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Synthesis of Succin-as-eins. III.[1] Dyes Derived from β-Benzoylpropionic, β-(3-Acenaphthoyl)propionic and β-(α-Thenoyl)propionic Acids

R. GOPAL,* P. C. GUPTA, and S. P. GARG**
Department of Chemistry, University of Allahabad, India

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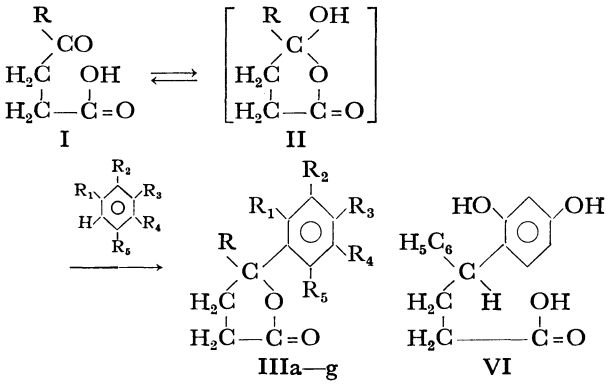
Synopsis. A number of succin-as-eins have been prepared by condensing β-benzoylpropionic, β-(3-acenaphthoyl)propionic and β-(α-thenoyl)propionic acids with phenol, resorcinol, catechol, quinol, phloroglucinol, pyrogallol and orcinol.

The γ-keto acids have been found to cyclize to their γ-hydroxylactones,[2] which yield acetyl derivatives[3-5] retaining their cyclic structures. The β-benzoylpropionic acid[6] (I: R=C_6H_5), β-(3-acenaphthoyl)propionic acid[7] (I: R=$C_{12}H_9$) and β-(α-thenoyl)propionic acid[8] (I: R=C_4H_3S) gave a new series of cyclic compounds succin-as-eins (IIIa—g)[1,9] on condensation with phenols such as phenol, resorcinol, catechol, quinol, phloroglucinol, pyrogallol and orcinol.

The IR (KBr) spectra of IIIa—g, IV and V show strong bands between 1760—1755 cm^{-1} (γ-lactone). The dye (IIIb: R=C_6H_5) (1760 cm^{-1}) on reduction with Zn-dust and acetic acid gave phenyl resorcinol succin-as-in (VI; IR (KBr) bands at 3600—3000 cm^{-1}, -OH in -COOH; 1700 cm^{-1}, >CO in -COOH) (*cf.*, methyl resorcinol succin-as-in[9]). The acid (VI) when left overnight was found changed into IIIb (R=C_6H_5).



IIIa: $R_1=R_2=R_4=R_5=H$; $R_3=OH$
IIIb: $R_2=R_4=R_5=H$; $R_1=R_3=OH$
IIIc: $R_3=R_4=R_5=H$; $R_1=R_2=OH$
IIId: $R_2=R_3=R_5=H$; $R_1=R_4=OH$
IIIe: $R_2=R_4=H$; $R_1=R_3=R_5=OH$
IIIf: $R_4=R_5=H$; $R_1=R_2=R_3=OH$
IIIg: $R_2=R_4=H$; $R_5=CH_3$; $R_1=R_3=OH$
IV: $R_2=R_4=R_5=H$; $R_1=R_3=OCOCH_3$
V: $R_5=H$; $R_2=R_4=Br$; $R_1=R_3=OH$

Scheme 1.

TABLE 1. PREPARATION AND PROPERTIES OF PHENYL SUCCIN-AS-EINS (III: R=C_6H_5) AND ACENAPHTHYL SUCCIN-AS-EINS (R=$C_{12}H_9$)

Dyes	Condensation Temp (°C)	Condensation Time (h)	Mp (°C)	Appearance	λ_{max}^{EtOH} (mm); ε Neutral	λ_{max}^{EtOH} (mm); ε at (pH)	Found % C	Found % H	Calcd % C	Calcd % H
IIIa (R=C_6H_5)	150	5	280	Brown	—	412 (9.2); 4572	75.32	5.44	75.59	5.51
IIIb (R=C_6H_5)	170	6	>300	Shining red	460; 2943, 480; 2808	500 (9.1); 3294	70.86	5.04	71.11	5.18
IIIc (R=C_6H_5)	140	5	>300	Light brown	—	a)	70.90	5.20	71.11	5.18
IIId (R=C_6H_5)	140	5	206	Black	—	a)	71.14	4.92	71.11	5.18
IIIe (R=C_6H_5)	150	2	255	Dark red	—	475 (8.2); 2803	66.88	5.04	67.13	4.89
IIIf (R=C_6H_5)	140	4	300	Black	—	a)	66.92	5.16	67.13	4.89
IIIg (R=C_6H_5)	140	3½	185	Dirty yellow	—	495 (9.5); 2158	71.64	5.38	71.83	5.63
IIIa (R=$C_{12}H_9$)	150	3	>300	Brown	—	430 (9.8); 2719	79.64	5.18	80.00	5.45
IIIb (R=$C_{12}H_9$)	170	1/2	140	Deep red	530; 761	580 (9.5); 1041	75.90	5.60	76.30	5.20
IIIc (R=$C_{12}H_9$)	150	1	200	Light brown	—	a)	76.02	4.94	76.30	5.20
IIId (R=$C_{12}H_9$)	170	1	160	Dark yellow	—	a)	76.68	4.88	76.30	5.20
IIIe (R=$C_{12}H_9$)	180	1/4	170	Brown red	—	430, 450 (9.2); 4344	72.54	4.59	72.92	4.97
IIIf (R=$C_{12}H_9$)	180	1/4	>300	Dark brown	—	a)	73.30	4.61	72.92	4.97
IIIg (R=$C_{12}H_9$)	170	1/2	195	Dark red	—	a)	76.39	5.26	76.66	5.55
IV (R=C_6H_5)	140	5	128	Pale yellow	360; 6372	—	67.56	4.82	67.79	5.08
IV (R=$C_{12}H_9$)	140	3½	95	Pale yellow	370; 8600	—	72.88	4.84	72.56	5.11
V (R=C_6H_5)	130	2	>300	Red	530; 1849	530 (9.1); 2825	Br, 37.52%		Br, 37.35%	
V (R=$C_{12}H_9$)	30	5	125	Deep red	590; 2460	590 (9.0); 2460	Br, 31.50%		Br, 31.12%	

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

* Present address: Defence Laboratory, Jodhpur, India.

** Present address: Dept. of Chemistry, University of Jodhpur, Jodhpur, India.

Table 2. Preparation and properties of thenyl succin-as-eins (III; $R=C_4H_3S$)

Dyes	Condensation Temp (°C)	Time (h)	mp (°C)	Appearance	λ_{max}^{EtOH} (mm); ε Neutral	at (pH)	Found % C	H	S	Calcd % C	H	S
IIIa ($R=C_4H_3S$)	110	6	215	Brown	—	420 (9.0); 5200	64.29	4.32	12.01	64.61	4.60	12.30
IIIb ($R=C_4H_3S$)	120	3	210	Brown	475; 2153	500 (8.8); 3174	60.67	4.64	11.28	60.87	4.34	11.59
IIIc ($R=C_4H_3S$)	110	13	>300	Brown	—	a)	60.49	4.01	11.21	60.87	4.34	11.59
IIId ($R=C_4H_3S$)	140	6	>300	Brown	—	a)	61.13	4.62	11.23	60.87	4.34	11.59
IIIe ($R=C_4H_3S$)	120	1½	>300	Brown	—	480 (9.0); 2014	57.86	4.43	10.76	57.53	4.10	10.95
IIIf ($R=C_4H_3S$)	120	2	>300	Brown	—	a)	57.26	3.98	10.80	57.53	4.10	10.95
IIIg ($R=C_4H_3S$)	120	1	>300	Brown	—	500 (8.8); 3625	61.81	4.48	10.76	62.07	4.82	11.03
IV ($R=C_4H_3S$)	140	3	250	Light Brown	355; 5040	—	59.74	4.29	8.52	60.00	4.40	8.80
V ($R=C_4H_3S$)	30	120	>300	Orange Red	550; 868	550 (8.4); 868	Br, 36.48%			Br, 36.84%		

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

The absorption maxima (λ_{max}) of acenaphthyl succin-as-eins (IIIa—g, V: $R=C_{12}H_9$) have been found much higher than their analogous succineins and phthaleins but those of phenyl succin-as-eins (IIIa—g, V: $R=C_6H_5$) and thenyl succin-as-eins (IIIa—g, V: $R=C_4H_3S$) are comparable with their analogues.

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 Spectrometer.

The preparation and purification of the compounds (IIIa—g) taking respective acids (I) and phenols (yield, 40—45%), and diacetyl (IV), and dibromo (V) compounds were done in identical manner as described earlier.[1,9-11]

Zn-dust reduction of IIIb ($R=C_6H_5$). The dye (IIIb; $R=C_6H_5$) (1 g) was refluxed in glacial acetic acid (100 ml) with Zn-dust (5 g) for 15 min to yield a light yellow crystalline acid (VI; 0.9 g) mp 180 °C, which does not give fluorescence in alkaline solution. Found: C, 70.42; H, 5.64%. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.88%.

The acid (VI) when left overnight changed to red compound IIIb ($R=C_6H_5$), superimposible IR and same λ_{max} values. The acetylation of the mixture of acid (VI) and red compound was carried out as in IV to give diacetyl (IV), mixed mp, identical IR, λ_{max} values and elemental analysis.

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