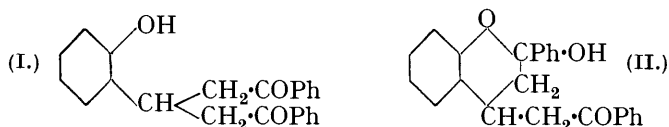


**261. Reactions of *o*-Hydroxybenzylidenediacetophenones. Part V.
Functional Group Reactions of Salicylidenediacetophenone.**

By A. S. GOMM and DOUGLAS W. HILL.

THE suggestion (Part I; J., 1934, 1255) that the *o*-hydroxybenzylidenediacetophenones (I) might be better formulated as chromanols (II), is supported by the following considerations. (a) The diketones are insoluble in alkali although the corresponding chalcones are readily soluble. (b) They give no coloration with ferric chloride. (c) Their dehydration

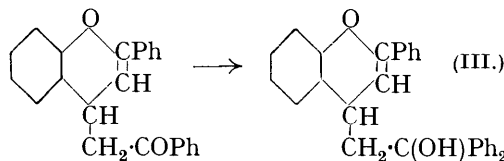


by glacial acetic acid to 4-phenacylflavens closely resembles the conversion of 2-chromanols into Δ^2 -chromenes (Löwenbein, *Ber.*, 1924, **57**, 1517; Heilbron and Hill, J., 1927, 2005). On the other hand, the formation of substituted pyrylium salts (Hill, this vol., p. 85) may be adduced as evidence in favour of (I).

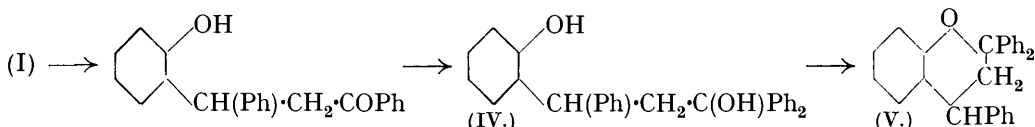
We have attempted to decide between these formulæ by a study of the reactions of the two functional groups—phenolic hydroxyl and ketone. Cornelson and Kostanecki (*Ber.*, 1896, **29**, 240) found that salicylidenediacetophenone could be acetylated by heating with acetic anhydride and sodium acetate. This method affords only poor yields, but that of Pratt and Robinson (J., 1925, **127**, 1184) gives yields exceeding 90%. Methylation of the phenolic group with, *e.g.*, methyl sulphate and alkali could not be used, since the alkali might easily open the ring in a chromanol of type (II). The use of diazomethane, which reacts normally only with acidic hydroxyls (Nierenstein, *Ber.*, 1927, **60**, 1820; Meerwein and Hinz, *Annalen*, 1930, **484**, 1), is not open to this criticism. The hydroxyl group is not easily methylated under the conditions employed, but small yields of a methyl derivative

were isolated which agreed in all respects with the *o*-methoxybenzylidenediacetophenone described by Pfeiffer (*Annalen*, 1917, **412**, 308).

Examination of the ketonic groups could not be made with reagents requiring acid solution for obvious reasons, and recourse was therefore had to a study of the reaction with phenylmagnesium bromide by a comparison of the products from the diketone and the 4-phenacylflavene derived from it. The latter compound reacted normally to form 4-(β -hydroxy- $\beta\beta$ -diphenylethyl)flavene (III), but the products resulting from the diaceto-



phenone were dependent on the conditions: in boiling benzene solution it yielded a compound from which 2 : 2 : 4-triphenylchroman (V) was obtained, but in cold ethereal solution the product was a colourless compound, m. p. 185°, which is probably the intermediate $\alpha\alpha\gamma$ -triphenyl- γ -(*o*-hydroxyphenyl)-*n*-propyl alcohol (IV). The isolation of this



compound is paralleled by the isolation by Heilbron and Hill (*loc. cit.*) of a similar intermediate compound from the reaction between phenylmagnesium bromide and 4 : 7-dimethylcoumarin. We submit that the formation of these three compounds appears to be explicable only on the basis of formula (I), since if (II) were correct, the diacetylflavene and the flavene should give the same products.

The formation of the carbinol (IV) and the triphenylchroman (V) may be accounted for by the ready elimination of one of the acetyl groups (see Part II; cf. also Klingemann, *Annalen*, 1895, **275**, 53). This behaviour would cause the diacetylflavene to resemble the $\alpha\beta$ -unsaturated ketones, so that the addition of the Grignard reagent would follow Kohler's rule (*Amer. Chem. J.*, 1907, **38**, 511), giving, in this instance, 1 : 4-addition as the first stage of the reaction to yield α -phenyl- α -(*o*-hydroxyphenyl)propionophenone, from which the carbinol and the chroman would result normally.

Attempts to effect reaction between phenylmagnesium bromide and 4-phenacylidene-flavene were unsuccessful (cf. Irvine and Robinson, *J.*, 1927, 2086, who could not induce 6-methoxy-4-phenacylidene-flavene to react).

The evidence presented here appears to favour the diketone formula (I), but its acceptance leaves us still without an explanation of the insolubility of the compounds in alkali or their failure to give a colour reaction with ferric chloride. It is more probable that the two forms (I) and (II) are tautomeric.

EXPERIMENTAL.

Acetylation of Salicylidenediacetophenone.—The diacetylflavene (5 g.) was dissolved in acetic anhydride (20 c.c.) by warming, and the solution was cooled while anhydrous potassium carbonate (5 g.) was added to it in small quantities. After standing over-night, it was poured into water. The light brown oil which separated soon solidified, and was purified by crystallisation from dilute alcohol; m. p. 83° (5.1 g.).

Methylation with Diazomethane.—The diacetylflavene (5 g.) suspended in ether (250 c.c.) was treated with diazomethane (from 5 c.c. of nitrosomethylurethane). After standing for 24 hours, the ether was evaporated, leaving a pale yellow oil (5 g.) which solidified on scratching. This was fractionally crystallised from alcohol and yielded 1.7 g. of pure unchanged starting material, m. p. 128°, and 0.6 g. of pure *o*-methoxybenzylidenediacetophenone, m. p. and mixed m. p. 113°.

*$\alpha\alpha\gamma$ -Triphenyl- γ -(*o*-hydroxyphenyl)-*n*-propyl Alcohol.*—Phenylmagnesium bromide (from

24 g. of bromobenzene) in ether (200 c.c.) was added slowly (2 hrs.) with stirring and cooling to a suspension of salicylidenediacetophenone (5 g.) in ether (200 c.c.). After standing over-night, the complex was decomposed by ice-cold 10% ammonium chloride. The residual oil, after steam distillation, solidified on cooling, and was extracted with ether which, after drying, was evaporated. It deposited a colourless solid, which was purified by several recrystallisations from alcohol; m. p. 185° (Found: C, 85.8; H, 6.0. $C_{27}H_{24}O_2$ requires C, 85.3; H, 6.3%).

2:2:4-Triphenylchroman.—A solution of phenylmagnesium bromide (from 30 g. of bromobenzene) in ether (200 c.c.) was added slowly to a boiling solution of salicylidenediacetophenone (10 g.) in benzene (250 c.c.). The reaction mixture was boiled for a further hour, then kept over-night, and decomposed by 2% hydrochloric acid; after removal of the solvent the residue was distilled in steam. A pale yellow solid remained in the flask. It was filtered off, and crystallised from alcohol several times, being obtained finally as hard, colourless rhombs, m. p. 216—217° (Found: C, 89.3; H, 6.0. $C_{27}H_{22}O$ requires C, 89.5; H, 6.1%).

4-(β -Hydroxy- $\beta\beta$ -diphenylethyl)flavene.—A solution of 4-phenacylflavene (2 g.) in boiling benzene (100 c.c.) was treated as described above with phenylmagnesium bromide (from 3 g. of bromobenzene) in ether (100 c.c.). The residue after steam distillation was a brown solid, which was repeatedly crystallised from alcohol and obtained as fine, colourless needles, m. p. 194° (Found: C, 85.9; H, 5.9. $C_{26}H_{24}O_2$ requires C, 86.1; H, 5.9%).

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