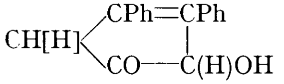
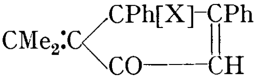
273. *Anionotropic and Prototropic Changes in Cyclic Systems. Part V. The System derived from 1-Hydroxyindene.*

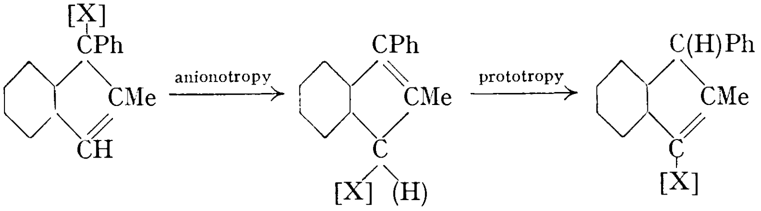
By HAROLD BURTON and CHARLES W. SHOPPEE.

PREVIOUS communications (J., 1933, 720; 1934, 197, 201, 205) have dealt with systems exhibiting consecutive anionotropic and prototropic changes, but possessing structural features additional to those solely required for the realisation of such changes. Thus, the possible participation of the methylenic hydrogen atom [H] in the prototropic changes undergone by the diphenyl*cyclo*pentenonol (I), and the possibility of anionotropic changes involving the double linking in the *iso*propylidene group of the analogous *iso*propylidene derivatives (II), were undesirable features. That such changes did not occur to any appreciable extent was proved only by laborious experimental work.

(I.) 

 (II; X = OH or Cl.)

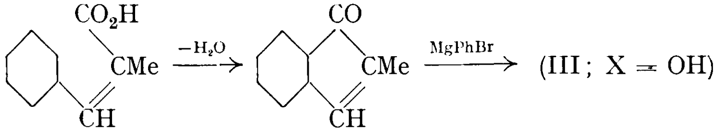
It seemed, therefore, of interest to examine the simplest system in which such consecutive tautomeric changes of opposite polar type might be expected to occur. Having regard to the constitutional factors which have been shown to control the occurrence of such changes (Burton, J., 1928, 1650; Ingold and Shoppee, J., 1929, 1199), an indene of type (III) appeared to represent the simplest system * complying with these conditions. The mobility of the anion [X] will be promoted by the presence of two phenyl groups attached to the carbon atom bearing the potential anion, and since the structure possesses the necessary Δ^2-unsaturation, substantially complete transformation into the isomeric indene (IV) should occur.



(III.) (IV.) (V.)

The structure (IV) contains a three-carbon prototropic system; the requisite grouping $C_\gamma = C_\beta - C_\alpha(H)$ is present as part of the indene ring, the high prototropic mobility of which is well known (Ingold and Piggott, J., 1923, **123**, 1469), and is related to the special properties of the indene structure (Goss and Ingold, J., 1928, 1268); hence the prototropic change (IV ⟶ V) should be very easily accomplished under the appropriate conditions.

The foregoing anticipations have been completely realised. 1-*Hydroxy*-1-*phenyl*-2-*methylindene* (III; X = OH) was synthesised from phenylmagnesium bromide and 2-methylindenone, the last compound being obtained by dehydration of *cis*-α-methylcinnamic acid (Stoermer and Vöht, *Annalen*, 1915, **409**, 55):



The hydroxyindene must possess the structure (III; X = OH), and not the isomeric structure (IV; X = OH), which might conceivably have arisen from anionotropy of the Grignard compound (III ⟶ IV; X = OMgBr) (cf. Gilman and Harris, *J. Amer. Chem. Soc.*, 1931, **53**, 3541), since it was completely unaltered by treatment with boiling alcoholic potassium hydroxide; in these circumstances the compound, had it possessed the constitution (IV), would have afforded the indanone (VI) (see below).

By treatment with boiling acetic anhydride, the hydroxyindene (III; X = OH) was completely converted into an *acetate*, which we regard as possessing structure (VIII), since hydrolysis does not regenerate the original compound. The acetate is undoubtedly formed by way of the isomeride (VII), which could not be isolated. We suggest that the ease of acetylation of the tertiary alcohol (III) is intimately connected with the circumstance that

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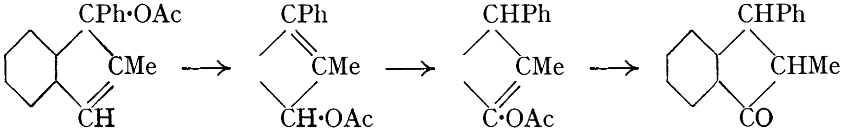
* The variants of X usually employed are OH, OAc, and Cl. The methyl group in position 2 was introduced to preclude the unlikely possibility of complications arising from elimination of HX.

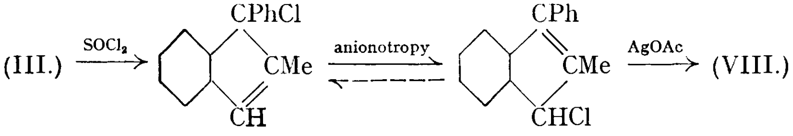
the hydroxyl group is the potential anion of an anionotropic system. The acetate (VIII) exists in two physical forms: (α) m. p. 75—76° to a turbid liquid, clearing at 91°; (β) m. p. 91—92°; they can be interconverted by nucleation of a solution in ligroin with the appropriate form. Ozonolysis of the acetate (VIII) in glacial acetic acid, and reduction of the ozonide with zinc dust in ethereal solution gave a neutral oil containing unidentified ketonic and/or aldehydic substances.



(VII.) (VIII.) (IX.) (VI.)

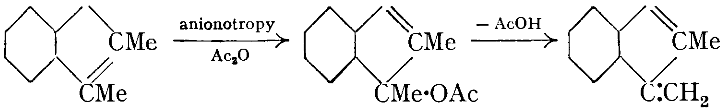
The acetate (VIII) when refluxed with 5% alcoholic potassium hydroxide passed almost quantitatively into 3-phenyl-2-methylindanone (VI), by way of the acetate (IX), which is that of the enolic form of (VI). The large degree of completion of the change (VIII ⟶ IX), which is contrary to the expected effect of the γ-phenyl group on the prototropic equilibrium (VIII $\rightleftharpoons$ IX) (cf. Shoppee, J., 1930, 973), is probably due to the continuous removal of (IX) by hydrolysis and subsequent ketonisation. The ketone (VI) was characterised by its 2 : 4-dinitrophenylhydrazone, identified by direct comparison with a specimen obtained by Ingold and Wilson's method (J., 1933, 1498).

When the alcohol (III; X = OH) is treated with thionyl chloride, a single crystalline *chloride* is formed; the chlorine atom of this is virtually ionic and reacts very easily with silver acetate in acetic acid to give an 85% yield of the acetate (VIII). We therefore regard the chloride as 1-*chloro*-3-*phenyl*-2-*methylindene* (XI), formed from the precursor (X) by anionotropic change. The reactivity of the chlorine atom is primarily dependent upon its participation in the triad anionotropic system $C = C - C[Cl]$. The present case constitutes a clear and unambiguous example; no alternative explanation for the reactivity of the chlorine atom is possible, as in previous examples containing an adjacent, activating carbonyl group.



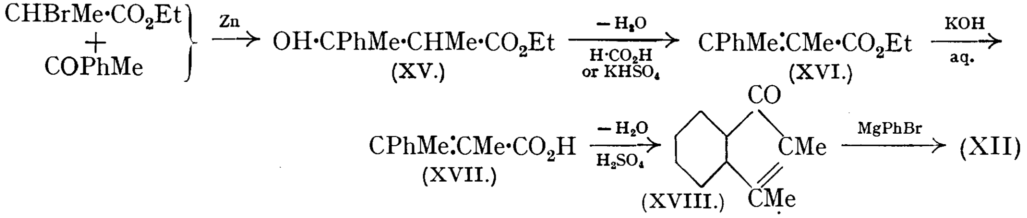
(X.) (XI.)

We have also investigated the homologous 1-*hydroxy*-1-*phenyl*-2 : 3-*dimethylindene* (XII). This alcohol should be capable of anionotropy but not of prototropy, owing to the presence of the methyl group in the 3-position, so acetylation should furnish a tertiary acetate (XIII), which might then pass, by loss of acetic acid, into the unsaturated hydrocarbon (XIV). Treatment of (XII) with boiling acetic anhydride gave a red amorphous polymeride, whilst the use of acetic anhydride containing a trace of sulphuric acid at 0° yielded a yellow amorphous polymeride. The analytical figures for the latter (O = 2·1% by difference) indicate the incomplete occurrence of some process analogous to [(XIII, O = 11·5%) ⟶ (XIV, O = nil)], with subsequent polymerisation.



(XII.) (XIII.) (XIV.)

Although Ingold and Wilson (*loc. cit.*) state that the product obtained by the action of zinc and an α-bromo-aliphatic ester on an aryl alkyl ketone, gives, on dehydration, an ethylene derivative of the wrong geometrical form for cyclisation, we experienced no difficulty in preparing 2 : 3-*dimethylindenone* (XVIII) by the following series of reactions :



Actually, Rupe, Steiger, and Fiedler (*Ber.*, 1914, **47**, 65) record that the mixture of isomeric αβ-dimethylcinnamic acids (XVII) obtained by using formic acid as the dehydrating agent, when treated with cold concentrated sulphuric acid, gave a ketonic substance, m. p. 78° ; this was not further investigated by these workers, but we have identified it as (XVIII), and have characterised it by the preparation of the 2 : 4-*dinitrophenylhydrazone* and the *semicarbazone.*

We record these observations in some detail, because von Braun (*Annalen*, 1926, **451**, 47) was unable to repeat the work of Rupe, Steiger, and Fiedler. He states that the hydroxy-ester (XV) undergoes partial dehydration on vacuum distillation, and that the mixture of ethyl αβ-dimethylcinnamates (XVI), obtained by completing the dehydration process with potassium hydrogen sulphate, on hydrolysis with potassium hydroxide under the conditions described by Rupe, Steiger, and Fiedler, undergoes almost complete fission to acetophenone. We find that the hydroxy-ester (XV) distils without decomposition, that dehydration with either 85% formic acid or potassium hydrogen sulphate gives the ester (XVI) (accompanied by traces of ethyl β-phenyl-α-methyl-Δ^{β}-butenoate), and that hydrolysis with potassium hydroxide of specimens of the esters prepared by either method, under Rupe's conditions, affords a mixture of *cis*- and *trans*-αβ-dimethylcinnamic acids (XVII) ; fission to acetophenone does occur, but to the extent of only 8%.

EXPERIMENTAL.

2-*Methylindenone.*—*trans*-α-Methylcinnamic acid, m. p. 81°, was readily obtained by condensation of ethyl propionate and benzaldehyde with sodium, and hydrolysis of the resulting ester (cf. Stoermer and Vöht, *loc. cit.*). Conversion into the *cis*-isomeride was accomplished by irradiation of the *trans*-acid, either molten or preferably in hot carbon tetrachloride solution, in a concentric quartz cell using a straight type of vacuum mercury burner, both supplied by the Thermal Syndicate. The apparatus was kept cool by compressed air playing on to the cell. With the molten acid, some discoloration occurred after 48 hrs.' irradiation; the melt was poured into a shallow dish, allowed to solidify, finely powdered, and added to concentrated sulphuric acid (500 c.c.) at — 2° with vigorous mechanical stirring during 5 mins. After a further 15 mins.' stirring, the purple liquid was poured on crushed ice, and the product extracted twice with ether. The combined extracts, after being washed with 2*N*-sodium carbonate, dried (potassium carbonate), and evaporated under a column, gave 2-methylindenone (6 g.), b. p. 121—123°/17 mm., m. p. 47°. Acidification of the alkaline washings yielded unaltered *trans*-acid (80 g.) ; this was purified by esterification with methyl alcohol containing 10% of sulphuric acid, vacuum distillation of the methyl ester (m. p. 38°), and hydrolysis of the last with aqueous methyl-alcoholic potassium hydroxide, and re-irradiated. A repetition of the irradiation process, using the *trans*-acid (70 g.) in carbon tetrachloride for 70 hrs., gave 5 g. of the indenone and 62 g. of recovered *trans*-α-methylcinnamic acid.

1-*Hydroxy*-1-*phenyl*-2-*methylindene* (III; X = OH).—To the freshly-prepared 2-methylindenone (6 g.), dissolved in ether (25 c.c.) at 0°, a filtered solution of phenylmagnesium bromide (1 mol. ; from magnesium, 1·2 g. ; bromobenzene, 7·8 g. ; ether, 50 c.c.) was added. The product, after standing for 3 hrs., was decomposed with ice-cold ammonium chloride solution, and extracted with ether. The dried and evaporated extract was fractionated in a vacuum, giving 1-*hydroxy*-1-*phenyl*-2-*methylindene* (4·5 g.), b. p. 157°/0·6 mm. The alcohol crystallised when a solution in ligroin was kept at 0° for some time; two recrystallisations from ligroin (b. p. 40—60°) gave colourless prisms, m. p. 59° (2·5 g.) (Found : C, 86·2; H, 6·3. $C_{16}H_{14}O$ requires C, 86·5; H, 6·35%). A small lower-boiling fraction was treated with semicarbazide acetate in aqueous alcohol; after 48 hrs. the precipitate was collected, dried, extracted with ligroin (b. p. 60—80°) which removed some diphenyl, and crystallised from alcohol, the yellow semicarbazone, m. p. 192° (decomp.), of 2-methylindenone being obtained (Found: C, 65·4; H, 5·5. Calc. for $C_{11}H_{11}ON_3$: C, 65·7; H, 5·5%) (cf. Stoermer and Vöht, *loc. cit.*).

1-*Acetoxy*-3-*phenyl*-2-*methylindene*.—1-Hydroxy-1-phenyl-2-methylindene (1·0 g.) was refluxed with acetic anhydride (10 c.c.) for 7 hrs.; after decomposition of the excess of acetic anhydride with cold water, the product was extracted with ether, the extract washed with 2*N*-sodium carbonate, dried (potassium carbonate), and evaporated. The residual oil soon crystallised, and the *acetate*, twice recrystallised from ligroin (first b. p. 40—60°, then b. p. 60—80°), slowly formed colourless, rhombic prisms of the α-*acetate*, m. p. 75—76°, to a turbid liquid which clears at 90—91°, and when allowed to cool and reheated has m. p. 91—92° [Found: C, 81·7; H, 6·0; *M*(Rast), 230, 221. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%; *M*, 264]. A second similar preparation was divided into two parts; one part was dissolved in ligroin (b. p. 60—80°) and the cooled solution seeded with a trace of material, m. p. 90—91°, whereupon the β-*acetate*, m. p. 90—91°, separated rapidly in well-formed needles [Found: C, 81·5; H, 6·2%; *M*(Rast), 233, 236]; similar seeding with a trace of the α-form slowly yielded the α-acetate. A mixture of the α- and the β-form in approximately equal parts melted sharply at 90—91°.

3-*Phenyl*-2-*methylhydrindanone* (VI).—The α-acetate, m. p. 75—76° (0·5 g.), was refluxed with 5% alcoholic potassium hydroxide for 2 hrs.; the product was poured into water, and extracted with ether. After drying (potassium carbonate) and evaporation, 3-phenyl-2-methylindanone remained as a pale yellow oil, which gave no colour with ferric chloride, and was characterised (see Brady, J., 1931, 756) as the 2 : 4-dinitrophenylhydrazone, red needles from alcohol, m. p. 179°, alone or mixed with an authentic specimen (Found: C, 65·3; H, 4·5; N, 13·7. Calc. for $C_{22}H_{18}O_4N_4$: C, 65·6; H, 4·5; N, 13·9%) (cf. Ingold and Wilson, *loc. cit.*). A similar experiment with the β-acetate, m. p. 91—92°, gave the same dinitrophenylhydrazone, m. p. 179°; in both cases the yields of hydrazone were nearly quantitative.

1-*Chloro*-3-*phenyl*-2-*methylindene* (XI.)—1-Hydroxy-1-phenyl-2-methylindene (1·5 g.) was refluxed with thionyl chloride (5 c.c.) for 0·5 hr., and the product poured on crushed ice. After ether extraction, washing of the extract with water, drying, and evaporation, a yellow oil remained which distilled at 150—160°/0·6 mm.; it then crystallised when rubbed with cold ligroin, and after two recrystallisations from ligroin (b. p. 40—60°), 1-*chloro*-3-*phenyl*-2-*methylindene* (0·8 g.) separated as yellow needles, m. p. 47° (Found: C, 79·5; H, 5·5; Cl, 15·0. $C_{16}H_{13}Cl$ requires C, 79·8; H, 5·45; Cl, 14·8%). The chloride (0·75 g.), an equal weight of silver acetate, and glacial acetic acid (5 c.c.) were heated under reflux; silver chloride was formed rapidly. The product was filtered from excess silver acetate, the filtrate poured into 2*N*-sodium carbonate, and extracted with ether. Drying and evaporation yielded a yellow oil which rapidly crystallised (0·66 g.); two recrystallisations from ligroin (b. p. 60—80°) gave the β-acetate, m. p. 91—92°, mixed m. p. 91—92°; a specimen of this, dissolved in ligroin and seeded with a trace of the α-form, slowly yielded the α-acetate, m. p. 75—76°.

Ethyl β-*Hydroxy*-β-*phenyl*-α-*methylbutyrate*.—This ester (145 g.), b. p. 141°/10 mm., was readily obtained by condensation of acetophenone (110 g.), ethyl α-bromopropionate (162 g.), and zinc (70 g.) in pure benzene (200 g.). No indication of dehydration during vacuum distillation was observed (cf. von Braun, *loc. cit.*).

Ethyl αβ-*Dimethylcinnamate*.—(*a*) The above hydroxy-ester (145 g.) was boiled under reflux for 6 hrs. with twice its volume of 85% formic acid (cf. Rupe, Steiger, and Fiedler, *loc. cit.*). The cooled product was poured into water, extracted with ether, washed repeatedly with 2*N*-sodium carbonate, and dried (potassium carbonate). Fractionation of the oil obtained by evaporation gave ethyl αβ-dimethylcinnamate (73 g.), b. p. 130°/12 mm.; a considerable quantity of lower-boiling material, probably αβ-dimethylstyrene (b. p. 80°/20 mm.), was also produced. Ozonolysis of the ester and decomposition of the ozonide with boiling water gave traces of formaldehyde, indicating the presence of a minute quantity of ethyl β-phenyl-α-methyl-Δ^{β}-butenoate. The non-volatile fission products were not further examined.

(*b*) The hydroxy-ester (60 g.) and potassium hydrogen sulphate ("AnalaR") (120 g.) were heated together at 150° for 4 hrs. (cf. von Braun, *loc. cit.*); the product was dissolved in ether, the ethereal solution dried (potassium carbonate) and evaporated; fractionation of the resulting oil yielded ethyl αβ-dimethylcinnamate (43 g.), b. p. 128—129°/10 mm.

cis- *and* trans-αβ-*Dimethylcinnamic Acids*.—(i) The foregoing product (*a*) (70 g.) was refluxed with aqueous potassium hydroxide (35 g. in 175 c.c. of water) until complete solution was effected (*ca.* 3 hrs.) (cf. Rupe, Steiger, and Fiedler, *loc. cit.*). The product was cooled, diluted, and extracted twice with ether; the ethereal extract, washed with water, dried (potassium carbonate), and evaporated, was distilled, whereby acetophenone (4 g.), b. p. 200—205° (semicarbazone, m. p. 201°), was obtained; a small residue of higher-boiling material, probably unhydrolysed ester, remained. The alkaline aqueous liquor was acidified with ice-cold 10*N*-sulphuric acid, and extracted with ether. The dried and evaporated solution gave an oil (55 g.), consisting principally of *cis*-αβ-dimethylcinnamic acid, which gave a deep blue colour with cold concentrated sulphuric acid. The oil slowly deposited a small quantity of the crystalline *trans*-acid.

(ii) Similarly, 43 g. of preparation (*b*) were hydrolysed, and there were obtained 2·5 g. of acetophenone (semicarbazone, m. p. 201°) and 30 g. of oily acid which also gave the above colour reaction.

2 : 3-*Dimethylindenone* (XVIII).—(*a*) The liquid mixture of *cis*- and *trans*-αβ-dimethylcinnamic acids (45 g.) was added during 15 mins. to concentrated sulphuric acid (500 c.c.) at 12—15°; the mixture was stirred for a further 5 mins., and poured on crushed ice. The product was extracted twice with ether, the ethereal extract washed with water, and with successive quantities of 2*N*-sodium carbonate until acidification of the washings gave no turbidity. After drying (potassium carbonate), and evaporation under a column, a yellow oil remained which crystallised rapidly. Thrice recrystallised from ligroin (b. p. 60—80°), 2 : 3-*dimethylindenone* separates in yellow plates, m. p. 80° (yield 9 g.) (Found: C, 83·3; H, 6·2. $C_{11}H_{10}O$ requires C, 83·5; H, 6·4%). The 2 : 4-*dinitrophenylhydrazone* forms crimson-red prisms from ethyl acetate; m. p. 273—274° (decomp. after darkening) (Found: C, 60·3; H, 4·2. $C_{17}H_{14}O_4N_4$ requires C, 60·35; H, 4·1%); the *semicarbazone* crystallises from alcohol in yellow prisms, m. p. 197° (decomp.) (Found: C, 67·0; H, 6·1; N, 19·5. $C_{12}H_{13}ON_3$ requires C, 67·0; H, 6·1; N, 19·5%).

The acid recovered from the alkaline washings gave a yellow colour when dissolved in cold concentrated sulphuric acid, and on keeping, set to a glass filled with minute crystals of the *trans*-acid.

(*b*) Ethyl β-hydroxy-β-phenyl-α-methylbutyrate (6 g.) was added during 5 mins. to concentrated sulphuric acid (60 c.c.) at 10—12°, with the instantaneous production of a deep blue solution. After being stirred for a further 15 mins., during which the temperature was allowed to fall to 3°, the mixture was poured on crushed ice, and extracted with ether. The extract, after removal of acidic substances, drying, and evaporation, crystallised in part to yield 2 : 3-dimethylindenone, m. p. 80° [2 : 4-dinitrophenylhydrazone, m. p. 273° (decomp.)]; the residual oil was not examined, but probably consisted of ethyl αβ-dimethylcinnamate and unchanged ester. Acidification of the alkaline washings yielded a small quantity of a crystalline acid; this, twice crystallised from ligroin (b. p. 40—60°), separated in well-formed prisms, m. p. 107—108°, and was identified as slightly impure *trans*-αβ-dimethylcinnamic acid (Found: C, 73·3; H, 6·8. Calc. for $C_{11}H_{12}O_2$: C, 74·9; H, 6·9%) (cf. Rupe, Steiger, and Fiedler, *loc. cit.*). The acid dissolved in cold concentrated sulphuric acid to a colourless solution.

1-*Hydroxy*-1-*phenyl*-2 : 3-*dimethylindene* (XII).—A filtered solution of phenylmagnesium bromide (2 mols.; from magnesium, 3·1 g.; bromobenzene, 20·4 g.; ether, 50 c.c.) was added to a solution of 2 : 3-dimethylindenone (10·2 g.) in ether (25 c.c.) at 0°. After standing for some hours, the mixture was decomposed with ice, 2*N*-hydrochloric acid added, the product extracted with ether, dried, and evaporated. Distillation afforded 1-*hydroxy*-1-*phenyl*-2 : 3-*dimethylindene* (10 g.) as a yellow oil, b. p. 175°/0·4 mm. (Found: C, 85·9; H, 7·0. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%), which could not be induced to crystallise. All attempts to convert this substance into a homogeneous acetate or unsaturated hydrocarbon failed. Prolonged treatment with boiling acetic anhydride gave a red amorphous substance, and acetic anhydride containing a trace of sulphuric acid at 0° afforded a yellow amorphous polymeride, decomp. *ca.* 200° after softening and darkening from 180° [Found: C, 91·6; H, 6·3%; *M*(Rast), 783]. Neither polymeride on ozonolysis gave detectable amounts of formaldehyde.

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