263. *The Interaction of Decalin and Friedel–Crafts Acetylating Agent.*

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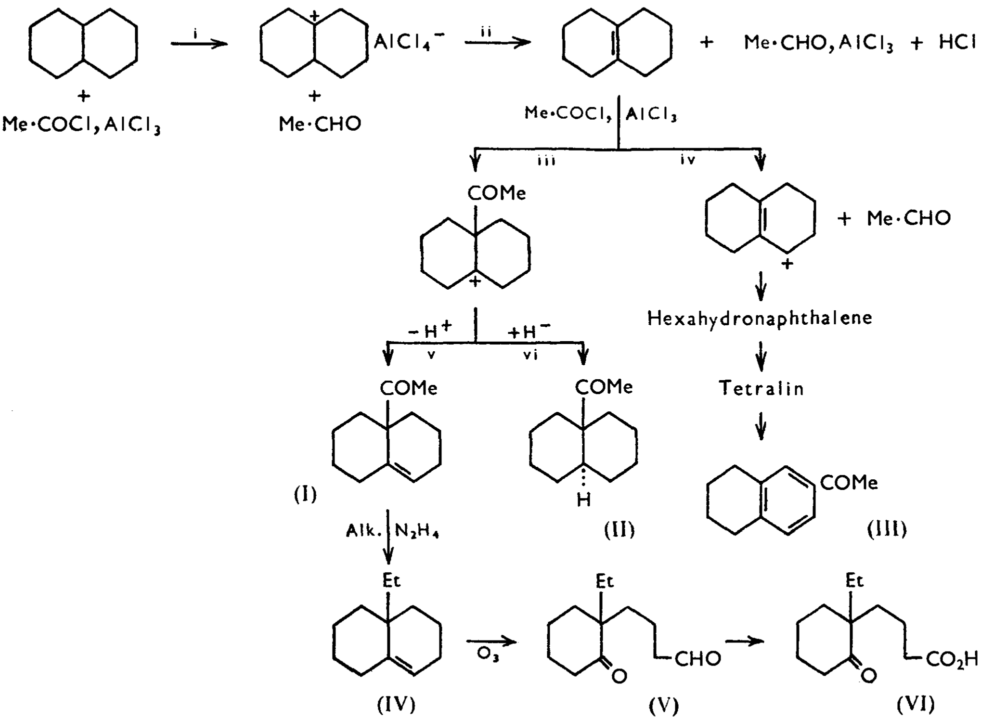
In methylene or ethylene chloride at room temperature, and in the presence of excess of aluminium chloride, decalin and acetyl chloride provide 9-acetyl-*trans*-decalin, 10-acetyl-$\Delta^{1:9}$-octahydronaphthalene, 6-acetyltetralin, and a hydroxy-ketone $C_{12}H_{20}O_2$, m. p. 107—108°, which will be discussed in a further communication. These compounds are obtained also by interaction of $\Delta^{9:10}$-octalin and the acetylating agent.

Decalin readily reacts with the acetyl chloride–aluminium chloride complex at room temperature; the best yields of 10-acetyl-$\Delta^{1:9}$-octahydronaphthalene (I) and 9-acetyl-*trans*-decalin (II) were obtained when a mixture of decalin (3·6 moles), aluminium chloride (6 moles), acetyl chloride (4 moles), and methylene chloride (700 c.c.) was kept at room temperature for two days and then added to water. Fractional distillation gave a mixture of ketones (I) and (II), b. p. 120—125°/15 mm., in 50% yield, and 6-acetyltetralin (III), b. p. 130—135°/15 mm., in 22% yield. Ketone (III) was identified by its 2 : 4-dinitrophenylhydrazone and semicarbazone, and by oxidation to tetralin-6-carboxylic acid. Separation of ketones (I) and (II) was facilitated by the fact that, the carbonyl group of the former being less hindered sterically, the former provides a semicarbazone under conditions which leave the latter unchanged. Thus the mixture was shown to consist of (I) 75% and (II) 25%.



Identifications.—Oxidation of 9-acetyl-*trans*-decalin (II), first with selenium dioxide and then with alkaline hydrogen peroxide, gave *trans*-decalin-9-carboxylic acid, m. p.

134°. This acid contained no terminal methyl group and was dehydrogenated to naphthalene, and its acid chloride, like other tertiary acid chlorides, evolved carbon monoxide when added to a mixture of benzene and aluminium chloride. The other product was a hydrocarbon $C_6H_5{\cdot}C_{10}H_{17}$. Catalytic hydrogenation of 10-acetyl-$\Delta^{1:9}$-octahydronaphthalene gave 9-acetyl-*trans*-decalin: identification of the octahydro-compound involved reduction by lithium aluminium hydride to the corresponding secondary alcohol and preparation of its α-naphthylurethane, m. p. 162°. Wolff–Kishner reduction of the octahydro-ketone (I) gave the hydrocarbon (IV) from which the keto-aldehyde (V) was obtained by ozonolysis and the keto-acid (VI) by further oxidation with alkaline hydrogen peroxide.

In the annexed scheme, which is now proposed, reaction (i) involves transfer of hydride ion from a decalin molecule to an acetyl cation and together with step (ii) gives acetaldehyde, hydrogen chloride, and 9 : 10-octalin. This octalin was not isolated, but it is presumably an intermediate since, when added to the acetylating agent, it gave a mixture of ketones (I), (II), and (III). Apparently, 9 : 10-octalin can be dehydrogenated [reaction (iv)] to tetralin which is acetylated, or it can combine with an acyl cation [reaction (iii)], forming a carbonium ion which can give the product (I) by losing a proton [reaction (v)] or the product (II) by gaining a hydride ion [reaction (vi)].

The products of interaction of decalin and the Friedel–Crafts acetylating agent in the presence of excess of acetyl chloride are different from those of interaction in the presence of excess of aluminium chloride and throw light on the course of the interaction. Further discussion of the mechanism is therefore postponed.

EXPERIMENTAL

Interaction of Decalin, Acetyl Chloride, and Aluminium Chloride.—After many experiments the following procedure was found to give the highest yields of the required fraction, b. p. 120—125°/15 mm. A mixture of decalin (500 g.), anhydrous aluminium chloride (840 g.), acetyl chloride (320 g.) and methylene chloride (700 c.c.) was kept at room temperature for 2 days and then poured on ice and dilute hydrochloric acid. The methylene chloride layer was separated, dried (K_2CO_3), and distilled, and gave a fraction (259 g.), b. p. 118—135°/15 mm. Repeated fractional distillation gave fractions (i) (175 g.), b. p. 120—125°/15 mm., and (ii) (75 g.), b. p. 130—135°/15 mm. The latter was mainly 6-acetyltetralin: it gave a 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 235° (Found: C, 60·9; H, 5·4; N, 16·6. Calc. for $C_{18}H_{18}O_4N_4$: C, 61·2; H, 5·1; N, 15·8%), a semicarbazone, m. p. and mixed m. p. 236° (Found: C, 67·5; H, 7·3; N, 18·3. Calc. for $C_{13}H_{17}ON_3$: C, 67·5; H, 7·4; N, 18·2%), and, by hypochlorite oxidation, tetralin-6-carboxylic acid, m. p. and mixed m. p. 153° (Found: C, 75·4; H, 6·7%; equiv., 172. Calc. for $C_{11}H_{12}O_2$: C, 75·0; H, 6·8%; equiv., 176). Fraction (i) very slowly deposited a solid *substance* (*ca.* 5 g.) which crystallized from light petroleum in needles, m. p. 107—108° (Found: C, 73·5; H, 10·2. $C_{12}H_{20}O_2$ requires C, 73·6; H, 10·2%), gave a 2 : 4-dinitrophenylhydrazone, a *semicarbazone*, m. p. 238° (Found: C, 61·2; H, 9·1; N, 16·6. $C_{13}H_{23}O_2N_3$ requires C, 61·6; H, 9·1; N, 16·6%), and an *α-naphthylurethane*, m. p. 162° (Found: C, 75·9; H, 7·3; N, 3·9. $C_{23}H_{27}O_3N$ requires C, 75·6; H, 7·4; N, 3·8%). Fraction (i) (47 g.), semicarbazide hydrochloride (74 g.), and potassium acetate (94 g.) in water (280 c.c.) and ethanol (235 c.c.) were refluxed for 2 hr. A small precipitate, m. p. 270° (decomp.) (Found: C, 19·7; H, 4·9; N, 41·8%), was separated and discarded and the filtrate was poured into water (1 l.). The oily precipitate thus obtained was isolated and, by extraction with boiling light petroleum, separated into a *semicarbazone*, m. p. 254° (45 g.) after recrystallisation from dilute ethanol (Found: C, 66·3; H, 8·9; N, 17·4. $C_{13}H_{21}ON_3$ requires C, 66·3; H, 8·9; N, 17·9%), and an oil (11 g.), b. p. 122—125°/15 mm. (Found: C, 80·4; H, 11·3. $C_{12}H_{20}O$ requires C, 80·0; H, 11·1%).

Identification of the oil. It was shown to be *9-acetyl-*trans*-decalin.* It did not decolorise bromine in carbon tetrachloride or aqueous potassium permanganate solution. A mixture of the oil (7·2 g.) and lithium aluminium hydride (3·2 g.) in dry ether (125 c.c.) was refluxed for 3 hr. and poured on ice and dilute sulphuric acid; the ethereal layer was separated, dried (K_2CO_3), and distilled, and gave *9-1′-hydroxyethyldecalin* (*ca.* 7 g.), b. p. 136—138°/15 mm. (Found:

C, 79·2; H, 11·9. $C_{12}H_{22}O$ requires C, 79·1; H, 12·1%), which formed an *α-naphthylurethane* which crystallised from ligroin in prisms, m. p. 162° (Found: C, 78·95; H, 8·1; N, 3·9. $C_{23}H_{29}O_2N$ requires C, 78·6; H, 8·3; N, 4·0%).

A mixture of the oil (2 g.) and selenium dioxide (1 g.) in dioxan (35 c.c.) and water (0·5 c.c.) was refluxed for 4 hr. It was freed from selenium by filtration, poured into water (100 c.c.), and extracted with chloroform (3 × 30 c.c.). The extracts were dried (Na_2SO_4), the solvent was removed, and the residue, in ethanol (100 c.c.), was treated with hydrogen peroxide (100-vol.; 10 c.c.) and 8% sodium hydroxide solution (15 c.c.) at 70° for 30 min. Removal of ethanol by distillation, and acidification of the residue, gave an oil which was extracted with ether (2 × 20 c.c.). Acidification of sodium hydrogen carbonate extracts of the ethereal solution gave prisms, m. p. 132—134° after recrystallisation from light petroleum (Found: C, 73·0; H, 9·5%; equiv., 170. Calc. for $C_{11}H_{18}O_2$: C, 72·5; H, 9·9%; equiv., 180), of *trans*-decalin-9-carboxylic acid (Dauben, Tweit, and Maclean [1] report m. p. 133—134°).

This acid (10 g.) was refluxed with thionyl chloride (30 c.c.) for 1 hr. Distillation of the product gave the acid chloride (8 g.), b. p. 115—118°/15 mm. This chloride in benzene (10 c.c.) was gradually added with stirring to a suspension of finely powdered aluminium chloride (6 g.) in benzene (30 c.c.). A vigorous reaction with evolution of hydrogen chloride and carbon monoxide ensued and the conventional working up gave an oil, b. p. 158—164°/15 mm., which was added to a mixture of acetyl chloride (2 g.) and aluminium chloride (3 g.) in methylene chloride (10 c.c.). The resulting acetyl derivative gave a *semicarbazone*, m. p. 196° (Found: C, 72·5; H, 8·4; N, 13·2. $C_{19}H_{27}ON_3$ requires C, 72·8; H, 8·6; N, 13·4%), and, therefore, was the product of acetylation of a hydrocarbon $C_6H_5{\cdot}C_{10}H_{17}$.

A mixture of the acid (0·5 g.) and 10% palladium–charcoal (0·5 g.) was heated at 220—240° for 48 hr. Carbon dioxide was liberated at 100°, and hydrogen (354 c.c. at 20°) was subsequently evolved. Naphthalene, m. p. and mixed m. p. 80°, condensed on the cooling thimble and gave a picrate of m. p. and mixed m. p. 149°.

Identification of the semicarbazone, m. p. 254°. Its hydrolysis with phthalic acid gave an oil, b. p. 120—122°/15 mm., in quantitative yield (Found: C, 80·4; H, 10·4. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%), which was *10-acetyl-*$\Delta^{1:9}$*-octalin*. Over palladium–charcoal at room temperature it absorbed 1 mol. of hydrogen and gave a saturated ketone which did not give a semicarbazone but was reduced by ethereal lithium aluminium hydride to 9-1′-hydroxyethyl-*trans*-decalin, b. p. 136—138°/15 mm. (Found: C, 79·2; H, 11·9. Calc. for $C_{12}H_{22}O$: C, 79·1; H, 12·1%), which gave an α-naphthylurethane, m. p. and mixed m. p. 162°. Reduction of the unsaturated ketone by lithium aluminium hydride gave *10-1′-hydroxyethyl-*$\Delta^{1:9}$*-octalin*, b. p. 135—136°/15 mm. (Found: C, 79·5; H, 11·1. $C_{12}H_{20}O$ requires C, 80·0; H, 11·1%) [*α-naphthylurethane*, m. p. 136° (Found: C, 79·3; H, 7·6; N, 4·3. $C_{23}H_{27}O_2N$ requires C, 79·1; H, 7·7; N, 4·0%)].

The unsaturated ketone (25 g.), 85% hydrazine hydrate solution (37·5 c.c.), and potassium hydroxide (52·5 g.) in diethylene glycol (375 g.) were refluxed for 4 hr. and gave a product (16 g.), b. p. 90—95°/15 mm., which did not form a semicarbazone or 2 : 4-dinitrophenylhydrazone and decolorised only 50% of the amount of bromine (in carbon tetrachloride) calculated for 10-ethyl-$\Delta^{1:9}$octalin.

Ozone was passed through a solution of the product (4·5 g.) in water (3 c.c.) and glacial acetic acid (12 c.c.) at 0° for 2·5 hr., and gave 4-(1-ethyl-2-oxo*cyclo*hexyl)butanal (V) as an oil (2 g.) which afforded an orange-yellow *bis*-2 : *4-dinitrophenylhydrazone*, m. p. 184° (Found: C, 51·4; H, 5·0; N, 19·7. $C_{24}H_{28}O_8N_8$ requires C, 51·8; H, 5·0; N, 20·1%).

Ozone was passed through another sample of the product (2 g.) in ethyl acetate (10 c.c.) for 1·5 hr. and gave an oil, b. p. >80°/15 mm., which was added to a mixture of 2N-sodium hydroxide (8 c.c.) and Merck's "Perhydrol" (15 c.c.); the mixture was warmed until the evolution of oxygen was complete. The alkali-soluble 4-(1-ethyl-2-oxo*cyclo*hexyl)butanoic acid was precipitated by addition of concentrated hydrochloric acid as an oil which gave an orange 2 : *4-dinitrophenylhydrazone*, m. p. 215° (Found: C, 55·0; H, 6·3; N, 14·5. $C_{18}H_{24}O_6N_4$ requires C, 55·1; H, 6·1; N, 14·3%).

Interaction of $\Delta^{9:10}$*-Octalin, Acetyl Chloride, and Aluminium Chloride.*—The octalin (8·4 g.) in methylene chloride (20 c.c.) was slowly added to a cooled mixture of aluminium chloride (9 g.) and acetyl chloride (10 g.) in methylene chloride (20 c.c.); there was a vigorous reaction with evolution of hydrogen chloride. After 10 min., the mixture was worked up in the usual way and gave the same products as were obtained from decalin, *i.e.*, the hydroxy-ketone,

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[1] Dauben, Tweit, and Maclean, *J. Amer. Chem. Soc.*, 1955, **77**, 48.

$C_{12}H_{20}O_2$, m. p. and mixed m. p. 107—108°, 10-acetyl-$\Delta^{1:9}$-octalin (semicarbazone, m. p. and mixed m. p. 254°), 9-acetyl-*trans*-decalin [identified by the α-naphthylurethane (m. p. and mixed m. p. 162°) of the alcohol obtained by lithium aluminium hydride], and 6-acetyltetralin (semicarbazone, m. p. and mixed m. p. 236°).

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