557. *Interaction of 6-Acetyltetralin and Excess of Friedel–Crafts Ethylating Agent.*

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Whereas acylating agent attacks the alicycle of acyltetralins (I $\longrightarrow$ II; R′ = H), ethylating agent effects aromatic substitution giving ethyltetralins (I; R′ = Et). The latter compounds, with acylating agent, give the dihydronaphthalenes (II; R′ = Et), whereas with ethylating agent they give 2 : 5-diacyl-7-ethyl-1-methylindenes (V). These compounds are also given by the action of ethylating agent on 5-acyl-1-methylindanes (IV; R′ = H). The latter have been prepared by the cyclisation of 3-*p*-acetylphenyl-1-chlorobutane (III).

6-ACETYLTETRALIN (I; R = Me, R′ = H) cannot be acylated in the aromatic ring; reaction with excess of acetylating agent occurs at 70—100°, the temperature of decomposition of the agent, affording first 6-acetyl-1 : 2-dihydronaphthalene and finally 3 : 6-diacetyl-1 : 2-dihydronaphthalene (II; R = Me, R′ = H).[1] The behaviour of 7-acetyl-5-ethyltetralin (I; R = Me, R′ = Et) towards excess of acetylating agent seems to be similar, the product being 3 : 6-diacetyl-8-ethyl-1 : 2-dihydronaphthalene (II; R = Me, R′ = Et).[2]

Reaction of ethylating agent with acetyltetralin requires raised temperatures and, as in the nuclear ethylation of acetophenone and benzonitrile,[3] is most conveniently effected when the agent is formed *in situ* by the decomposition at about 100° of the diethyl ether–aluminium chloride complex :

$$\mathrm{Et_2O,AlCl_3 + AlCl_3 \longrightarrow EtCl,AlCl_3 + EtOAlCl_2}$$

This agent, in contrast to acylating agent, effects nuclear substitution; the product is mainly 7-acetyl-5-ethyltetralin (I; R = Me, R′ = Et). This compound gave benzene-1 : 2 : 3 : 5-tetracarboxylic acid by nitric acid oxidation and 1 : 3-diethylnaphthalene by Clemmensen reduction followed by catalytic dehydrogenation of the product, and was thereby identified. Thus, in accordance with earlier work, the alkylating agent is the more powerful agent of aromatic substitution.

In compounds (I; R′ = Et) only positions *ortho* to the carbonyl group are available for nuclear substitution and further ethylation must be expected to proceed with difficulty; in fact, reaction of the tetralin (I; R = Me, R′ = Et) with ethylating agent requires a temperature of about 140°; 2 : 5-diacetyl-7-ethyl-1-methylindene (V; R = Me) is the main isolable product. We suggest that ethylation occurs in the benzene ring affording an *o*-alkylacetophenone which, like other compounds of this type,[4] is deacylated by aluminium chloride–hydrogen chloride; the resulting acylating agent then reacts with the indane (IV; R = Me, R′ = Et), a product of rearrangement of the tetralin (I; R = Me, R′ = Et), to give the indene (V; R = Me). In accordance with this mechanism (*a*) interaction of the tetralin (I; R = Et, R′ = H) and ethylating agent gives the indene (V; R = Et), (*b*) the tetralin (I; R = Me, R′ = Et) is rearranged in the presence of fused aluminium chloride at 140°, and (*c*) interaction of ethylating agent and 5-acetyl-1-methylindane (IV; R = Me, R′ = H), which has been prepared by the cyclisation of 3-*p*-acetylphenyl-1-chlorobutane (III), gives the indene (V; R = Me).

That the tetralins (I) rearrange when R′ = Et but not when R′ = H is a further illustration that isomerisation and other reactions of aromatic compounds in the presence of aluminium and hydrogen chlorides occur the more readily the larger the number of alkyl substituents and the greater the overcrowding.

Like 2 : 5-diacetylindene (VI), which forms the deep red anion (VII), the indene (V; R = Me or Et) gives a red solution in ethanolic sodium hydroxide; however, whereas

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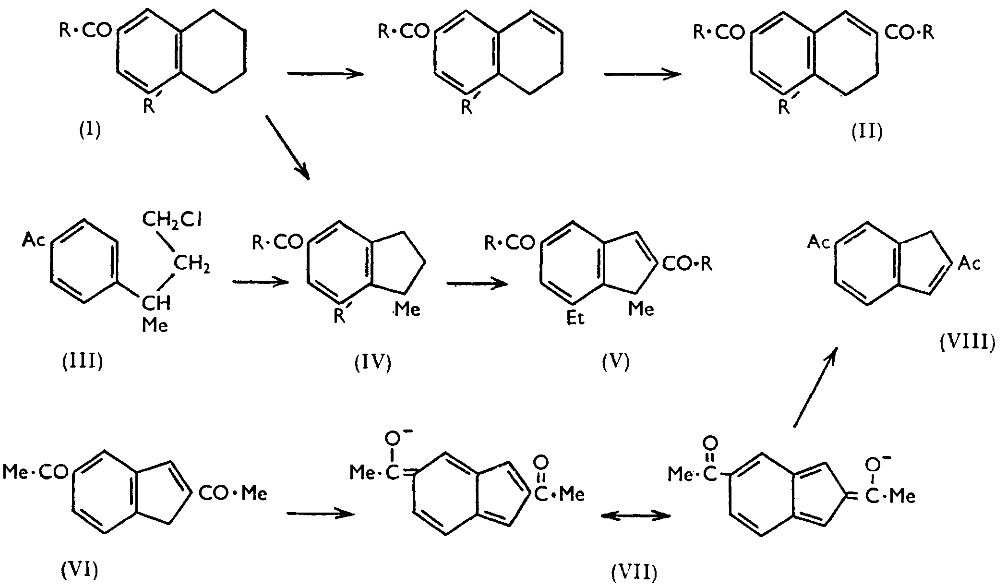
[1] Baddeley, Wrench, and Williamson, *J.*, 1953, 2110.

[2] See Experimental section.

[3] Baddeley, *J.*, 1949, S 229.

[4] Baddeley, *Quart. Reviews*, 1954, **8**, 355.

2 : 5-diacetylindene (VI) is rearranged to the 2 : 6-compound (VIII) in the presence of alkali, the indene (V) is not rearranged. Rearrangement of the latter similar to that of (VI ⟶ VIII) would bring the 1-methyl group into the plane of the benzene ring and is probably hindered by steric interaction of methyl and ethyl groups.



EXPERIMENTAL

Reactants.—6-Acetyltetralin, b. p. 155°/11 mm. (oxime,[5] m. p. 106°), and 6-propionyltetralin, b. p. 170°/13 mm. (semicarbazone,[6] m. p. 220°), were prepared in 75% yield by the Friedel–Crafts acylation of tetralin in ethylene chloride. They were recovered unchanged after fusion with aluminium chloride (3 mol.) at 140° for 3 hr. *5-Acetyl-1-methylindane* was prepared : A mixture of crotonic acid (86 g.) and aluminium chloride (280 g., 2 mol.) in benzene (400 c.c.) was saturated with dry hydrogen chloride and set aside at room temperature for 4 days. It gave β-phenylbutyric acid[7] (139 g., 85%), b. p. 168—170°/15 mm. This acid (85 g.) gave 3-phenylbutan-1-ol[8] (74 g., 92%), b. p. 132°/14 mm., by reduction with lithium aluminium hydride. The action of thionyl chloride (1·5 mol.) on the butanol gave the *chloride* (63 g., 83%), b. p. 108°/12 mm. (Found : Cl, 19·8. $C_{10}H_{13}Cl$ requires Cl, 21·1%). Acetylation[9] of the chloride (34 g.) then gave *3-p-acetylphenyl-1-chlorobutane* (32 g., 75%), b. p. 180—184°/12 mm. (Found : Cl, 16·7. $C_{12}H_{15}OCl$ requires Cl, 16·9%) [the *2 : 4-dinitrophenylhydrazone* separated from ethanol in red needles, m. p. 181° (Found : C, 55·8; H, 5·0; N, 14·2. $C_{18}H_{19}O_4N_4Cl$ requires C, 55·4; H, 4·9; N, 14·4%)]. Fusion of the chloro-ketone (20 g.) with aluminium chloride (68 g.) and sodium chloride (7 g.) at 100° for an hour gave *5-acetyl-1-methylindane* (10 g., 61%), b. p. 142—145°/11 mm. (Found : C, 82·5; H, 8·0. $C_{12}H_{14}O$ requires C, 82·8; H, 8·0%) [*semicarbazone*, m. p. 196° (Found : C, 67·1; H, 7·7; N, 17·7. $C_{13}H_{17}ON_3$ requires C, 67·6; H, 7·4; N, 18·2%)].

6-Acetyltetralin and Ethylating Agent.—(i) *At* 100°. A mixture of the ketone (87 g.), diethyl ether (37 g.), and aluminium chloride (210 g.) was heated at 100° for 3 hr., and then decomposed with ice. The product was worked up in the usual way and gave 6-acetyltetralin (20 g.) and a fraction, b. p. 120—130°/0·8 mm. (52 g.), which was mainly *7-acetyl-5-ethyltetralin*; this separated from light petroleum in needles, m. p. 35° (Found : C, 83·6; H, 8·6. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%), gave a *semicarbazone*, needles (from ethanol), m. p. 163° (Found : C, 69·8; H, 8·5; N, 16·2. $C_{15}H_{21}ON$ requires C, 69·5; H, 8·1; N, 16·2%), and was identified as

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[5] Scharwin, *Ber.*, 1902, **35**, 2511.
[6] Barbot, *Bull. Soc. chim. France*, 1930, **47**, 1314.
[7] Tiffeneau, *Compt. rend.*, 1904, **138**, 987.
[8] Cohen, Marshall, and Woodman, *J.*, 1915, 901.
[9] Baddeley and Williamson, *J.*, 1953, 2120.

follows: (*a*) A sample (0·4 g.), nitric acid (4 c.c.; *d* 1·4), and water (6 c.c.) were heated at 180° for 6 hr. and gave benzene-1 : 2 : 3 : 5-tetracarboxylic acid (tetramethyl ester, m. p. and mixed m. p. 109—110°). (*b*) A sample (1 g.) was reduced by Clemmensen's method and gave 5 : 7-diethyltetralin which was dehydrogenated by palladised charcoal (30%; 1 g.) at 250° to 1 : 3-diethylnaphthalene (picrate,[10] m. p. 102°).

(ii) *At* 140°. A mixture of 6-acetyltetralin (87 g.), diethyl ether (46 g.), and aluminium chloride (280 g.) effervesced vigorously at 120—130° evolving hydrogen chloride, ethyl chloride, and ethane. After 3 hr. at 135—140° the mixture was decomposed with ice and gave unsaturated ketonic material (23 g.), b. p. 134—200°/12 mm., and 2 : 5-*diacetyl*-7-*ethyl*-1-*methylindene* (24 g.), b. p. 185—190°/0·1 mm., long needles, m. p. 150° (from ethanol) (Found: C, 78·9; H, 7·3%; *M*, 236 in nitrobenzene. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%; *M*, 242). Similarly, this compound (2·5 g.) was prepared from 7-acetyl-5-ethyltetralin (8·5 g.) and 5-acetyl-1-methylindane (8·5 g.) severally. It was obtained in better yield (15 g.) when a mixture of 6-acetyltetralin (44 g.), acetyl chloride (20 g.), diethyl ether (19 g.), and aluminium chloride (175 g.) was heated at 130° for 3 hr.

Reactions of 2 : 5-*diacetyl*-7-*ethyl*-1-*methylindane.* (i) It gave a *dioxime*, m. p. 235° (decomp.) (Found: C, 70·1; H, 7·5; N, 10·2. $C_{16}H_{20}O_2N_2$ requires C, 70·5; H, 7·4; N, 10·3%). (ii) Oxidation with dilute nitric acid gave benzene-1 : 2 : 3 : 5-tetracarboxylic acid (tetramethyl ester, m. p. and mixed m. p. 109°). (iii) Oxidation with permanganate in anhydrous acetone at 0° gave 2 : 5-*diacetyl*-3-*ethylbenzoic acid*, long needles, m. p. 115° (from ligroin) (Found: C, 67·0; H, 6·2%; equiv., 235. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%; equiv., 234). This acid gave a 2 : 4-dinitrophenylhydrazone and with hypochlorite solution gave chloroform and 6-*ethylbenzene*-1 : 2 : 4-*tricarboxylic acid*, m. p. 203° (decomp.) (Found: C, 55·0; H, 4·3%; equiv., 84·8. $C_{11}H_{10}O_6$ requires C, 55·5; H, 4·2%; equiv., 79·3). (iv) With Adams's catalyst in glacial acetic acid, the compound absorbed hydrogen (5 mol.) affording a hydrocarbon which did not evolve hydrogen when heated with palladised charcoal at 260°. (v) It dissolved in ethanolic sodium hydroxide solution to give a deep red solution, and was recovered by acidification.

6-*Propionyltetralin and Ethylating Agent.*—A mixture of the tetralin (47 g.), diethyl ether (23 g.), and aluminium chloride (140 g.) was heated first at 95—100° and then for 3 hr. at 135—140°, giving unsaturated ketonic material (17 g.), b. p. 130—200°/12 mm., and 7-*ethyl*-1-*methyl*-2 : 5-*dipropionylindene* (15 g.), b. p. 190—200°/0·1 mm., needles, m. p. 119° (from light petroleum) (Found: C, 79·9; H, 8·0. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·1%). It gave a *dioxime*, m. p. 170° (Found: C, 72·3; H, 8·0; N, 9·7. $C_{18}H_{24}O_2N_2$ requires C, 72·0; H, 8·0; N, 9·3%), slowly decolorised bromine in carbon tetrachloride and aqueous permanganate, formed a deep red solution in ethanolic sodium hydroxide, and gave benzene-1 : 2 : 3 : 5-tetracarboxylic acid when oxidised with dilute nitric acid. Its ultraviolet absorption spectrum is the same as that of 2 : 5-diacetyl-7-ethyl-1-methylindene and similar to that of 2 : 5-diacetylindene [1] (see Table).

Acetylation of 7-*Acetyl*-5-*ethyltetralin.*—This compound (4·0 g.) with aluminium chloride (4·2 g., 1·5 mol.) in methylene chloride (25 c.c.) was added to acetyl chloride (4·0 g., 20 mol.) and aluminium chloride (5·0 g., 3 mol.) in methylene chloride (25 c.c.). The solvent was volatilised under reduced pressure and the residue was heated at 100° for 2 hr. The mixture was decomposed with ice and the organic product was isolated in the usual manner. It contained a fraction (2·0 g.), b. p. 195—200°/0·1 mm., needles, m. p. 108° (from light petroleum) (Found: C, 79·4; H, 7·1. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%), which is probably 3 : 6-*diacetyl*-8-*ethyl*-1 : 2-*dihydronaphthalene.* Its ultraviolet absorption spectrum resembles that of 3 : 6-diacetyl-1 : 2-dihydronaphthalene [1] (see Table). Both compounds slowly decolorise solutions of aqueous permanganate and bromine in carbon tetrachloride, and their solutions in ethanolic sodium hydroxide are colourless.

Ultraviolet absorption spectra (*by Dr. A. R. Thompson*).

	$\lambda_{max.}$, Å.	$\varepsilon_{max.}$	$\lambda_{max.}$, Å.	$\varepsilon_{max.}$
2 : 5-Diacetylindene (VI)	2950	22,000	2550	23,000
2 : 5-Diacetyl-7-ethyl-1-methylindene (V; R = Me)	2945	16,500	2570	18,500
7-Ethyl-1-methyl-2 : 5-dipropionylindene (V; R = Et)	2945	16,800	2590	18,300
3 : 6-Diacetyl-1 : 2-dihydronaphthalene (II; R′ = H)	3000	16,600	2600	32,500
3 : 6-Diacetyl-8-ethyl-1 : 2-dihydronaphthalene (II; R′ = Et)	3000	16,600	2610	21,000

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[10] Arnold and Barnes, *J. Amer. Chem. Soc.*, 1944, **66**, 960.