

75. The Effect of Bond Structure on the Transformation of *o*-Aroyloxy-acetoarones into *o*-Hydroxydiaroylmethanes. Baker-Venkataraman Transformation.

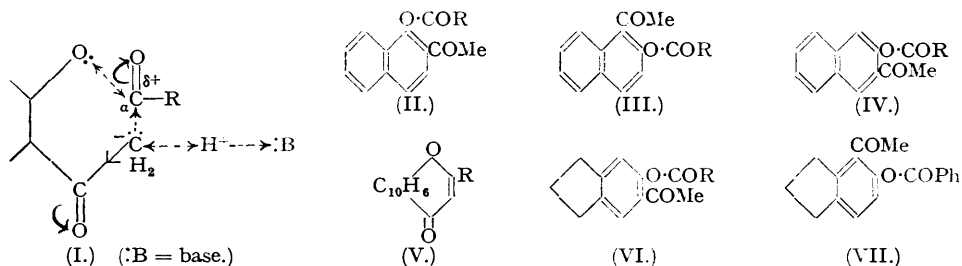
By N. V. NOWLAN, P. A. SLAVIN, and T. S. WHEELER.

The experimental results indicate that the Baker-Venkataraman transformation of *o*-aroyloxyacetoarones into *o*-hydroxydiaroylmethanes takes place more rapidly across the 2 : 3-bond (single bond) in naphthalene than across the 1 : 2-bond (double bond). This is attributed to ester-type neutralisation across the double bond, and is in accordance with the view (Doyle *et al.*, *Proc. Roy. Dublin Soc.*, 1948, **24**, 291) that the transformation involves a base-catalysed intramolecular Claisen condensation. Preliminary results with *o*-aroyloxyacetylindanes do not seem to be in accord with the Mills-Nixon view of bond distribution in indane.

The tendency of *o*-hydroxydiaroylmethanes, $\text{HO}-\text{C}(\text{COR})_2-\text{CO}-\text{R}$, to undergo spontaneous cyclisation to the corresponding flavones when R contains an electrophilic (nitro-) group is discussed. A number of new 4-pyrones are described.

It has not been found possible to transform *o*-arylsulphonyloxyacetophenones.

THE transformation of *o*-aroyloxyacetoarones into *o*-hydroxydiaroylmethanes (Baker, *J.*, 1933, 1381; Mahal and Venkataraman, *J.*, 1934, 1767) has been shown by Doyle *et al.* (*Proc. Roy. Dublin Soc.*, 1948, **24**, 291) to be a base-catalysed intramolecular Claisen condensation involving a nucleophilic displacement of oxygen on carbon as indicated by the transition compound (I). This paper describes an investigation of this transformation across the $\text{C}_{(1)}-\text{C}_{(2)}$ and $\text{C}_{(2)}-\text{C}_{(3)}$ bonds of naphthalene, which have as regards the chemical reactivity of naphthalene compounds the quality, respectively, of double and single bonds [cf. Fieser, "Organic Chemistry" (Gilman), 1943, Vol. I, 145]. The experimental work was concerned mainly with the base-catalysed transformation of *o*-(nitrobenzoyloxy)acetophenones (II, III, and IV;



R = *o*-, *m*-, or *p*-nitro- or 3 : 5-dinitro-phenyl) into the corresponding *o*-hydroxy-diketones, $\text{C}_{10}\text{H}_6(\text{OH})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R}$, which in some instances cyclised spontaneously to form the benzoflavanone (V). The transformation of other 2-acyloxy-3-acetonaphthones (IV; R = Me, Ph, styryl, or 2-methoxy-3-naphthyl), and of some esters of *o*-hydroxyacetylindanes (VI; R = Me, Ph, and *p*-nitrophenyl) and (VII), was also investigated. Attempts to transform benzene- and toluene-sulphonyl esters of the *o*-hydroxyacetonaphthones (see Table III) using a variety of basic catalysts (see Doyle *et al.*, *loc. cit.*) were unsuccessful: the sulphonyl group, though electrophilic, is less so than the carbonyl group (Kohler and Potter, *J. Amer. Chem. Soc.*, 1935, **57**, 1316; Connor *et al.*, *ibid.*, 1936, **58**, 1386). When 2-benzenesulphonyloxy-3-acetonaphthone was treated with triphenylmethylsodium, a compound giving analytical figures corresponding to $\text{C}_{56}\text{H}_{44}\text{O}_2\text{S}$ [? 2 : 3- $\text{C}_{10}\text{H}_6(\text{COMe})\cdot\text{O}\cdot\text{SPh}(\text{CPh}_3)_2$] was obtained. Transformation of the sulphonyl esters was also attempted using boron trifluoride as an acid catalyst (see Breslow and Hauser, *J. Amer. Chem. Soc.*, 1940, **62**, 2385) but without success.

Results with o-Acyloxyacetonaphthones.—The trend of the results obtained with the nitroesters summarised in Table I, while not conclusive, indicates that generally transformation takes place across the $\text{C}_{(2)}-\text{C}_{(3)}$ single-type bond more rapidly than across the $\text{C}_{(1)}-\text{C}_{(2)}$ double-type bond. Comparative experiments with 2-benzoyloxy-1-acetonaphthone (III; R = Ph) (Bhalla *et al.*, *J.*, 1935, 870) and 2-benzoyloxy-3-acetonaphthone (IV; R = Ph) gave, similarly, more rapid transformation with the latter compound. Smooth and rapid transformation was also obtained with 2-cinnamoyloxy-3-acetonaphthone (IV; R = styryl) and 2-(2-methoxy-3-naphthoyloxy)-3-acetonaphthone (IV; R = 2-methoxy-3-naphthyl). It was not found possible to transform 2-acetoxy-3-acetonaphthone (IV; R = Me) (Fries and Schimmelschmidt, *Ber.*,

TABLE I.

Results with nitrobenzoyloxyacetoneaphthones.

(II, III, and IV; R = *o*-, *m*-, or *p*-nitro- or 3 : 5-dinitro-phenyl.)

Aroyl radical.	Acetonaphthone.					
	1-Hydroxy-2-acetonaphthone (II).		2-Hydroxy-1-acetonaphthone (III).		2-Hydroxy-3-acetonaphthone (IV).	
	Reaction time, mins.	Yield, ¹ %.	Reaction time, mins.	Yield, ¹ %.	Reaction time, mins.	Yield, ¹ %.
2-Nitrobenzoyl-	2	26 D	6	2 DF	2	30 DF
3-Nitrobenzoyl-	7	22 D	8	21 F	1	30 D
4-Nitrobenzoyl-	5	58 D	7	28 D	<1	46 D
3 : 5-Dinitrobenzoyl-	5	Tar	6	50 F ²	1	3 F

These transformations were carried out under controlled conditions in boiling pyridine with potassium hydroxide as base. For details see the Experimental section. Potassium hydroxide was chosen after a number of the bases used by Doyle *et al.* (*loc. cit.*) had been tested.

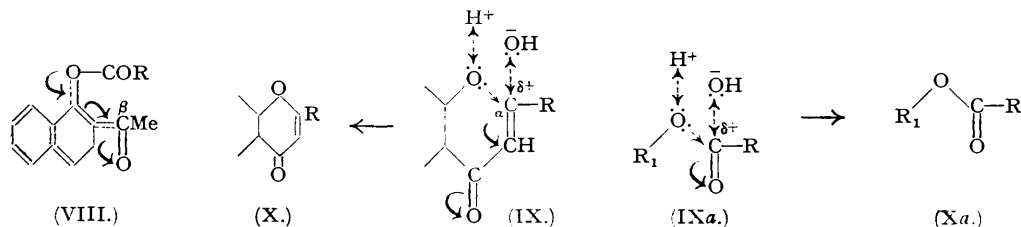
¹ Yields are calculated on the aroyloxyacetoneaphthone. D indicates yield of diketone; F shows yield of flavone when produced by spontaneous cyclization of diketone; DF gives yield of flavone obtained by cyclization of material (crude diketone) which could not readily be purified.

² 3' : 5'-Dinitro-3-(3 : 5-dinitrobenzoyl)-5 : 6-benzflavone was the probable product of the transformation.

1925, 58, 2835). *o*-Acetoxyacetoarones (I; R = Me) are difficult to transform (cf. Baker, *loc. cit.*; Virkar and Wheeler *J.*, 1939, 1679; Geissman, *J. Amer. Chem. Soc.*, 1949, 71, 1498) as the anionoid effect of the methyl group reduces the electrophilic nature of C_(a) (I). Gowan (private communication) has, however, succeeded in transforming *o*-acetoxyacetophenone into *o*-hydroxybenzoylacetone using triphenylmethylsodium as the basic catalyst.

These results support the view of Doyle *et al.* (*loc. cit.*) as to the mechanism of the transformation. The mobile π electrons of the C₍₁₎-C₍₂₎ bond facilitate ester-type neutralisation of the carbonyl carbon C_(β) (VIII); such neutralisation occurs less readily across the C₍₂₎-C₍₃₎ bond in which the density of electrons is low (see Pullman, *Ann. Chim.*, 1947, 2, 5). The occurrence of such neutralisation across the C₍₁₎-C₍₂₎ bond is shown by the exceptionally high basic strength of 2-nitro-3-naphthylamine as compared with 2-nitro-1-naphthylamine and 1-nitro-2-naphthylamine (cf. Bryson, *Trans. Faraday Soc.*, 1949, 45, 257; Hodgson and Turner, *J.*, 1943, 635). The argument is supported by the non-existence of 2 : 3-naphthaquinone; an *o*-quinonoid form is involved in the type of neutralisation shown in (VIII) (see Waters, *J.*, 1948, 727).

Preliminary Results with o-Aroyloxyacetylindanes.—5-Benzoyloxy-6-acetylindane (VI; R = Ph) was found in comparative experiments to be transformed into the corresponding diketone more rapidly than was 5-benzoyloxy-4-acetylindane (VII). This result is unexpected if the Mills-Nixon structure (*J.*, 1930, 2510), which is shown in (VI) and (VII), is assumed for indane.



However, though Baker's well-known investigation on chelation effects (*J.*, 1937, 476) supports this structure for *o*-hydroxyacetylindanes, the results of extensive work on the reactivity of indane and of its derivatives indicate that, if bond fixation is present, it is not so well-defined as in the naphthalene series, but is more sensitive to the substituents present and to the reagents employed [see Fieser, *op. cit.*, p. 139; Hippchen, "On the arrangement of the double bonds in hydrindene (indane)," F.I.A.T. Final Report, No. 1033 (1947); "Elsevier's Encyclopædia of Organic Chemistry," 1948, 12, A, 103; Springall *et al.*, *J.*, 1949, 1524]. It is hoped to investigate further the transformation of esters of the type shown in (VI) and (VII). 5-Acetoxy-6-acetylindane (VI; R = Me) (Baker, *loc. cit.*) could not be transformed.

Flavone Formation.—It will be seen from Table I that three of the nitro-diketones (indicated

by F) cyclised, when formed, to the flavone (cf. Doyle *et al.*, *loc. cit.*). This cyclisation is of course analogous to esterification (IX; IXa; X; Xa); it involves a nucleophilic displacement of hydroxyl on carbon (see Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686) and is therefore promoted by the presence, in R, of an electrophilic (nitro-) group, which increases the cationoid activity of C_(a) (IX). It will be noted that 2-(3:5-dinitrobenzoyloxy)-1-acetonaphthone (III; R = 3:5-dinitrophenyl) yielded directly a compound giving analytical figures corresponding to the related 3-arylated flavone (Table I, footnote 2).

EXPERIMENTAL.

Preparation of o-Hydroxyacetovanones and their Esters.—1-Hydroxy-2-acetonaphthone (Witt and Braun, *Ber.*, 1914, **47**, 3216), 2-hydroxy-1-acetonaphthone (Fries, *Ber.*, 1921, **54**, 709), 2-hydroxy-3-acetonaphthone (Fries and Schimmelschmidt, *Ber.*, 1925, **58**, 2835), 5-hydroxy-6-acetylinthane, and 5-hydroxy-4-acetylinthane (Baker, *J.*, 1937, 476) were synthesised as described by the authors cited. In this preparation of 1-hydroxy-2-acetonaphthone it was found essential to keep the temperature of the reaction mixture below 140°, otherwise 1-hydroxy-2:4-diacetylnaphthalene was produced.

The esters were prepared by the pyridine-acid chloride method (cf. Doyle *et al.*, *Proc. Roy. Dublin Soc.*, 1948, **24**, 291); the yields were usually over 60%. Completion of esterification was determined by extracting an acidified sample of the reaction mixture with chloroform, diluting the extract with alcohol, and testing for free *o*-hydroxy-diketone with alcoholic ferric chloride. Serial numbers have been assigned to the carboxylic esters to facilitate cross-reference.

Those of the sulphonic esters which did not solidify rapidly when the reaction mixture was acidified were extracted with chloroform, and the extracts were washed with aqueous sodium carbonate and with water and dried (Na₂SO₄). The residue obtained on removal of the solvent was distilled at about 10⁻³ mm. before recrystallisation.

Mononitrobenzoyloxyacetanaphthones.—These compounds (see Tables I and II) were colourless to yellow, excepting No. 4 which was red.

TABLE II.

y-(*x*-Nitrobenzoyloxy)-*z*-acetanaphthones.

(II, III, and IV; R = *o*-, *m*-, and *p*-nitrophenyl) (C₁₉H₁₃O₅N requires C, 68.1; H, 3.9; N, 4.2%).

Serial no.	Ester.			M. p.	Crystallizing solvent.	Found, %.		
	<i>x</i> .	<i>y</i> .	<i>z</i> .			C.	H.	N.
1	2'	1	2	115—116°	Alcohol-dioxan	68.0	4.1	4.3 ¹
2	3'	1	2	151—152	Alcohol	—	—	4.4 ²
3	4'	1	2	150—151	Alcohol-dioxan	68.3	3.9	4.3 ²
4	2'	2	1	146—148	Acetone-aqueous alcohol	67.3	3.9	4.3 ¹
5	3'	2	1	174—176	Chloroform	68.1	3.9	4.5 ¹
6	4'	2	1	137—138	Acetone-aqueous alcohol	67.3	3.9	4.2 ¹
7	2'	2	3	165	Alcohol-dioxan	68.2	4.1	4.2 ¹
8	3'	2	3	146—148	Alcohol-dioxan	67.8	3.9	4.0 ¹
9	4'	2	3	177—179	Alcohol-dioxan	67.7	3.9	4.0 ¹

¹ New compound.

² Virkar, *J. Univ. Bombay*, 1942, **11**, 136.

Dinitrobenzoyloxyacetanaphthones (see Table I).—The molecular formula, C₁₉H₁₂O₇N₂, for these compounds requires C, 60.0; H, 3.1; N, 7.4%. 1-(3:5-Dinitrobenzoyloxy)-2-acetonaphthone (II; R = 3:5-dinitrophenyl) (10) (from chloroform), m. p. 209—212° (decomp.) (Found: C, 59.7; H, 3.3; N, 7.4%), 2-(3:5-dinitrobenzoyloxy)-1-acetonaphthone (III; R = 3:5-dinitrophenyl) (11) [from chloroform-light petroleum (b. p. 60—80°)], m. p. 200—202° (Found: C, 60.2; H, 3.2; N, 7.8%), and 2-(3:5-dinitrobenzoyloxy)-3-acetonaphthone (IV; R = 3:5-dinitrophenyl) (12) [from chloroform-light petroleum (b. p. 40—60°)], m. p. 173° (Found: C, 59.9; H, 3.2; N, 7.3%), were readily obtained (ca. 80% yield) as pale yellow crystals by the pyridine-acid chloride method.

Other Carboxylic Acid Esters.—2-Benzoyloxy-3-acetonaphthone (IV; R = Ph) (13) (from ligroin), m. p. 111° (Found: C, 78.5; H, 4.7. C₁₉H₁₄O₃ requires C, 78.6; H, 4.8%), 2-cinnamoyloxy-3-acetonaphthone (IV; R = styryl) (14) (from ligroin), m. p. 121° (Found: C, 79.6; H, 5.2. C₂₁H₁₆O₃ requires C, 79.7; H, 5.1%), 2-(2-methoxy-3-naphthoyloxy)-3-acetonaphthone (IV; R = 2-methoxy-3-naphthyl) (15) (from benzene and alcohol), m. p. 191° (Found: C, 77.7; H, 5.0. C₂₄H₁₆O₄ requires C, 77.8; H, 4.9%), 5-benzoyloxy-6-acetylinthane (VI; R = Ph) (16) (from aqueous alcohol), m. p. 87—88° (Found: C, 77.0; H, 5.9. C₁₈H₁₄O₃ requires C, 77.1; H, 5.7%), 5-(*p*-nitrobenzoyloxy)-6-acetylinthane (VI; R = *p*-nitrophenyl) (17) (from aqueous alcohol), m. p. 104—105° (Found: C, 66.6; H, 4.8; N, 4.3. C₁₈H₁₃O₅N requires C, 66.5; H, 4.6; N, 4.3%), and 5-benzoyloxy-4-acetylinthane (VII) (18) (from aqueous methyl alcohol and ligroin), m. p. 89—90° (Found: C, 77.1; H, 5.6. C₁₈H₁₄O₃ requires C, 77.1; H, 5.7%), were obtained as colourless crystals.

Sulphonic Acid Esters.—Results for these compounds, all colourless, are given in Table III.

Action of Triphenylmethylsodium on 2-Benzenesulphonyloxy-3-acetonaphthone.—2-Benzenesulphonyloxy-3-acetonaphthone (0.5 g.) contained in a reaction flask filled with nitrogen was treated with an ethereal solution of triphenylmethylsodium, prepared, stored, and delivered into the reaction flask in an atmosphere of nitrogen using the procedure of Hauser and Hudson ("Organic Reactions," 1942, Vol. I, 286). Addition of the reagent was discontinued when the red colour of its solution was no longer discharged. The mixture was shaken for 1 hour and treated with water. The insoluble product (0.5 g.)

separated from chloroform and from glacial acetic acid in colourless crystals, m. p. 184°, insoluble in aqueous alkali, acetone, and ether, soluble in chloroform, and unaffected by hot hydrobromic acid in glacial acetic acid (Found : C, 86.5, 86.4, 86.3, 86.5; H, 5.8, 5.9, 5.5, 5.6; S, 4.4, 4.7. $C_{58}H_{44}O_8S$ requires C, 86.2; H, 5.6; S, 4.1%).

TABLE III.

*Sulphonic acid esters, x-R-sulphonyloxy-y-acetonaphthones.*¹

(A; R = benzene : $C_{18}H_{14}O_4S$ requires C, 66.3; H, 4.3; S, 9.8%.
B; R = toluene : $C_{19}H_{16}O_4S$ requires C, 67.1; H, 4.7; S, 9.4%.)

R.	Ester.		M. p.	Crystallizing solvent.	Found, %.		
	x.	y.			C.	H.	S.
A; Benzene	2	1	72—74°	Aqueous alcohol	66.2	4.4	9.6
"	2	3	84—86	Alcohol	66.1	4.3	9.4
B; <i>o</i> -Toluene	1	2	63—65	Alcohol	66.9	4.9	9.5
"	2	1	60—62	Light petroleum (b. p. 60—80°)	67.0	4.8	9.4
"	2	3	110—112	Alcohol	67.0	4.8	9.0
<i>p</i> -Toluene	1	2	99—101	Aqueous alcohol	66.9	4.7	9.6
"	2	1	98—99	Alcohol	67.3	4.9	9.3
"	2	3	84—86	Alcohol	66.8	4.7	9.0

¹ These compounds are new.

Preparation of 1:3-Diketones.—Transformation into ketones of the nitro-esters listed in Table II. Potassium hydroxide (ca. 0.1 g.) was crushed between warm dry filter-papers and rapidly transferred to a boiling pyridine solution (5 ml.) of the ester (0.5 g.) to be transformed. Heating under reflux was continued until the solution, at first red, became brown, and solid separated. The mixture was cooled, diluted with water (20 ml.), and filtered. The filtrate was brought to pH 6 (glass electrode) with glacial acetic acid (ca. 0.4 ml.), and after an hour the precipitated diketone was collected and crystallised or, if difficult to purify, cyclised to the flavone. The presence of a nitro-group, particularly in the *ortho*-position, promotes the formation of resin and, if heating was continued until the solution became black, an unworkable product was obtained. Acidification beyond pH 6 caused precipitation of resin. Results for the nitrobenzoyl-*o*-hydroxynaphthoilmethanes prepared in this way are given in Table IV. The colour of these compounds varied from yellow to orange.

TABLE IV.

x-Nitrobenzoyl-y-hydroxy-z-naphthoilmethanes.

($C_{19}H_{13}O_5N$ requires C, 68.1; H, 3.9; N, 4.2%.)

Corresponding ester no. of Table II.	Diketone.			M. p.	Crystallizing solvent.	Found, %.		
	x.	y.	z.			C.	H.	N.
1	2	1'	2'	173—175°	Aqueous acetone	67.8	4.1	4.1 ¹
2	3	1'	2'	191	Acetone	68.4	3.9	4.3 ²
3	4	1'	2'	222—224	Tetrahydrofurfuryl alcohol	67.5	4.0	4.2 ²
6	4	2'	1'	168—170	Alcohol	67.9	4.0	4.2 ¹
8	3	2'	3'	182—183	Acetone	67.7	3.9	4.5 ¹
9	4	2'	3'	228—230	Acetone	68.1	4.2	4.2 ¹

¹ New compound.

² Virkar, *loc. cit.*

Transformation of other esters of o-hydroxyacetanaphthones. Benzoyl-2-hydroxy-3-naphthoilmethane. A solution of 2-benzoyloxy-3-acetonaphthone (IV; R = Ph) (ester no. 13) (1.2 g.) in pyridine (5 ml.) was treated with alcoholic sodium ethoxide (3 ml. of a solution containing 1 g. of sodium in 25 ml. of alcohol). The sodium salt of the diketone separated rapidly. The mixture was diluted with water and acidified with 10% hydrochloric acid. The solid (1.0 g.) thus obtained crystallised from aqueous alcohol in yellow needles, m. p. 129—130° (Found : C, 78.4; H, 4.8. $C_{19}H_{14}O_3$ requires C, 78.6; H, 4.8%). In comparative experiments (ester, 45 mg.; pyridine, 1 ml.; sodium ethoxide, 0.5 ml. of the solution referred to above) 2-benzoyloxy-1-acetonaphthone (Ullal, Shah, and Wheeler, *J.*, 1940, 1499) showed a slower rate of transformation. No effect was apparent until 30 minutes after addition of the base, as compared with the immediate precipitate obtained with the 2:3-compound.

Cinnamoyl-2-hydroxy-3-naphthoilmethane (from glacial acetic acid), m. p. 160° (Found : C, 79.3; H, 4.9. $C_{21}H_{16}O_3$ requires C, 79.7; H, 5.1%), and *2-hydroxy-2'-methoxy-3:3'-dinaphthoilmethane* (from glacial acetic acid), m. p. 181—182° (Found : C, 77.1; H, 5.0. $C_{24}H_{18}O_4$ requires C, 77.8; H, 4.9%), were prepared as yellow crystals from the corresponding esters (nos. 14 and 15 respectively). As with 2-benzoyloxy-3-acetonaphthone (see above) the transformations were immediate.

Transformation of esters of o-hydroxyacetylindanes. 5-Hydroxy-6-benzoylacetylindane. A solution of 5-benzoyloxy-6-acetylindane (VI; R = Ph) (ester No. 16) (0.5 g.) in pyridine (5 ml.) was treated with solid potassium hydroxide (0.15 g.) previously crushed in a hot mortar, and the mixture was kept overnight. The yellow solid (0.47 g.) obtained when the reaction product was mixed with excess of 10% hydrochloric acid separated from aqueous alcohol in yellow needles, m. p. 99—101° (Found : C, 77.1; H, 5.8. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.7%). *5-Hydroxy-6-p-nitrobenzoylacetylindane* (from

aqueous dioxan), m. p. 225—227° (Found: C, 66.1; H, 4.5; N, 4.3. $C_{18}H_{15}O_5N$ requires C, 66.5; H, 4.6; N, 4.3%), and 5-hydroxy-4-benzoylacetylindane (from aqueous alcohol), m. p. 114—115° (Found: C, 77.2; H, 5.8. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.7%), were similarly prepared as yellow crystalline solids from the corresponding esters (nos. 17 and 18). The yields were respectively 75 and 85%.

Comparative experiments were made on the rates of transformation of 5-benzoyloxy-6-acetylindane (VI; R = Ph) and 5-benzoyloxy-4-acetylindane (VII) using solid potassium hydroxide in pyridine as described above. With 5-benzoyloxy-6-acetylindane there was an immediate colour change and separation of the salt of the diketone was complete in 30 minutes. With the 5:4-isomer, 30 minutes elapsed before separation of the diketone salt commenced, and complete reaction required some hours.

Preparation of 4-Pyrones.—These compounds (flavones; benzchromones; indanopyrones) were obtained from esters, through diketones, by the following three methods:

A. The diketone was boiled with glacial acetic acid containing a few drops of concentrated hydrochloric acid, and the pyrone formed was separated by addition of hot water until a permanent opalescence was produced. The liquid was then slowly cooled (see Doyle *et al.*, *loc. cit.*). The yields were usually quantitative.

B. The crude product (diketone) of the transformation which could not readily be purified was cleaned by Method A.

C. The flavone resulted directly by spontaneous cyclisation of the diketone formed in the transformation reaction.

Mononitrobenzoflavones. Table V summarises results for the mononitrobenzoflavones obtained from the esters listed in Table II.

TABLE V.

x-Nitro-*y*:*z*-benzflavones.(C₁₉H₁₁O₄N requires C, 71.9; H, 3.5; N, 4.4%)

Corresponding ester no. in Table II.	Nitrobenzflavone.			M. p.	Found, %.			Method of preparation of flavone.
	<i>x</i> .	<i>y</i> .	<i>z</i> .		C.	H.	N.	
1	2'	7	8	222—224°	71.7	3.9	4.1	A ¹
2	3'	7	8	258	71.7	3.5	—	A ²
3	4'	7	8	296	72.2	3.7	4.2	A ²
4	2'	5	6	214—215	71.5	3.8	4.4	B ¹
5	3'	5	6	256—257	72.3	3.9	4.4	C ¹
6	4'	5	6	282—284	71.4	3.6	4.3	A ¹
7	2'	6	7	192—194	71.7	3.2	4.6	B ¹
8	3'	6	7	248—250	72.0	3.7	4.8	A ¹
9	4'	6	7	264	71.7	3.7	4.5	A ¹

These compounds, No. 1 excepted, were crystallised from glacial acetic acid; for No. 1 acetone-alcohol was used. They separated from the solvent in colourless to pale yellow crystals.

¹ New compound.² Virkar, *loc. cit.*

Dinitrobenzflavones. 3':5'-Dinitro-3-(3:5-dinitrobenzoyl)-5:6-benzflavone (from glacial acetic acid and tetrahydrofurfuryl alcohol), m. p. 267—269° (Found: C, 56.8; H, 2.5; N, 10.0. $C_{26}H_{12}O_{11}N_4$ requires C, 56.1; H, 2.2; N, 10.1%), was obtained directly (method C) as a red powder in the transformation of 2-(3:5-dinitrobenzoyloxy)-1-acetonaphthone (III; R = 3:5-dinitrophenyl) (ester no. 11). 3':5'-Dinitro-6:7-benzflavone (from dioxan), m. p. 330° (decomp.) (Found: C, 62.5; H, 2.9; N, 7.6. $C_{19}H_{10}O_6N_2$ requires C, 63.0; H, 2.8; N, 7.7%), was similarly obtained as a yellow powder from 2-(3:5-dinitrobenzoyloxy)-3-acetonaphthone (IV; R = 3:5-dinitrophenyl) (ester no. 12).

Other pyrones. The following 4-pyrones were prepared from the corresponding diketones using method A. The number of the ester corresponding to the diketone is given in brackets. 6:7-Benzflavone (linear naphthaflavone) (13) (colourless; from benzene-ligroin), m. p. 173° (Virkar and Wheeler, *J.*, 1939, 1682, give 171—172°) (Found: C, 83.3; H, 4.5. Calc. for $C_{18}H_{12}O_2$: C, 83.8; H, 4.4%); 2-styryl-6:7-benzchromone (14) (pale yellow; from benzene-ligroin), m. p. 168° (Found: C, 84.2; H, 4.9. $C_{21}H_{14}O_2$ requires C, 84.6; H, 4.7%); 2-(2-methoxy-3-naphthyl)-6:7-benzchromone (15) (pale yellow; from benzene-ligroin), m. p. 214° (Found: C, 81.3; H, 3.5. $C_{24}H_{18}O_3$ requires C, 81.8; H, 4.5%); 6-phenylindano(5':6'-2:3)-4-pyrone (16) (colourless; from aqueous acetic acid), m. p. 161—162° (Found: C, 82.3; H, 5.5. $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.3%); 6-(*p*-nitrophenyl)indano(5':6'-2:3)-4-pyrone (17) (yellow; from aqueous acetic acid), m. p. 265—267° (Found: C, 70.3; H, 4.3; N, 4.7. $C_{18}H_{13}O_4N$ requires C, 70.4; H, 4.2; N, 4.6%).

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