-[b]	28.0	...	...	0.9	..
Polymer	4.8	15.3	...	73.5	..
Olefin consumed	80.7	101.8	101.9	79.7	84.7

[a] Wt. % of diisobutene consumed ending up as substituent group or polymer. [b] Mixture of dodecyl, octyl-butyl, tributyl.

***p*-*t*-Octylbenzoic Acid, 4-(1,1,3,3-Tetramethylbutyl)-benzoic Acid.**—Oxidation of 8 g. of the *t*-octyltoluene with 12 g. of potassium permanganate in 65 g. of pyridine at 88° for 7 hours, following the general procedure of Nightingale and Janes,[8] yielded 4 g. of colorless platelets after recrystallization from isoöctane; m.p. after two recrystallizations, 158.5–159.5°.

Anal. Calcd. for $C_{15}H_{22}O$: C, 76.88; H, 9.46; neut. equiv., 234.3. Found: C, 76.87, 76.98; H, 9.52, 9.51; neut. equiv., 236, 236.6.

We have extended this study of the intact alkylation of aromatics to include various isobutene polymers and a variety of catalysts and operating conditions. A complete report of these results will be made at a later date.

(8) D. Nightingale and J. R. Janes, THIS JOURNAL, **66**, 155 (1944).

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Effect of Ultraviolet Light on Steroids during Paper Chromatography[1]

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Since the first description of the paper chromatographic separation and purification of corticosteroids[2] this technique has been rapidly adopted by many workers in the field.[3] Two of the difficulties often encountered in the application of this technique are the frequent inability to measure steroids quantitatively following chromatography, and to obtain from paper chromatograms samples of steroids (despite their apparent crystalline purity) completely free from contaminants which can best be described by their appearance in subsequent chromatograms of the sample in question, as highly polar material which does not migrate from the starting line. This latter problem is particularly noticeable in dealing with radioactive steroids containing carbon-14 (and has been observed by others working with C^{14}-desoxycorticosterone and progesterone[4]). The occurrence of this immobile material persists despite the distance the steroid has traversed from the starting line in earlier chromatograms, and its intensity has been related to the *interval of time between the removal of the chromatogram for drying and the subsequent elution* of the steroid. The two aspects of this problem have been investigated independently in these laboratories and the following preliminary observations are presented in order to acquaint workers employing these techniques with what is at best an aggravating phenomenon.

(1) Supported in part by Contract No. DA-49-007-MD-184, Medical Research and Development Board, Office of the Surgeon General, Department of the Army; and in part by a grant from the Division of Grants and Fellowships, National Institute of Health, U. S. Public Health Service.

(2) (a) A. Zaffaroni, R. B. Burton and E. H. Keutman, *Science*, **111**, 6 (1950); (b) R. B. Burton, A. Zaffaroni and E. H. Keutman, *J. Biol. Chem.*, **188**, 763 (1951).

(3) (a) D. Kritchevsky and M. Calvin, THIS JOURNAL, **72**, 4330 (1950); (b) O. Schindler and T. Reichstein, *Helv. Chim. Acta*, **34**, 108 (1951); (c) T. H. Kritchevsky and A. Tiselius, *Science*, **114**, 299 (1951); (d) I. E. Bush, *Biochem. J.*, **50**, 370 (1952); (e) R. Neher and A. Wettstein, *Helv. Chim. Acta*, **35**, 276 (1952); (f) C. D. Kochakian and G. Stidworthy, *J. Biol. Chem.*, **199**, 607 (1952); (g) L. R. Axelrod, *ibid.*, **201**, 59 (1953); (h) K. Savard, *ibid.*, **202**, 357 (1953).

Experimental

Effect of Ultraviolet Light on Testosterone-3-C^{14}.—Six milligrams of testosterone-3-C^{14} (49,000 c./min./mg.)[5] was chromatographed on a sheet of filter paper (8 × 50 cm.) in the solvent system ligroin–propylene glycol[2b] for 48 hours; the distribution of radioactivity and the area occupied by the testosterone are shown in Fig. 1a. After the usual interval (16–24 hours) allowed for drying in air, the area of the chromatogram containing the testosterone was cut out and eluted with methanol; the testosterone was reapplied to a second sheet of filter paper and chromatographed in ligroin–propylene glycol for 48 hours. Again after drying, the testosterone was located and the distribution of radioactivity determined; these are shown in Fig. 1b. The small amount of polar material at the starting line appeared in the expected manner. The chromatogram was exposed, on both sides, to the irradiation of an ultraviolet source (Mineralite, Ultraviolet Products, Pasadena, California) at a distance of 12 cm. for 2 hours. The area of the testosterone was then eluted and chromatographed on a third sheet of filter paper for 48 hours in ligroin–propylene glycol. The distribution of radioactivity in this chromatogram is shown in Fig. 1c, together with the colored areas which appeared when the strip was exposed to the Zimmermann reagent. As can be seen, there is a major increase in the amount of polar material at the starting line with a corresponding decrease in the area and radioactivity of the testosterone zone. Even more impressive is the appearance in serious concentration of at least *five* additional steroid areas, all of which gave positive (violet and blue) color reactions with the Zimmermann reagent. Interpretation of the location of these zones, as well as the colors they gave with the Zimmermann reagent[2b] suggest that the following reactions had occurred: saturation of the 4,5-double bond, or its migration from that position in conjugation with the 3-ketone, or both; formation of 17-ketosteroids (violet Zimmermann color) indicating oxidation of the 17β-hydroxyl group.

Recovery of Steroids from Irradiated Chromatograms.—In the following experiments 200 γ of steroid was applied to each of several 1-cm. strips of filter paper and chromatographed in ligroin–propylene glycol for the time required to move the steroid in question to approximately half the length of the paper strip (24 hours for testosterone, 16 hours for Δ^4-androstene-3,17-dione, 8 hours for progesterone). A completed chromatogram containing each steroid was dried in an air-oven at 60° for 30 minutes, while duplicate chromatograms were exposed to the Mineralite source of ultraviolet light for 2 hours. The steroid areas were then eluted with methanol and the absorption at 240 mμ was measured in methanol in the Beckman spectrophotometer. Correction was made in all these readings for absorbing material by the elution from each chromatogram of an area of paper equal to that occupied by the steroid being measured; this was accomplished by utilizing an eluate of the non-steroid area of the chromatogram as blank. The results are listed in Table I, along with the results obtained with cortisone after chromatography in toluene–propylene glycol[2b] for 96 hours.

Evidence for the destruction of the α,β-unsaturated ketone structure of the steroids by ultraviolet light was ob-

(4) R. D. H. Heard, private communication.

(5) Prepared by Dr. Marcel Gut.