The Effect of Bond Structure on the Baker–Venkataraman Transformation of Acetylanisoyloxyindanes and Benzoyloxytetrahydroacetonaphthones.

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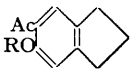
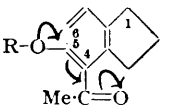
Further work on the Baker–Venkataraman transformation in the indane series is described (see Nowlan, Slavin, and Wheeler, *J.*, 1950, 340). A study of this reaction applied to *vic.*-benzoyloxytetrahydroacetonaphthones supports the view that the 1 : 2-bond in 5 : 6 : 7 : 8-tetrahydronaphthalene derivatives has a higher order than the 2 : 3-bond. The existence of steric strain in the acetyl group of 5 : 6 : 7 : 8-tetrahydro-2-hydroxy-1-acetonaphthone is demonstrated and its effects are discussed.

Nowlan, Slavin, and Wheeler (*J.*, 1950, 340) suggested on the basis of experiments with *vic.*-aroyloxyacetonaphthones that the Baker–Venkataraman transformation could be employed to study the bond structures of certain aromatic compounds. An advantage of using this reaction is that neither the aromatic bond nor the terminal carbon atoms of that bond are directly involved, as with other reactions (*e.g.*, Claisen rearrangement or ozonisation) used to study bond structure. Nowlan *et al.* (*loc. cit.*) showed that 5-acetyl-6-benzoyloxyindane (I*a*) rearranged to form the corresponding diketone, 5-benzoylacetyl-6-hydroxyindane more rapidly than 4-acetyl-5-benzoyloxyindane (II*a*) yields 4-benzoylacetyl-5-hydroxyindane. This result has now been confirmed by a study of 5-acetyl-6- and 4-acetyl-5-*p*-anisoyloxyindane (I*b* and II*b*); the transformation takes place more readily across the 5 : 6- than the 4 : 5-bond. These results suggest that the 5 : 6 bond in the indane derivatives studied is of a lower order than the 4 : 5-bond. The mobile π electrons in a double bond facilitate ester-type neutralisation of the carbonyl group in the

(I*a*; R = Bz)
(I*b*; R = *p*-MeO·C$_6$H$_4$·CO)
(I*c*; R = H)

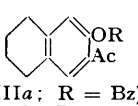




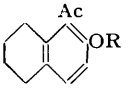
(II*a*; R = Bz)
(II*b*; R = p-MeO·C$_6$H$_4$·CO)
(II*c*; R = H)

acetyl radical. This hinders the Baker–Venkataraman transformation, which is to be regarded as a base-catalysed intramolecular condensation of the Claisen type (see II*a*, and Nowlan *et al.*, *loc. cit.*). The same conclusion with regard to bond order follows also from Wibaut and de Jong's ozonisation studies (*Bull. Soc. chim. France*, 1950, 996) and from Lothrop's results (*J. Amer. Chem. Soc.*, 1940, **62**, 132) on the Claisen rearrangement in indane compounds. It agrees, too, with the bond structure proposed for indane by Berthier and Pullman (*Bull. Soc. chim. France*, 1950, 88),* and is not contradicted by some recent infrared studies on indane derivatives by Hunsberger, Lednicer, Gutowsky, Bunker, and Taussig (*J. Amer. Chem. Soc.*, 1955, **77**, 2466).

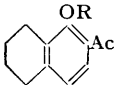
Transformation of Tetralin Derivatives.—The study has been extended to tetralin derivatives, and the transformations of 3-benzoyloxy-5 : 6 : 7 : 8-tetrahydro-2- (III*a*) and



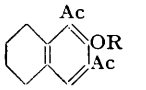
(III*a*; R = Bz)
(III*b*; R = H)
(III*c*; R = Ac)



(IV*a*; R = Bz)
(IV*b*; R = H)
(IV*c*; R = Me)



(V*a*; R = Bz)
(V*b*; R = H)



(VI*a*; R = Bz)
(VI*b*; R = H)

2-benzoyloxy-5 : 6 : 7 : 8-tetrahydro-1-acetonaphthone (IV*a*) and 1-benzoyloxy-5 : 6 : 7 : 8-tetrahydro-2-acetonaphthone (V*a*) into the corresponding diketones have been examined.

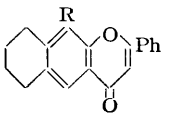
These diketones were cyclised to the respective flavone derivatives (VII*a*), (VIII*a*), and

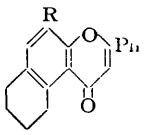
* [Added, 1.10.55.] See also Horning and Amstutz, *J. Org. Chem.*, 1955, **20**, 1069.

(IX). The transformation of 1 : 3-diacetyl-2-benzoyloxy-5 : 6 : 7 : 8-tetrahydronaphthalene (VI*a*) gave two diketones, 4-acetyl-3-benzoylacetyl- (X) and 3-acetyl-1-benzoylacetyl-5 : 6 : 7 : 8-tetrahydro-2-naphthol (XI). These diketones were separated and cyclised to the corresponding flavone derivatives (VII*b*) and (VIII*b*) respectively, the structures of which are discussed below.

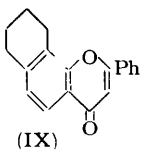
The rates of the transformations were in the order (VI*a* > III*a* > IV*a* > V*a*). The results with (III*a*), (IV*a*), and (V*a*) indicate that the order of the 1 : 2-bond is greater than that of the 2 : 3-bond, in agreement with Berthier and Pullman's theory (*loc. cit.*). However, the matter is complicated by stereochemical factors which now require discussion and which became apparent in the synthesis of the parent hydroxy-ketone of the ester (IV*a*).

(VII*a*; R = H)
(VII*b*; R = Ac)

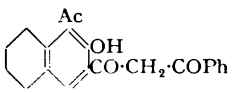




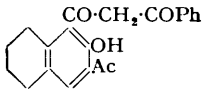
(VIII*a*; R = H)
(VIII*b*; R = Ac)



(IX)



(X)



(XI)

Preparation of Hydroxy-ketones.—The hydroxy-ketones (III*b*), (IV*b*), and (VI*b*) are new. 5 : 6 : 7 : 8-Tetrahydro-3-hydroxy-2-acetonaphthone (III*b*) was obtained by Fries rearrangement of 5 : 6 : 7 : 8-tetrahydro-2-naphthyl acetate. The position of the acetyl group was confirmed by dehydrogenation of the product to 3-hydroxy-2-acetonaphthone; a new route to this not easily obtainable compound was thus provided (cf. Fries and Schimmelschmidt, *Ber.*, 1925, **58**, 2835; Virkar and Wheeler, *J.*, 1939, 1681).

1 : 3-Diacetyl-5 : 6 : 7 : 8-tetrahydro-2-naphthol (VI*b*) was prepared by Fries rearrangement of 3-acetoxy-5 : 6 : 7 : 8-tetrahydro-2-acetonaphthone (III*c*); it was separated from accompanying phenol (III*b*) by virtue of its insolubility in light petroleum. 5 : 6 : 7 : 8-Tetrahydro-2-hydroxy-1-acetonaphthone (IV*b*) was obtained from 1-bromo-5 : 6 : 7 : 8-tetrahydro-2-naphthyl methyl ether (Arnold, Zaugg, and Sprung, *J. Amer. Chem. Soc.*, 1941, **63**, 1314) which was converted into the Grignard compound, and thence, by treatment with acetonitrile, or with cadmium chloride followed by acetyl chloride, into 5 : 6 : 7 : 8-tetrahydro-2-methoxy-1-acetonaphthone (IV*c*), which was demethylated.

Demethylation of 5 : 6 : 7 : 8-*Tetrahydro-2-methoxy-1-acetonaphthone* (IV*c*).—This was investigated by three methods:

(*a*) A solution of the ether (IV*c*) in benzene was refluxed with aluminium chloride, and the phenol (IV*b*) was obtained. This was confirmed by remethylation to the initial methoxy-compound—the possibility of rearrangement (cf. Baddeley, *Quart. Rev.*, 1954, **8**, 355) was thus eliminated.

(*b*) A mixture of 5 : 6 : 7 : 8-tetrahydro-2-methoxy-1-acetonaphthone (IV*c*), aluminium chloride, and sodium chloride was heated at 170—190° (cf. Bruce, Sorrie, and Thomson, *J.*, 1953, 2403), and 5 : 6 : 7 : 8-tetrahydro-3-hydroxy-2-acetonaphthone (III*b*) was isolated. Demethylation was accompanied by a rearrangement which involved either a rearrangement of the reduced ring (Schroeter, *Ber.*, 1924, **57**, 1990) or an acyl-group migration (Baddeley, *J.*, 1944, 232).

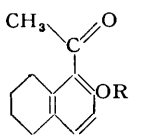
(*c*) A solution of the methoxy-ketone in a mixture of hydriodic acid and acetic anhydride, when kept at 45° for 48 hours (cf. Hutchins and Wheeler, *J.*, 1939, 91), formed 5 : 6 : 7 : 8-tetrahydro-2-naphthol. Demethylation was thus accompanied by an acid-catalysed deacylation (cf. Schubert and Latourette, *J. Amer. Chem. Soc.*, 1952, **74**, 1829).

The rearrangement reaction (method *b*) and the deacylation reaction (method *c*) suggest that the acetyl group in the phenol (IV*b*) is sterically hindered. Steric interference by the " alkyl " ring in tetralin with groups substituted in the positions *ortho* to the alkyl ring has previously been observed (see Van Helden, Verkade, and Wepster, *Rec. Trav. chim.*,

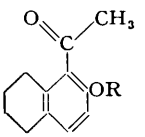
1954, **73**, 39; Fenton, DeWald, and Arnold, *J. Amer. Chem. Soc.*, 1955, **77**, 979). Accordingly, the ultraviolet spectra of the phenols (III*b*) and IV*b*) were examined for evidence of steric strain. The curve for the former corresponds closely with that for *o*-hydroxyacetophenone (Morton and Stubbs, *J.*, 1940, 1347) when allowance is made for the bathochromic effect of the " alkyl " ring in (III*b*) (Jones, *Chem. Rev.*, 1943, **32**, 1). The peak in (III*b*) ($\lambda_{max.}$ 265 mμ, log ε 4·11) is largely suppressed in the isomer (IV*b*) ($\lambda_{max.}$ 255·5 mμ, log ε 3·35), presumably by steric inhibition of conjugation between the carbonyl group and the aromatic ring in the latter (cf. Braude, Sondheimer, and Forbes, *Nature*, 1954, **173**, 117). The second peak in the spectrum of (IV*b*) is at $\lambda_{max.}$ 296 mμ, log ε 3·31. This is probably due mainly to the hydroxyl group conjugated to the ring, for there is a peak in the curve of 5 : 6 : 7 : 8-tetrahydro-2-naphthol at $\lambda_{max.}$ 282·5 mμ, log ε 3·40, and Morton and Sawires (*J.*, 1940, 1052) report the maximum for phenol at $\lambda_{max.}$ 273 mμ, log ε 3·30. The peak at 296 mμ is broad, so in addition to the hydroxyl absorption there may be a contribution from the hindered conjugation of the carbonyl group with the aromatic ring. Such conjugation gives an absorption at $\lambda_{max.}$ 278 mμ, log ε 3·02 (Morton and Stubbs, *loc. cit.*). The bathochromic effect of the " alkyl " ring would shift this absorption into the region of the observed peak.

Discussion.—As stated above, the faster rearrangement of the ester (III*a*) than of its isomers (IV*a*) and (V*a*) is considered to be due to the low bond order of the 2 : 3-bond; this militates against ester-type neutralisation of the acetyl group and therefore promotes the Baker–Venkataraman transformation. In view of the strained nature of the acetyl group in (IV*b*) it is necessary to consider a possible steric effect in the transformation of (IV*a*). Examination of models of the Courtauld type (Hartley and Robinson, *Trans. Faraday Soc.*, 1952, **48**, 847) of the compounds (IV*a*) and (IV*b*) shows that the acetyl group in the 1-position is a hindered group in that the methyl group cannot pass across the reduced ring if the acetyl group is rotated about the bond joining it to the aromatic ring; on the other hand, there is no great hindrance as the carbonyl group is passed across the reduced ring. Thus it appears that of the two extreme positions for the acetyl group, (XII) and (XIII), the conformation (XIII) involves little strain and is favoured. This conclusion is similar to that of Kadesch (*J. Amer. Chem. Soc.*, 1944, **66**, 1207) for 2-methylacetophenone. The favoured orientation of the acetyl group in (XIII) is that required for the Baker–Venkataraman transformation, so that it would seem that the hindrance to rotation of the acetyl group can be ignored in considering the results of the Baker–Venkataraman reaction.

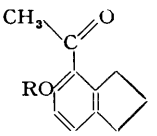
It has been shown that the steric effects of the trimethylene ring in indane are less than those of the tetramethylene ring in tetralin (Van Helden *et al.*, *loc. cit.*; Fenton, *et al.*, *loc. cit.*; Kooyman and Strang, *Rec. Trav. chim.*, 1953, **72**, 342). The study of models suggests that the orientation of the acetyl group in (II*a*), (II*b*), and (II*c*) is as in (XIV) rather than as in (XV). So in (II*a*) and (II*b*), as in (IV*a*), the steric hindrance of the acetyl group does does not affect the results of the Baker–Venkataraman transformation.



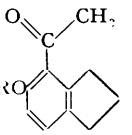
(R = H or Bz)
(XII)



(R = H or Bz)
(XIII)



(R = H, Bz, or *p*-MeO·C_6H_4·CO)
(XIV)



(R = H, Bz, or *p*-MeO·C_6H_4·CO
(XV)

With the Fries reaction, however, the hindered nature of the 1-position in 5 : 6 : 7 : 8-tetrahydronaphthalene derivatives, and of the 4-position in indanes, probably opposes the entrance of the acyl group migrating from the *ortho*-position. There is evidence that an intramolecular Fries migration to an *ortho*-position requires the formation of a bulky cyclic transition complex involving the ester grouping, aluminium chloride, and the *ortho*-carbon atom (Baltzly, Ide, and Phillips, *J. Amer. Chem. Soc.*, 1955, **77**, 2522). Hence, as indicated above, in the Fries rearrangement of 5 : 6 : 7 : 8-tetrahydro-2-naphthyl acetate, the migration is preferentially to the 3-position (cf. Sergievskaya and Morozovskaya,

J. Gen. Chem., U.S.S.R., 1945, **15**, 319; *Chem. Abs.*, 1946, **40**, 7187). Similarly, Baker (*J.*, 1937, 476) showed that acetyl migration in 5-acetoxyindane is preferentially to the 6-position. Thus with both the tetralin and the indane compounds the Fries migration is to the non-hindered position, although consideration of bond structure suggests that the alternative hindered position would be preferred. Baker's observation (*loc. cit.*) that 5-acetyl-6-hydroxyindane (I*c*) is more highly chelated than 4-acetyl-5-hydroxyindane (II*c*) may be related to steric resistance to conformation (XV).

One possibly anomalous result remains for mention. As stated above, the transformation of (VI*a*) leads to two diketones (X) and (XI) which were separated and then cyclised to the flavones (VII*b*) and (VIII*b*). The results of the transformations of (III*a*), (IV*a*), and (V*a*) suggest that the transformation of (VI*a*) should give (X) in greater yield than (XI). The recovery of purified (X) and (XI) from the crude transformation product was not quantitative, but in all experiments the yield of (XI) was greater than (X).

Structures of Acetyl-diketones and -flavones.—The structures of the acetyl-diketones and -flavones prepared were determined by deacylation of the acetylflavone (VII*b*) to give (VII*a*) by refluxing with 85% phosphoric acid (cf. Arnold and Rondestvedt, *J. Amer. Chem. Soc.*, 1946, **68**, 2176). This assignment of structures is supported by a study of the ultraviolet spectra of (VII*a*), (VII*b*), (VIII*a*), (VIII*b*), and (IX). The linear compounds (VII*a*) and (VII*b*) both show a peak at about 300 mμ, more intense than a second peak at 260 mμ. The curve of (VII*a*) differs from that of flavone (Davis and Geissman, *J. Amer. Chem. Soc.*, 1954, **76**, 3507) by the expected bathochromic shift caused by the " alkyl " ring. The peaks at about 300 mμ in the spectra of the angular-type compounds (VIII*a*) and (VIII*b*) are similar to each other and are less intense than second peaks at 260 mμ. Compound (IX) has also an angular structure but differs from (VIII*a*) and (VIII*b*) in that the point of fusion of one end of the alkyl ring is *ortho* to the position of fusion of the oxygen of the γ-pyrone ring. In the spectrum of (IX), the peak at 300 mμ is lower than that at 260 mμ but the difference in intensity is not as marked as that in the isomeric flavone (VIII*a*) or its acetyl derivative (VIII*b*).

It should be stressed that, although the transformation experiments support the Berthier–Pullman view of the bond structure of indane and tetralin, yet the results apply strictly only to the compounds studied.

Experimental

Ethanol was used for crystallisation and for absorption measurements unless otherwise stated.

Anisates of o-*Hydroxyacetylindanes.*—*Preparation.* 5-Acetyl-6- (I*c*) and 4-acetyl-5-hydroxyindane (II*c*) were prepared as described by Baker (*J.*, 1937, 476). 5-*Acetyl*-6-p-*anisoyloxyindane* (I*b*), obtained from (I*c*) by the pyridine–acid chloride method and crystallised from ethanol or ligroin, had m. p. 128—129° (Found : C, 73·2; H, 5·7. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·9%). The isomeric 4-*acetyl*-5-p-*anisoyloxyindane* (II*b*), m. p. 81—83° (aqueous ethanol or ligroin) (Found : C, 72·9; H, 5·9%), was prepared from (II*c*) in a similar manner.

Baker–Venkataraman transformation. A solution of the ester (I*b*) (0·5 g.) in pyridine (5 ml.) was shaken with potassium hydroxide (0·5 g.) which had previously been powdered in a hot mortar. The product was acidified, and the precipitate collected. 5-p-*Anisoylacetyl*-6-*hydroxyindane* (0·3 g.) separated in yellow needles, m. p. 142—143° (Found : C, 73·2; H, 6·0. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·9%); the 4-p-*anisoylacetyl*-5-*hydroxy-analogue* [from (II*b*)] formed orange crystals, m. p. 114—115° (Found : C, 73·3; H, 5·6%). When the transformations were carried out simultaneously under standard conditions, reaction with ester (I*b*) commenced immediately and was complete in 20 min., whereas ester (II*b*) did not react for 20 min. and complete separation of the salt of the diketone required several hours.

Preparation of 4′-*Methoxy*cyclo*pentenoflavones.*—A solution of the diketone from ester (I*b*) (0·2 g.) in glacial acetic acid (2 ml.) was boiled with a few drops of concentrated hydrochloric acid for 1 min. Hot water was added until an opalescence appeared, and the mixture was boiled again and cooled to separate 4′-*methoxy*-6 : 7-cyclo*pentenoflavone*,* m. p. 198—199° (Found : C, 77·5; H, 5·6. $C_{19}H_{16}O_3$ requires C, 78·1; H, 5·5%). 4′-*Methoxy*-5 : 6-cyclo*pentenoflavone*,* obtained from (II*b*), had m. p. 176—177° (from aqueous acetic acid) (Found :

* In these compounds the primed numerals refer to positions in the phenyl group of flavone.

C, 77·3; H, 5·6%). These flavones in sulphuric acid showed a blue ultraviolet fluorescence. The first isomer was also prepared (mixed m. p.) by heating a solution of (I*b*) (0·2 g.) in distilled glycerol (2 ml.) for 30 min. at 250° in an atmosphere of nitrogen (cf. Lynch, O'Toole, and Wheeler, *J.*, 1952, 2063) and pouring the hot solution into water (20 ml.).

Preparation of Tetrahydrohydroxyacetonaphthones.—5 : 6 : 7 : 8-Tetrahydro-1-hydroxy-2-acetonaphthone (V*b*) was prepared by Sergievskaya and Morozovskaya's method (*J. Gen. Chem., U.S.S.R.*, 1944, **14**, 1107; *Chem. Abs.*, 1946, **40**, 7186).

5 : 6 : 7 : 8-*Tetrahydro-3-hydroxy-2-acetonaphthone* (III*b*). A mixture of 2-acetoxy-5 : 6 : 7 : 8-tetrahydronaphthalene (Schroeter, *Annalen*, 1922, **426**, 83) (116 g.) and aluminium chloride (116 g.) was heated at 120° for 1¾ hr., and the product decomposed by ice and hydrochloric acid. The resulting 5 : 6 : 7 : 8-*tetrahydro-3-hydroxy-2-acetonaphthone* (III*b*) separated from ethanol or aqueous acetone in pale yellow needles (64 g.), m. p. 72—73°, which gave a violet ethanolic ferric colour (Found : C, 75·9; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%). For confirmation of structure a mixture of (III*b*) (2 g.) and 30% palladised charcoal (0·2 g.) was heated at 270—300° in carbon dioxide (2 hr.). Extraction with ether gave a solid which crystallised in yellow plates, m. p. 106—108°, raised to 111—113° by addition of 3-hydroxy-2-acetonaphthone (m. p. 112—113°).

1 : 3-*Diacetyl*-5 : 6 : 7 : 8-*tetrahydro-2-naphthol* (VI*b*). Acetylation of the acetonaphthone (III*b*) (25 g.) (sodium acetate–acetic anhydride) gave its 2-*acetate* (III*c*) which crystallised in colourless prisms (24·5 g.), m. p. 55—57° (Found : C, 72·1; H, 6·6. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·9%). A mixture of this (7·5 g.) and aluminium chloride (7·5 g.) was kept at 75—80° for 6 hr. and the product was decomposed by ice and hydrochloric acid. The resulting black solid was washed with cold light petroleum (b. p. 40—60°). The residual 1 : 3-*diacetyl*-5 : 6 : 7 : 8-*tetrahydro-2-naphthol* (VI*b*) crystallised from ethanol (charcoal) or acetone in pale yellow rhombs (1·5 g.), m. p. 128—130°, which gave a purple ethanolic ferric colour (Found : C, 72·2; H, 6·8%).

5 : 6 : 7 : 8-*Tetrahydro-2-hydroxy-1-acetonaphthone* (IV*b*). 1-Bromo-5 : 6 : 7 : 8-tetrahydro-2-naphthol (Schroeter, *loc. cit.*) was methylated by potassium carbonate–methyl sulphate–acetone to form 1-bromo-5 : 6 : 7 : 8-tetrahydro-2-naphthyl methyl ether; Arnold, Zaugg, and Sprung's method (*loc. cit.*) was less satisfactory. Alternatively, 5 : 6 : 7 : 8-tetrahydro-2-naphthol was methylated as above (cf. Schroeter, *loc. cit.*) and treated with bromine in acetic acid to yield the bromo-methoxy-compound.

5 : 6 : 7 : 8-*Tetrahydro-2-methoxy-1-acetonaphthone* (IV*c*). (i) A solution of acetonitrile (5·5 ml.) in ether (25 ml.) was added dropwise during 20 min. to a stirred boiling Grignard solution from 1-bromo-5 : 6 : 7 : 8-tetrahydro-2-naphthyl methyl ether (32·7 g.), ether (170 ml.), magnesium (4·9 g.), iodine (trace), and ethyl bromide (trace) (cf. Arnold, Zaugg, and Sprung, *loc. cit.*). Stirring and refluxing were continued for 2 hr. Next day, the Grignard complex was decomposed by ice (300 ml.) and concentrated hydrochloric acid (200 ml.), the ether evaporated, and the acid solution refluxed for 2 hr. The ethereal solution of the resulting oil was washed with dilute aqueous sodium hydroxide and dried (Na_2SO_4). Evaporation of the solvent gave an oil; the fraction of this oil with b. p. 158—170°/8 mm. solidified. 5 : 6 : 7 : 8-*Tetrahydro-2-methoxy-1-acetonaphthone* (IV*c*) crystallised from light petroleum (b. p. 60—80°) or methanol in needles, m. p. 81—82° (2·2 g.) (Found : C, 76·4; H, 8·2. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%).

(ii) Cadmium chloride (5·4 g.) was added rapidly with stirring to a cooled Grignard solution from the bromo-ether (12 g.), ether (60 ml.), magnesium (1·6 g.), ethyl bromide (trace), and iodine (trace), and the mixture was refluxed for 2½ hr. More cadmium chloride (0·5 g.) was added, and the heating continued for 1½ hr. Gilman and Schulze's colour test (*J. Amer. Chem. Soc.*, 1925, **47**, 2002) was negative. Ether was then replaced by benzene and the final solution volume was adjusted to 50—60 ml. (cf. Cason, *J. Amer. Chem. Soc.*, 1946, **68**, 2078). Acetyl chloride (4 ml.) in benzene (60 ml.) was added dropwise to the stirred boiling cadmium aryl solution, and the mixture was refluxed for 8 hr. and poured on ice and dilute sulphuric acid. Removal of the solvent from the washed (dilute aqueous NaOH) and dried benzene solution afforded 5 : 6 : 7 : 8-tetrahydro-2-methoxy-1-acetonaphthone (IV*c*) (1·8 g.) (mixed m. p. confirmation with the product of the acetonitrile reaction).

Demethylation. (*a*) By aluminium chloride in benzene: a solution of (IV*c*) (1·3 g.) in benzene (130 ml.) was refluxed with aluminium chloride (13 g.) for 45 min. The solid formed was decomposed by ice and hydrochloric acid, followed by boiling of the mixture for 30 min. The product was collected in ether, extracted from the ethereal solution with dilute aqueous sodium hydroxide, and recovered by acidification. 5 : 6 : 7 : 8-*Tetrahydro-2-hydroxy-1-acetonaphthone* (IV*b*) crystallised from light petroleum (b. p. 40—60°) or methanol in needles, m. p. 112—113°

(Found : C, 75·2; H, 7·5. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%), which gave a faint green ethanolic ferric colour. Remethylation of the product (methyl sulphate–potassium carbonate –acetone) gave (IV*c*) (mixed m. p. confirmation).

(*b*) By aluminium chloride in fused sodium chloride (cf. Bruce, Sorrie, and Thomson, *J.*, 1953, 2403) : a mixture of (IV*c*) (0·5 g.), sodium chloride (0·5 g.), and aluminium chloride (2·5 g.), which had been heated at 170—190° for 3 min., was poured on ice and hydrochloric acid, and decomposition of the aluminium chloride complex was completed by heating the mixture on a steam-bath for 15 min. The product was collected in ether, the ethereal solution washed with dilute aqueous sodium hydroxide, and the hydroxide solution acidified. The precipitate of 5 : 6 : 7 : 8-tetrahydro-3-hydroxy-2-acetonaphthone (III*b*) was again collected in ether. It crystallised in pale yellow needles (0·012 g.), m. p. 68—69° alone or mixed with authentic (III*b*) (Found : C, 75·2; H, 7·6. Calc. for $C_{12}H_{14}O_2$: C, 75·8; H, 7·4%).

(*c*) By hydriodic acid and acetic anhydride (cf. Hutchins and Wheeler, *J.*, 1939, 91) : a mixture of (IV*c*) (1·4 g.), acetic anhydride (12 ml.), and hydriodic acid (12 ml., 55%) was kept for 48 hr. at 45° and poured into saturated aqueous sodium hydrogen sulphite. 5 : 6 : 7 : 8-Tetrahydro-2-naphthol, isolated by ether-extraction, crystallised from light petroleum in rhombs (0·4 g.), m. p. and mixed m. p. 59—62° (Found : C, 80·6; H, 8·2. Calc. for $C_{10}H_{12}O$: C, 81·0; H, 8·2%).

Preparation of the benzoates of (III*b*), (IV*b*), (V*b*), and (VI*b*). The following benzoates (the first three are isomers) were prepared by using pyridine and benzoyl chloride : 1-*benzoyloxy*-5 : 6 : 7 : 8-*tetrahydro*-2-*acetonaphthone* (V*a*) separated in rhombs from methanol, ethanol, or light petroleum (b. p. 60—80°), m. p. 102—104° (Found : C, 77·4; H, 6·1. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%); 3-*benzoyloxy*-5 : 6 : 7 : 8-*tetrahydro*-2-*acetonaphthone* (III*a*) formed plates, m. p. 81—82°, from ethanol or aqueous acetone (Found : C, 77·0; H, 5·8%); 2-*benzoyloxy*-5 : 6 : 7 : 8-*tetrahydro*-1-*acetonaphthone* (IV*a*) crystallised in needles, m. p. 62—63° from ligroin or methanol (Found : C, 77·7; H, 6·6%); 1 : 3-*diacetyl*-2-*benzoyloxy*-5 : 6 : 7 : 8-*tetrahydronaphthalene* (VI*a*) separated in rhombs, m. p. 116—117° (Found : C, 74·5; H, 5·8. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%).

Transformation of foregoing benzoates. The method of transformation was that used in transforming the *o*-acetylanisoyloxyindanes. The following products were isolated (the colours given with ethanolic ferric chloride are noted in parentheses) :

From (V*a*) : 2-*Benzoylacetyl*-5 : 6 : 7 : 8-*tetrahydro*-1-*naphthol* (0·28 g.), orange needles, m. p. 117—119° (green) (Found : C, 75·4; 75·6; H, 5·8, 6·0. $C_{19}H_{18}O_3,\frac{1}{2}H_2O$ requires C, 75·2; H, 6·3%).

From (III*a*) : 3-*Benzoylacetyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthol* (0·325 g.), yellow-orange needles, m. p. 107—108° (brown) (Found : C, 78·0; H, 6·3. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%).

From (IV*a*) : the crude product (0·41 g.) (red-brown) exhibited in sulphuric acid a green ultraviolet fluorescence. About 10% of it was insoluble in sodium hydroxide; this indicated that the reaction had yielded 1-benzoylacetyl-5 : 6 : 7 : 8-tetrahydro-2-naphthol and 5 : 6-*cyclo*hexenoflavone (VIII*a*). The crude diketone was directly cyclised to the flavone (see below).

From (VI*a*) : a mixture of 1-*acetyl*-3-*benzoylacetyl*- (X) (practically insoluble in cold ether) and 3-*acetyl*-1-*benzoylacetyl*-5 : 6 : 7 : 8-*tetrahydro*-2-*naphthol* (XI) (soluble in cold ether) was obtained. Compound (X) crystallised from acetone in orange rhombs, m. p. 166—168° (0·065 g.) (brown) (Found : C, 74·8; H, 5·8. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%). Compound (XI) (0·14 g.) was obtained in light yellow needles, m. p. 118—119° (red) (Found : C, 74·8; H, 5·7%).

When the four transformations were carried out under standard conditions the following results were obtained (yields of crude diketones are given in parentheses) :

Compound	Colour deepens in	Salt separates in	Reaction complete in	Yield (%)
(V*a*)	2—5 min.	25—35 min.	180—240 min.	80
(III*a*)	5 ,,	10—15 ,,	30—60 ,,	89
(IV*a*)	10—15 ,,	20 ,,	120—180 ,,	83
(VI*a*)	At once	5 ,,	15—60 ,,	90

The general conclusion is that the relative transformation rates were : (VI*a*) > (III*a*) > (IV*a*) > (V*a*).

Preparation of cyclo*Hexenoflavones.*—These were prepared by cyclising the corresponding diketones by the method described for the preparation of the 4′-methoxy*cyclo*pentenoflavones. The following flavones were thus prepared (the colours noted in parentheses are those of the fluorescence in concentrated sulphuric acid) :

7 : 8-cyclo*Hexenoflavone* (IX), needles, m. p. 194—195° (Found : C, 82·3; H, 5·8. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%) (blue-green). 6 : 7-cyclo*Hexenoflavone* (VII*a*), small needles, m. p. 170—171° (Found : C, 82·0; H, 5·8%) (blue). 5 : 6-cyclo*Hexenoflavone* (VIII*a*) [from cyclisation of crude product obtained by transformation of (IV*a*)], needles, m. p. 130—131° (Found : C, 82·9; H, 6·0%). The flavone was purified by vacuum-sublimation followed by crystallisation (green). 8-*Acetyl*-6 : 7-cyclo*hexenoflavone* (VII*b*), rhombs, m. p. 188—190° (Found : C, 79·4; H, 6·0. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%) (blue). 8-*Acetyl*-5 : 6-cyclo*hexenoflavone* (VIII*b*), pale yellow needles, m. p. 175—177° (Found : C, 78·7; H, 5·4%) (green). Cyclisation was not complete and it was necessary to remove uncyclised diketone by extraction with ether in which the flavone was almost insoluble. The flavone was purified by sublimation at 2 mm., followed by crystallisation.

Confirmation of Structures assigned to the Acetylflavones (cf. Arnold and Rondestvedt, *J. Amer. Chem. Soc.*, **1946**, **68**, 2176). A solution of (VII*b*) (0·15 g.) in phosphoric acid (85%; 10 ml.) was refluxed for 5 hr. and poured into water. The resulting precipitate crystallised from ethanol (charcoal) in needles, m. p. 169—171°, alone or mixed with (VII*a*).

Table of maxima observed in ultraviolet spectra.

Compound	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε	$\lambda_{max.}$	log ε
5 : 6 : 7 : 8-Tetrahydro-3-hydroxy-2-acetonaphthone (III*b*)	339·5	3·60	265·5	4·11	—	—
Product from demethylation of 5 : 6 : 7 : 8-tetrahydro-2-methoxy-1-acetonaphthone by use of $AlCl_3$–NaCl at 170—190° (III*b*)	340·5	3·58	264	4·10	—	—
5 : 6 : 7 : 8-Tetrahydro-2-hydroxy-1-acetonaphthone (IV*b*)	296	3·31	255·5	3·35	—	—
5 : 6 : 7 : 8-Tetrahydro-2-naphthol	331	2·36	282·5	3·40	225	4·11
6 : 7-*cyclo*Hexenoflavone (VII*a*)	304	4·41	260·5	4·39	—	—
8-Acetyl-6 : 7-*cyclo*hexenoflavone (VII*b*)	302	4·41	260·0	4·30	—	—
5 : 6-*cyclo*Hexenoflavone (VIII*a*)	297	4·26	265·5	4·45	—	—
8-Acetyl-5 : 6-*cyclo*hexenoflavone (VIII*b*)	300	4·23	258·5	4·30	220	4·50
7 : 8-*cyclo*Hexenoflavone (IX)	300·5	4·30	260·5	4·35	—	—

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