Rearrangements of Chromanones and Dihydrocoumarins by Aluminium Chloride.

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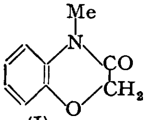
[Reprint Order No. 5625.]

By fusion with aluminium chloride chromanones and 3 : 4-dihydrocoumarins are rearranged to hydroxyindanones. 5 : 6-Benzochromanone and 3 : 4-dihydro-5 : 6-benzocoumarin respectively yield 9-hydroxy- and 4-hydroxy-perinaphthen-1-one (*via* dihydroperinaphthenones) while 4 : 5-benzocoumaranone yields 8-hydroxyacenaphthenone.

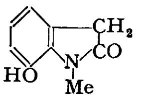
Chromanones are readily prepared by cyclisation of β-aryloxypropionic acids by means of polyphosphoric acid.

The rearrangement of 2 : 3-dihydro-4-methyl-3-oxobenz-1 : 4-oxazine (I) to the oxindole derivatives (II) and (III), through fusion with aluminium chloride (Cook, Loudon, and McCloskey, *J.*, 1952, 3904; Cook, Loudon, and Ogg, forthcoming publication), prompted investigation of similar fusion applied to compounds of the chromanone and dihydrocoumarin types. It was particularly desired to ascertain whether " abnormal " rearrangement, analogous to the change from (I) to (III), occurred. When fused with aluminium chloride chromanone (IV) afforded in good yield the known 7-hydroxyindanone (V), whereas dihydrocoumarin (VI) gave 4-hydroxyindanone (VII), which was identified by Clemmensen-reduction to 4-hydroxyindane, a compound similarly obtained from (V). Both rearrangement products are, therefore, normal. Moreover they were obtained throughout a range of fusion temperatures and it may be added that had (V) been formed from (VI) in significant amount its steam-volatility would have ensured its detection. On being fused with aluminium chloride 6-phenylchroman-4-one and 7-methoxychroman-4-one (the latter reacting *via* 7-hydroxychromanone) likewise afforded products which, on the basis of colour tests indicative of the *o*-hydroxy-ketonic structure, are also regarded as normal and, accordingly, as 7-hydroxy-4-phenylindanone and 5 : 7-dihydroxyindanone, respectively.

A convenient synthesis of chromanone derivatives is described by Bachman and Levine (*J. Amer. Chem. Soc.*, 1947, **69**, 2343; 1948, **70**, 599) who cyclised β-aryloxypropionitriles by means of concentrated sulphuric acid. The nitriles are readily available through cyanoethylation of phenols (cf. Cook and Reed, *J.*, 1945, 920) but the method of cyclisation fails when applied to the preparation of chromanone from β-phenoxypropionitrile and difficulty arising from sulphonation may be foreseen in other cases. However, β-aryloxypropionic acids are readily prepared by acid-hydrolysis of the nitriles and we have now found that these acids are smoothly cyclised to chromanones by polyphosphoric acid. This is the method of choice for preparing chromanone itself and it has given satisfactory results in the other cases here examined.



(I)



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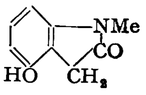

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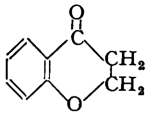

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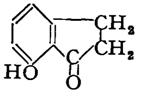
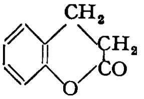
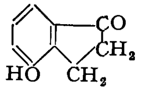


(V)

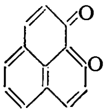


(VI)

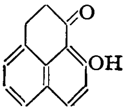


(VII)

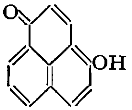
This route to chromanones, coupled with their rearrangement when fused with aluminium chloride, affords access to some interesting compounds. For instance, 5 : 6-benzochroman-4-one, prepared from β-naphthol, is converted into a mixture of 9-hydroxyperinaphthen-1-one (VIII) and the corresponding dihydro-compound (IX). The incidental dehydrogenation is commonly observed in cyclisation of β-1-naphthylpropionic acids (cf. Ansell and Berman, *J.*, 1954, 1792). The two products are interconvertible by hydrogenation–dehydrogenation procedures and are separable through the formation of a hydrochloride from (VIII). 9-Hydroxyperinaphthen-1-one was first described by Koelsch and Anthes (*J. Org. Chem.*, 1941, **6**, 558) who obtained it through cyclisation and incidental dephenylation of 1-cinnamoyl-2-methoxynaphthalene by aluminium chloride in benzene. Re-examination of its properties confirms its character as a strongly hydrogen-bonded compound. This emerges from its comparison with the dihydro-compound (IX) and with the isomeric 4-hydroxyperinaphthen-1-one (X). This last compound was prepared by fusing 3 : 4-dihydro-5 : 6-benzocoumarin with aluminium chloride and dehydrogenating the product. Of the three compounds, (VIII), (IX), and (X)—for which ultra-violet absorption data are given in the experimental section—only the first persistently resisted reaction with the usual reagents at the carbonyl or hydroxyl centres. On the other hand substitution in the ring-system of (VIII) is quite readily achieved, and in these laboratories Mr. J. K. Sutherland prepared monobromo- and mononitro-derivatives which, however, were not oriented.



(VIII)



(IX)



(X)

Fusion of 4 : 5-benzocoumaranone with aluminium chloride likewise afforded a phenolic product which is regarded as 8-hydroxyacenaphthenone.

EXPERIMENTAL

Petroleum as solvent refers to light petroleum, b. p. 40—60°. Except where otherwise stated fusion with aluminium chloride means that the mixture was gradually heated to the given temperature(s) where it was maintained for the stated time before being cooled, powdered, and treated with ice–hydrochloric acid; thereafter the product was extracted with ether, the extract washed with aqueous sodium carbonate and then with dilute sodium hydroxide, and phenolic material, liberated by acidification of the latter solution, was recovered in ether. All m. p.s were uncorrected.

Chromanone.—β-Phenoxypropionitrile (1 g.) (Cook and Reed, *loc. cit.*) was heated under reflux (2 hr.) with concentrated hydrochloric acid (40 c.c.) and water (20 c.c.), the cooled solution depositing β-phenoxypropionic acid as needles, m. p. 96—97° (from water). The powdered acid (3·1 g.) was slowly added to a mixture of phosphoric oxide (96 g.) and phosphoric acid (40 c.c.; *d*, 1·7) which had been pre-heated at 100° (30 min.) with exclusion of moisture. After 2 hr. at 100° the whole was added to ice–water and the gum, recovered in benzene and distilled at 130—132°/15 mm., afforded chromanone (2·4 g.), m. p. 39° (from petroleum), which was characterised as the semicarbazone, m. p. 227°.

7-*Hydroxyindanone.*—A mixture of chromanone (1·5 g.) and anhydrous, powdered aluminium chloride (2·7 g.) was fused at 180—190° (20 min.) and then at 200° (15 min.). 7-Hydroxyindanone was recovered in steam as silky needles, m. p. 111° (from methanol). Light absorption in ethanol: $\lambda_{\text{max.}}$ 3175, 2755, 2200 Å; log ε 3·52, 4·1, 4·32. The compound gave the characteristic deep-blue colour with ferric chloride in ethanol and afforded the semicarbazone, m. p. 242° (from ethanol) (cf. von Auwers and Hillinger, *Ber.*, 1916, **49**, 2412). Examination of the alkali-soluble, non-volatilised portion of the product gave only more of the same compound (total yield 65—70%) and similar results were obtained when the initial reaction was conducted at 220° (¾ hr.).

A mixture of 7-hydroxyindanone (0·2 g.), amalgamated zinc (2 g.), water (200 c.c.), and concentrated hydrochloric acid (10 c.c.) was heated for 1 hr. with occasional addition of dilute hydrochloric acid and then for 2 hr. with similar addition of concentrated acid. The gum, recovered in ether from the cooled solution, afforded 4-hydroxyindane, m. p. 49° (from petroleum) (cf. Arnold and Zaugg, *J. Amer. Chem. Soc.*, 1941, **63**, 1317) (Found: C, 80·4; H, 7·3. Calc. for $C_9H_{10}O$: C, 80·5; H, 7·5%).

7-*Methoxyindanone.*—A mixture of 7-hydroxyindanone (0·3 g.), potassium carbonate (0·75 g.), methyl iodide (1 c.c.), and acetone (20 c.c.) was heated under reflux for 4 hr. After removal of solvent, water (30 c.c.) was added; recovery in benzene afforded 7-*methoxyindanone* as plates, m. p. 102—103° (from benzene–petroleum) (Found: C, 74·4; H, 6·3. $C_{10}H_{10}O_2$ requires C, 74·0; H, 6·2%).

4-*Hydroxyindanone.*—Dihydrocoumarin (1·5 g.) (cf. Borsche and Weinheimer, *Ber.*, 1952, **85**, 200) was fused with aluminium chloride at 170—180° (3 hr.). 4-*Hydroxyindanone*, as platelets (0·7 g.), m. p. 239—240° (from methanol), was the sole phenolic product, no steam-volatile material being detected and similar results being obtained when fusion was effected at 210° (1 hr.) and 230° (1 hr.) (Found: C, 72·7; H, 5·6. $C_9H_8O_2$ requires C, 72·9; H, 5·4%). Light absorption in ethanol: $\lambda_{\text{max.}}$ 3125, 2575, 2250 Å; log ε 4·43, 4·94, 5·4. With ferric chloride in ethanol the compound gave a red-brown colour and on Clemmensen-reduction it afforded 4-hydroxyindane, m. p. and mixed m. p. 48—49°.

4-*Methoxyindanone.*—The 4-methoxy-compound, m. p. 102—103° (from methanol), was prepared as described for its isomer, with which a mixed m. p. was 68—82° (Found: C, 74·0; H, 6·5%).

6-*Phenylchromanone.*—4-Hydroxydiphenyl (3 g.), acrylonitrile (8 g.), and sodium methoxide (0·2 g.) were heated in an autoclave at 140—150° for 5 hr. The excess of acrylonitrile was removed *in vacuo*, and the resultant solid, after being washed with aqueous sodium hydroxide, afforded β-p-*phenylphenoxypropionitrile*, m. p. 124° (from methanol) (Found: C, 81·1; H, 6·0; N, 6·5. $C_{15}H_{13}ON$ requires C, 80·8; H, 5·8; N, 6·4%). The nitrile (1 g.), when heated (1·5 hr.) with sulphuric acid (20 c.c.; 50%), gave β-p-*phenylphenoxypropionic acid* as plates, m. p. 173° (from ethanol) (Found: C, 74·1; H, 6·0. $C_{15}H_{14}O_3$ requires C, 74·3; H, 5·8%). This acid, treated with phosphoric oxide–phosphoric acid as described for chromanone, yielded 6-*phenylchromanone* as fine needles, m. p. 71—72° (from ethanol) (Found: C, 80·0; H, 5·6. $C_{15}H_{12}O_2$ requires C, 80·3; H, 5·4%).

7-*Hydroxy*-4-*phenylindanone.*—To a melt of sodium chloride (2·5 g.) and aluminium chloride (2 g.) at 160° powdered 6-phenylchromanone (0·5 g.) was added and heating was continued at 185—190° for 40 min. The phenolic product was conveniently purified by passage in methanol through a short column of charcoal, affording 7-*hydroxy*-4-*phenylindanone* as plates, m. p. 123—124° (from methanol) (Found: C, 80·5; H, 5·7. $C_{15}H_{12}O_2$ requires C, 80·3; H, 5·4%). Light absorption in ethanol: $\lambda_{\text{max.}}$ 3275, 2425 Å; log ε 3·55, 4·46. The compound gave an intense blue colour with ferric chloride in ethanol and with sodium hydroxide formed a sparingly soluble, pale yellow sodium salt, m. p. 275—277°.

7-*Methoxychromanone.*—β-*m*-Methoxyphenoxypropionitrile (15 g.) (Bachman and Levine, *loc. cit.*) when heated (2·5 hr.) with concentrated hydrochloric acid (150 c.c.) and water (75 c.c.) afforded the corresponding acid, m. p. 80—81° (Pfeiffer and Oberlin, *Ber.*, 1924, **57**, 210, give m. p. 81—83°), which was cyclised, by phosphoric oxide–phosphoric acid, to 7-methoxychromanone, m. p. 52—54° (cf. Bachman and Levine, *loc. cit.*). This chromanone (1 g.), when fused with aluminium chloride (1·5 g.) at 130—140° (½ hr.), was demethylated, forming 7-*hydroxy*-

chromanone, m. p. 140°, from boiling water (charcoal) then from ethyl acetate (Found: C, 65·8; H, 4·55. $C_9H_8O_3$ requires C, 65·85; H, 4·9%). This was identified by remethylation to 7-methoxychromanone, m. p. and mixed m. p. 52—53°, and was characterised by acetylation to 7-*acetoxychromanone*, m. p. 94—95° (from methanol) (Found: C, 64·3; H, 4·9. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%).

4 : 7-*Dihydroxyindanone*.—When the foregoing fusion was carried out at 210° (½ hr.) the phenolic product was a gum. This was extracted with boiling light petroleum (b. p. 80—100°) to which a few drops of ethanol had been added. Slow evaporation of the solvent then gave a small quantity of 4 : 7-*dihydroxyindanone* as needles, m. p. 195—196° (from ethanol) (Found: C, 65·6; H, 4·8. $C_9H_8O_3$ requires C, 65·85; H, 4·9%). Light absorption in ethanol: $\lambda_{max.}$ 2780, 2300, 2200 Å; log ε 4·24, 4·23, 4·24. The compound gave an intense violet colour with ferric chloride in ethanol, and a deep yellow colour when heated with boroacetic anhydride in acetic anhydride. With hot acetic anhydride containing a trace of concentrated sulphuric acid it formed 4 : 7-*diacetoxyindanone*, m. p. 90—91° (from ethanol) (Found: C, 62·8; H, 4·9. $C_{13}H_{12}O_5$ requires C, 62·9; H, 4·9%).

9-*Hydroxyperinaphthen*-1-*one* (VIII).—(*a*) 5 : 6-Benzochroman-4-one (2 g.) (Bachman and Levine, *loc. cit.*) was heated with powdered aluminium chloride (2·7 g.) first at 100° and then for 1 hr. at 190—200° with stirring. The phenolic products were isolated as sparingly soluble sodium salts which were treated with acid, and the resultant yellow solid was recovered in ether and sublimed at 190°/20 mm. A solution of the sublimate in benzene was treated with dry hydrogen chloride causing precipitation of a hydrochloride. This was hydrolysed by hot ethanol from which 9-hydroxyperinaphthen-1-one crystallised as yellow plates (1 g.), m. p. 199—200° (Found: C, 79·4; H, 4·2. Calc. for $C_{13}H_8O_2$: C, 79·5; H, 4·1%). (*b*) A mixture of the dihydro-compound (IX; cf. below) (0·05 g.) and palladised charcoal (0·02 g.; 20%) was heated (45 min.) at 180°; the foregoing compound (VIII), m. p. and mixed m. p. 200°, was recovered in methanol.

9-Hydroxyperinaphthen-1-one had light absorption in ethanol: $\lambda_{max.}$ 4400, 4300, 4150, 3500, 2650, 2350 Å; log ε 4·08, 3·87, 3·95, 4·25, 3·95, 4·4. It gave a deep red-brown colour with ferric chloride in ethanol and was recovered unchanged from treatment with: acetic anhydride–sulphuric acid; diazomethane in ether or ether–methanol; methyl toluene-*p*-sulphonate and potassium carbonate in boiling nitrobenzene; methyl sulphate (on the sodium salt) in boiling xylene; and hydroxylamine in boiling ethanol. When added to fuming nitric acid (5 c.c.; *d*, 1·51) or heated (10 min. at 100°) with concentrated nitric acid (5 c.c.; *d*, 1·42) it (0·5 g.) yielded a *nitro*-derivative, m. p. 235° (decomp.) (from acetic acid) (Found: C, 64·6; H, 3·2; N, 6·1. $C_{13}H_7O_4N$ requires C, 64·7; H, 2·9; N, 5·8%) and, when brominated in cold acetic acid, afforded a *bromo*-derivative, m. p. 184—186° (from acetic acid) (Found: C, 56·5; H, 2·7; Br, 29·0. $C_{13}H_7O_2Br$ requires C, 56·7; H, 2·6; Br, 29·1%).

2 : 3-*Dihydro*-9-*hydroxyperinaphthen*-1-*one* (IX).—(*a*) The benzene filtrate from the preparation of (VIII) (*a*, above) was washed with aqueous sodium carbonate and then with water, dried, and concentrated *in vacuo*. The resultant solid afforded the *dihydro*-compound (IX) as stout, straw-coloured needles (0·4 g.), m. p. 137—138° (from methanol) (Found: C, 78·7; H, 5·2. $C_{13}H_{10}O_2$ requires C, 78·8; H, 5·1%). (*b*) The same compound was obtained, m. p. and mixed m. p. 137°, when (VIII) was hydrogenated (4 hr.) over palladium-black in acetic acid. 2 : 3-Dihydro-9-hydroxyperinaphthen-1-one had light absorption in ethanol: $\lambda_{max.}$ 3625, 3225, 2400, 2225 Å; log ε 3·76, 3·8, 4·16, 4·67. With ferric chloride in ethanol it gave a red-brown colour which gradually became green. It afforded a 2 : 4-*dinitrophenylhydrazone* as red needles, m. p. 265—266° (decomp.) (from benzene) (Found: C, 60·5; H, 3·5; N, 14·7. $C_{19}H_{14}O_5N_4$ requires C, 60·3; H, 3·7; N, 14·8%). When its solution in acetic anhydride was treated with a drop of concentrated sulphuric acid and heated just to boiling, then cooled and diluted with water, the *acetate* was obtained, m. p. 104—105° (from methanol) (Found: C, 74·8; H, 5·1. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%). Attempts to prepare the methyl ether yielded neutral gums which did not crystallise.

4-*Hydroxyperinaphthen*-1-*one* (X).—3 : 4-Dihydro-5 : 6-benzocoumarin (1 g.) (Hardman, *J. Amer. Chem. Soc.*, 1948, **70**, 2119) was fused (10 min.) with aluminium chloride (1·35 g.) at 140—145°. The recovered phenolic gum was heated (4 hr.) with palladised charcoal (0·1 g.; 20%) in trichlorobenzene. The product, recovered in alkali and precipitated by acid, afforded 4-*hydroxyperinaphthen*-1-*one* as orange needles (0·3 g.), m. p. 266—267° (from ethanol; charcoal) (Found: C, 79·5; H, 4·1. $C_{13}H_8O_2$ requires C, 79·6; H, 4·1%. Microhydrogenation with palladium in acetic acid indicated 0·94 double bond). Light absorption in ethanol: $\lambda_{max.}$ 4225, 3375, 3200, 2625 Å; log ε 4·12, 3·52, 3·50, 4·43. The compound gave a red-brown colour with ferric chloride in ethanol; afforded an *acetate*, m. p. 120° (from aqueous acetic acid) (Found:

C, 75·4; H, 4·4. $C_{15}H_{10}O_3$ requires C, 75·6; H, 4·25%), and a *methyl ether*, m. p. 53° (from ethanol–water) (Found: C, 79·8; H, 4·8. $C_{14}H_{10}O_2$ requires C, 79·9; H, 4·8%), and reacted with 2 : 4-dinitrophenylhydrazine although a crystalline product was not obtained.

8-*Hydroxyacenaphthenone*.—4 : 5-Benzocoumaranone (0·9 g.) (Ingham, Stephen, and Timpe, *J.*, 1931, 895) was fused with aluminium chloride (1·4 g.) at 180—190° (1 hr.) affording in poor yield 8-*hydroxyacenaphthenone* as pale-yellow crystals, m. p. 156—157° (from ethanol; charcoal) (Found: C, 78·3; H, 4·3. $C_{12}H_8O_2$ requires C, 78·3; H, 4·4%). It gave an intense green colour with ferric chloride in ethanol.

Our thanks are due to Professor J. W. Cook, F.R.S., for his interest in this work, and one of us (R. K. R.) is indebted to the Government of India and to the University of Glasgow for a Maintenance Allowance.

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[*Received, August* 16*th*, 1954.]