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ACID-CATALYSED CONDENSATION OF FORMALDEHYDE WITH SOME PHENOLIC KETONES

IN connection with the synthesis of homocupressuflavone hexamethyl ether, the required intermediate, *viz.*, 3, 3′-methylenebis phloracetophenone-4, 6-O-dimethyl ether was prepared by the acid-catalysed condensation of formaldehyde (formalin) with phloracetophenone-4, 6-O-dimethyl ether[1,2]. We have studied similar condensations with other phenolic ketones and some of the results are reported in this communication.

Resacetophenone-4-O-methyl ether gave, on reaction with formalin and aqueous sulphuric acid (35%), four products A, B, C and D which were separated by fractional crystallisation from acetone: Compound A, m.p. 204–5° (diacetate, 188–9°), compound B, m.p. 255–6° (diacetate, 161–2°), Compound C, m.p. 161–2° and Compound D, m.p. 181–2° (acetate, 161–2°). Their PMR spectral data (60 MHz, δ, $CDCl_3$) are given below:

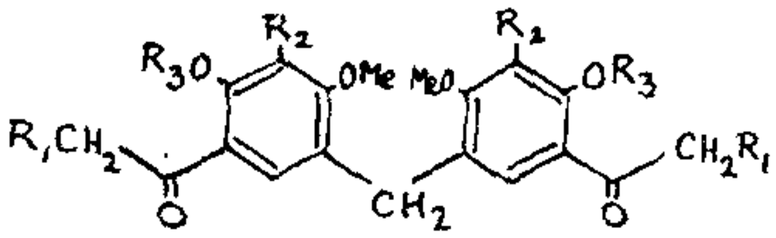
Compound A: 2·58 (s, 6H, two $CO-CH_3$), 3·96 (s, 2H, $-CH_2-$), 4·06 (s, 6H, two OCH_3), 6·75 (s, 2H two C_3–Ar H), 7·26 (s, 2H, two C_6–Ar H), 10·09 (s, 2H, two chelated OH).

Compound B diacetate: Since the compound B is not easily soluble in deuterochloroform, the PMR spectrum of its diacetate was recorded.

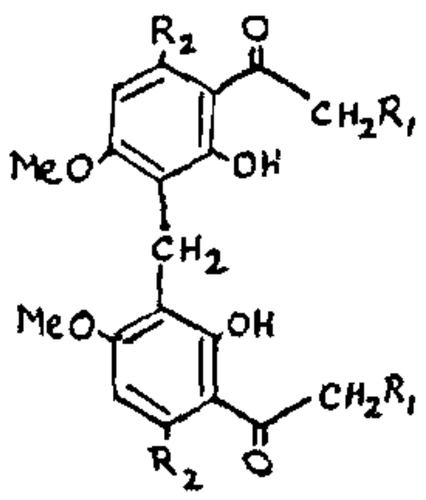
2·2 (s, 6H, two $CO-CH_3$), 2·45 (s, 6H, two $O-COCH_3$), 3·82 (s, 6H, two OCH_3), 3·9 (s, 2H, $-CH_2-$), 6·78 (d, 2H, J=9 Hz, two C_5–Ar H), 7·76 (d, 2H, J=9 Hz, two C_6–Ar H).

Compound C (90 MHz): 2·24 (s, 3H, $CO-CH_3$), 2·6 (s, 3H, $CO-CH_3$), 3·92 (s, 2H, $-CH_2-$), 3·98 (s, 6H, two $-OCH_3$), 6·55 (s, 1H, C_3–Ar–H), 6·7 (d, 1H, J=12 Hz, C_5–Ar H), 7·32 (s, 1H, C_6'–ArH), 7·95 (d, 1H, J=12 Hz, C_6–Ar H), 13·08 (s, 1H, chelated OH), 13·2 (s, 1H, chelated OH).

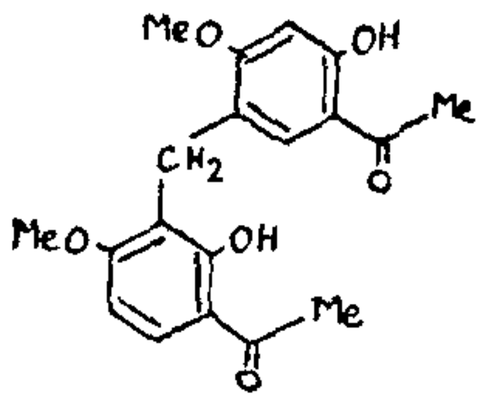
On the basis of the analytical and the PMR data the structures Ia, IIa and III were assigned to A, B and C respectively. The structure of the compound D is under investigation.



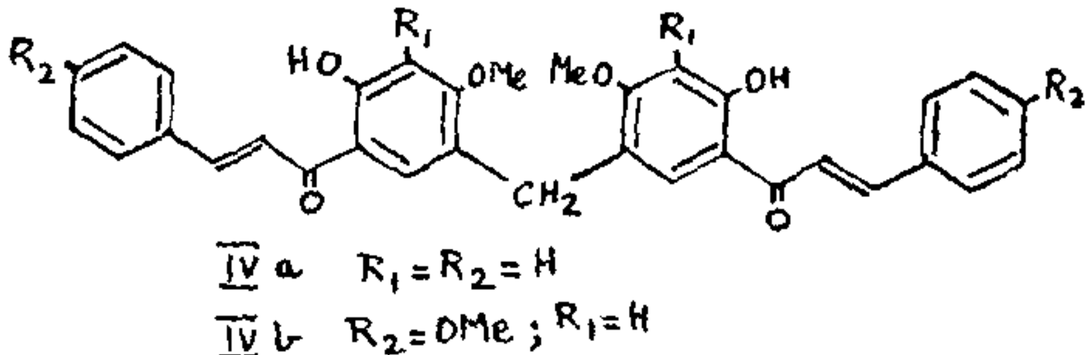
Ia $R_1=R_2=R_3=H$
Ib $R_2=OMe$; $R_1=R_2=H$
Ic $R_1=OMe$; $R_2=R_3=H$
Id $R_3=Bz$; $R_1=R_2=H$



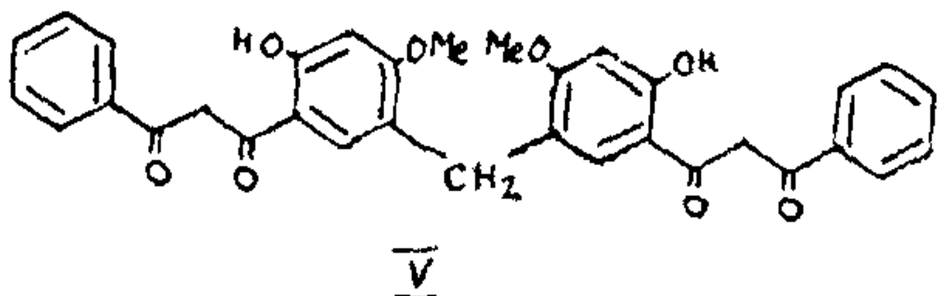
IIa $R_1=R_2=H$
IIb $R_1=R_2=OMe$



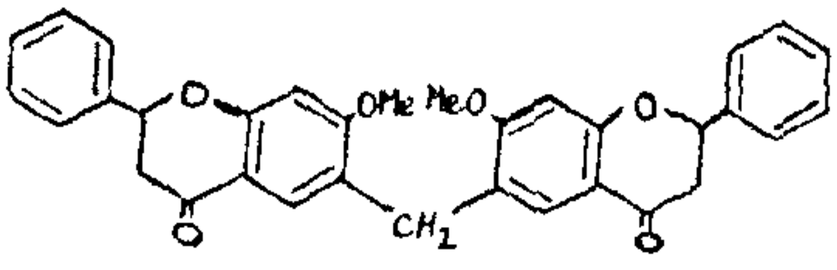
III



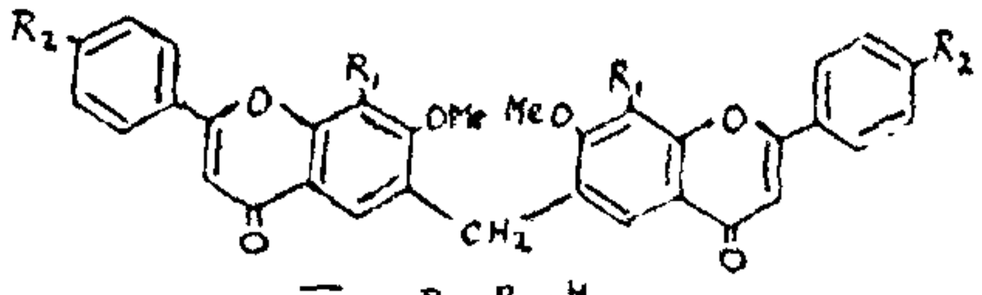
IVa $R_1=R_2=H$
IVb $R_2=OMe$; $R_1=H$
IVc $R_1=OMe$; $R_2=H$
IVd $R_1=R_2=OMe$



V



VII



VIa $R_1=R_2=H$
VIb $R_2=OMe$; $R_1=H$
VIc $R_1=OMe$; $R_2=H$

Compound Ia was converted into the homobichalcones (IV *a*), m.p. 219–21° (IV *b*), m.p. 239–40°. (IV *a*), was isomerised to the homobiflavanone, (VII), m.p. 233–5° by refluxing with alcoholic sulphuric acid. The homobichalcones (IV *a*) and (IV *b*), on oxidative cyclisation with selenium dioxide in boiling isoamyl alcohol solution yielded the homobiflavones (VI *a*) and (VI *b*), which did not melt below 360°. The homobiflavone (VI *a*) was also synthesised from (I *a*) via the dibenzoate, (I *d*), m.p. 201–3° and the tetraketone (V), m.p. 195–6°.

Gallacetophenone-3, 4-O-dimethyl ether gave, on refluxing with formalin and aqueous sulphuric acid, (I *b*), m.p. 141–2°. This compound was converted into the homobichalcones (IV *c*), m.p. 194–6° and (IV *d*), m.p. 186–7°. (IV *c*), could be oxidized with selenium dioxide in boiling isoamyl alcohol solution to the homobiflavone, (VI *c*) m.p. 275°. Similarly, ω-methoxy-resacetophenone-4-O-methyl ether yielded (I *c*) m.p. 152° (dibenzoate, m.p. 95–6) and ω-methoxy-4, 6-O-dimethyl ether gave (II *b*), m.p. 232–4° (monobenzoate, m.p. 176–8°).

The formation of only one condensation product from gallacetophenone-3, 4-di-O-methyl ether is as expected since the condensation will take place only in the position para to the phenolic hydroxyl group. However, similar condensation with ω-methoxy-phloracetophenone-4, 6-di-O-methyl ether yielded only one isolable product while four products could be obtained in pure form from the reaction with resacetophenone-4-O-methyl ether. TLC examination of the mother liquors from the crystallisation of (I *c*) showed the presence of at least three compounds, but attempts to isolated them in pure condition were not successful.

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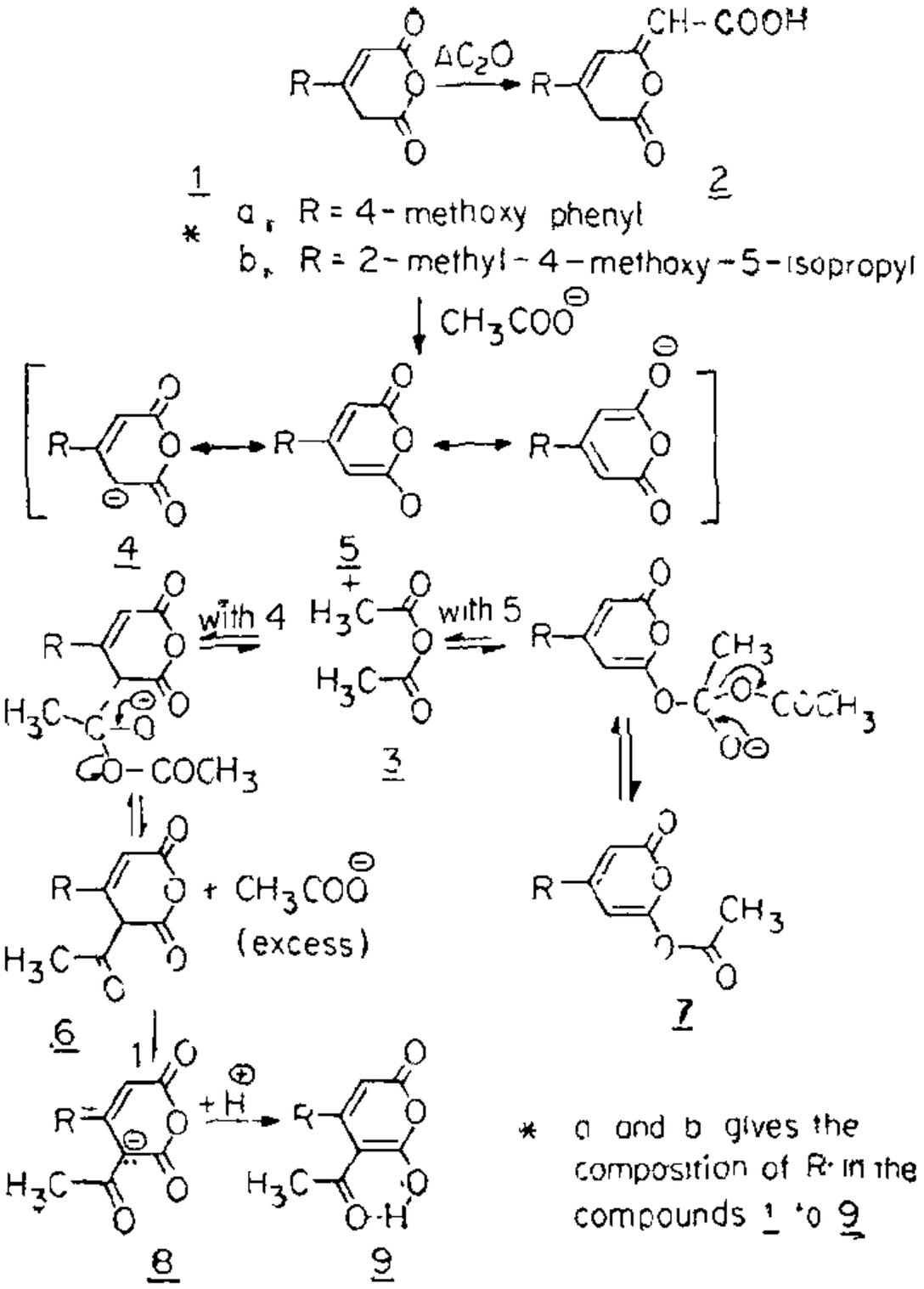
A REGIOSPECIFIC C-ACYLATION OF 3-ARYL PENT-2-ENE-1, 5, DIOIC ANHYDRIDES UNDER CONDITIONS OF THE PERKIN REACTION

(ON mechanistic grounds the 3-aryl pent-2-ene-1, 5-dioic anhydrides should undergo a regiospecific C-acylation with sodium acetate-acetic anhydride mixture and not yield the α, β-unsaturated carboxylic acids as reported by earlier workers. This postulation has been confirmed on the basis of ir and nmr studies of the condensation products).

Under condition of the Perkin reaction anhydrides of 3-aryl pent-2-ene-1, 5-dioic acids **1**, are reported to yield the corresponding glutaconyl acetic acids **2**[1,2] (Chart 1) similar to products obtained by application of the Perkin reaction to phthalic anhydride[3,4].

On mechanistic grounds the attack of the enolate anion of Ac_2O on the carbonyl carbon to yield **2** seems remote in view of the fact that the carbonyl carbon would not be susceptible to a nucleophilic attack due to the extensive delocalization possible with the adjoining π-system.



A more probable mechanism operating in this condensation would be one which has some of the flavour of both the aldol addition and the claisen condensation (Chart 1). Thus, the 3-aryl pent-2-ene-1, 5-dioic anhydrides would undergo a regiospecific C-acylation to yield the 4-acetyl-3-aryl pent-2-ene-1, 5-dioic anhydrides 6. This would naturally be expected to exist exclusively in the enol form because of the stabilization possible in this form by delocalization of the π-bond and the formation of an intra-molecular hydrogen bond.

These postulations stood confirmed on subjecting the condensation product to a spectral scrutiny. Spectral evidence positively identified the product as a C-acylated anhydride in the enol form **9**. In the ir spectrum the strong absorption band at 1,760 cm^{-1} with a slight split associated with νC=O, along with the