Synthesis of Succin-as-eins*

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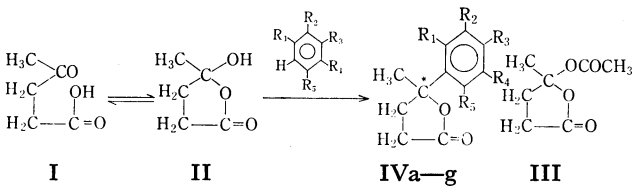
(Received February 12, 1973)

A new series of compounds, succin-as-eins(SAE)—methyl phenol SAE, methyl resorcinol SAE, methyl catechol SAE, methyl quinol SAE, methyl phloroglucinol SAE, methyl pyrogallol SAE and methyl orcinol SAE have been prepared by condensing 2-acetyl propionic acid with appropriate phenols. The structure of methyl resorcinol SAE, based on chemical reactions and spectral data is discussed. The λ_{max} values for few of the dyes are comparable with their analogous succineins and phthaleins.

2-Acetyl propionic acid (I) has been shown to be a mixture of ring (II) and chain (I) tautomers by various workers.[2-4] The lactol (II), which yields well crystalline acetyl derivative (III),[5] on condensation with phenols gave a new series of compounds, succin-as-eins (IV). The condensation process proceeds through the equilibrium process of lactol (II) of acid (I) and with excess of phenol whole of the acid reacts as lactol.

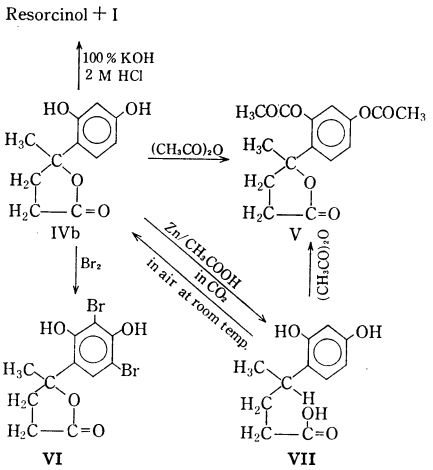
Seven succin-as-eins (SAE)—methyl phenol SAE (IVa), methyl resorcinol SAE (IVb), methyl catechol SAE (IVc), methyl quinol SAE (IVd), methyl phloroglucinol SAE (IVe), methyl pyrogallol SAE (IVf) and methyl orcinol SAE (IVg) have been prepared by condensing acid (I) with respective phenols.



I II IVa—g III

(IVa) $R_1=R_2=R_4=R_5=H$; $R_3=OH$
(IVb) $R_2=R_4=R_5=H$; $R_1=R_3=OH$
(IVc) $R_3=R_4=R_5=H$; $R_1=R_2=OH$
(IVd) $R_2=R_3=R_5=H$; $R_1=R_4=OH$
(IVe) $R_2=R_4=H$; $R_1=R_3=R_5=OH$
(IVf) $R_4=R_5=H$; $R_1=R_2=R_3=OH$
(IVg) $R_2=R_4=H$; $R_5=CH_3$; $R_1=R_3=OH$
(V) $R_2=R_4=R_5=H$; $R_1=R_3=OCOCH_3$
(VI) $R_5=H$; $R_2=R_4=Br$; $R_1=R_3=OH$

The column chromatography, supplemented with thin-layer chromatography, was used for the purification of condensed products. Their IR (KBr) spectra show a strong band at 1760 cm^{-1} due to γ-lactone. The KOH treatment of IVb followed by acid hydrolysis yielded resorcinol and the acid (I). The dye (IVb; 1760 cm^{-1}) when refluxed with Zn-dust and acetic acid gave methyl resorcinol succin-as-in[6] (VII; IR (KBr) bands at 3600—3000 cm^{-1}, -OH in -COOH; 1700 cm^{-1}, >CO in -COOH). The acid (VII) on acetylation gave diacetyl compound (V). The diacetyl (V; IR (KBr) bands at 1760, 1200, and 1125 cm^{-1} due to γ-lactone and phenolic acetate) and dibromo (VI; 1760 cm^{-1}, γ-lactone) derivatives of IVb are also indicative of resorcinol molecule in it.



The absorption maxima (λ_{max}) of SAE (IV) given in Table 1 have been found comparable with their analogous succineins and phthaleins.

Experimental

All melting points are uncorrected. The λ_{max} (UV and visible) have been recorded on model DU-2 Beckmann Spectrophotometer and IR determined using a Perkin-Elmer Infracord.

The phenols have been taken in a little excess of molecular proportion than the acid (I). Conc H_2SO_4 (4—6 drops) was used as a condensing agent throughout.

Methyl Resorcinol SAE (IVb). An intimate mixture of acid (I) (5 g) and resorcinol (5 g) was heated at 120 °C for 2 hr. Conc H_2SO_4 (4—6 drops) was added cautiously and the heating was continued for additional 6 hr at 160 °C. The brittle product was extracted with 3% NaOH and precipitated with dil HCl. The precipitate was chromatographed over silica gel with chloroform–acetone mixture (80: 20). The third fraction (200 ml) on crystallization gave a red crystalline dye (6.4 g), mp 300 °C, which dissolved with yellow-red colour in ethanol while in alkali (pH, 8) gave a bright pink-violet colour with light green fluorescence.

The preparation of the rest of compounds given in Table 1 was done in identical manner as described in IVb above taking acid (I) and appropriate phenols (yield, 60—65%).

* Owing to unsymmetric central carbon atom (C*) present in IV they may be named as succin-as-eins; -as representing unsymmetry and -ein the class of compound (Succin-ein[1]).

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TABLE 1. PREPARATION AND PROPERTIES OF METHYL SUCCIN-AS-EINS (IV)

Dyes	Condensation Temp (°C)	Condensation Time (hr)	Mp (°C)	Appearance	λ_{max}^{EtOH} (mμ); ε Neutral	λ_{max}^{EtOH} (mμ); ε at (pH)	Found % C	Found % H	Calcd % C	Calcd % H
IVa	110	12	225	Brown	—	411(9.0); 426	68.92	5.98	68.75	6.25
IVb	160	6	300	Red	480; 850	500(8.3); 1183	63.42	5.70	63.46	5.77
IVc	170	4	300	Dark brown	—	465(10.2); 619	63.74	5.54	63.46	5.77
IVd	170	4	300	Dark brown	—	a)	63.66	5.62	63.46	5.77
IVe	180	2.5	300	Dark red	—	470(8.4); 1142	58.82	5.54	58.92	5.36
IVf	160	5	300	Dark brown	—	485(8.6); 1366	58.86	5.44	58.92	5.36
IVg	140	1.5	300	Brown	—	500(10.0); 1966	65.10	6.12	64.86	6.30

a) The alkaline solution decomposed during the measurement of λ_{max} value.

Acetylation of IVb. The dye (IVb) (0.5 g), acetic anhydride (10 ml) and fused sodium acetate (1 g) were refluxed at 130—140 °C for 3 hr to give pale yellow crystalline diacetyl compound (V) (0.5 g), mp 190 °C (from 80% ethanol); $\lambda_{max}^{EtOH}(\varepsilon)$ 330 (3358).

Found: C, 61.82; H, 5.28; CH_3CO, 29.28%. Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.48; CH_3CO, 29.45%.

Bromination of IVb. The dye (0.5 g) was dissolved in ethanol (10 ml) and to this solution Br_2 (1 ml) was slowly added with stirring. It was refluxed for 45 min, on a water bath to give red crystalline dibromo compound (from 90% ethanol) (VI; 0.6 g), mp 300 °C; λ_{max}^{EtOH} (at neutral and at pH, 8.5) (ε) 530 (1390).

Found: Br, 43.96%. Calcd for $C_{11}H_{14}O_4Br_2$: Br, 43.7%.

Potassium-hydroxide Treatment of IVb. The dye (IVb) (2 g) and aqueous KOH (100%, 25 ml) were refluxed for 1 hr. The solution was diluted with 500 ml water and acidified with dil HCl, filtered and washed well with water. The solid residue was boiled with acidic water (50 ml, 1 ml 2 M HCl) to give the acid (I), mp 37 °C (lit,[4] mp 33—35 °C); bp 137—139 °C/10 mmHg (lit,[4] bp 137—139 °C/10 mmHg); amide, mp 106 °C (lit,[5] mp 107 °C); acetyl, mp 77 °C (lit,[5] mp 78 °C).

The light brown filtrate from solid residue was extracted with ether to give resorcinol (0.9 g), mixed mp 110 °C and identical IR with its authentic sample.

Zn-dust Reduction of IVb. The dye (IVb) (2 g) was refluxed in glacial acetic acid (100 ml) with Zn-dust (5 g) for 15 min, to yield a colourless crystalline acid (VII; 1.7 g), mp 245 °C, which does not give fluorescence in alkaline solution.

Found: C, 63.02; H, 6.48%. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.66%.

The acid (VII) when left overnight changed to red compound IVb, with superimposible IR and the same λ_{max} values. The acetylation of the mixture of acid (VII) and red compound was carried out as in V above to give diacetyl (V), mixed mp and identical IR, λ_{max} values and elemental analysis.

The authors are grateful to Dr. J. D. Tewari for his useful suggestions. A grant and fellowship (to R. G.) from CSIR, New Delhi is acknowledged.

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6) The nomenclature is according to "The Chemistry of Carbon Compounds" Vol. IIIB, ed. by E. H. Rodd, Elsevier, New York (1956), p. 1110.