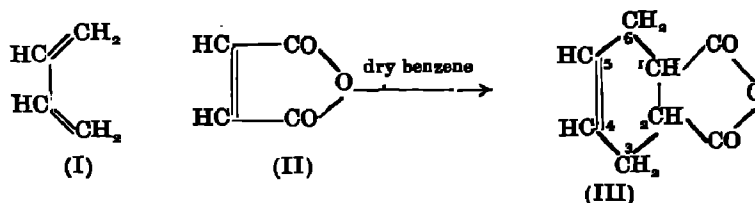


Dyes Derived from Substituted Phthalic Acids. Part III. *cis*- Δ^4 -Tetrahydrophthalic Acid. Effect of Decreasing Unsaturation in the Phthalic Acid Portion of Phthalein Dyes

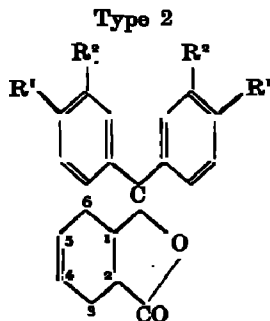
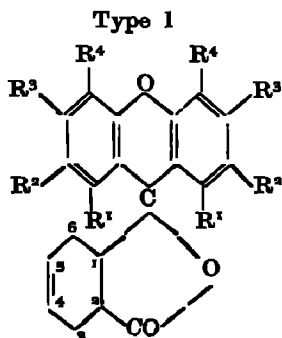
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cis- Δ^4 -Tetrahydrophthalic anhydride has been prepared and condensed with a number of aromatic hydroxy (phenols) and hydroxyamino (*m*-diethylaminophenol) compounds. The phthalein and rhodamine types of compounds, thus obtained, have been studied analytically and spectrophotometrically. The resorcinol compound has also been brominated and acetylated. The effect of decreasing unsaturation in the phthalic acid portion of phthaleins has been studied.

The investigation on the dyes derived from substituted phthalic acids¹ has been extended to the dyes derived from *cis*- Δ^4 -tetrahydrophthalic anhydride (III)², obtained from 1,3-butadiene (I) and maleic anhydride (II). The absorption maxima obtained have been compared with those of phthaleins and rhodamines obtained from phthalic anhydride and the results discussed.



The phthaleins and rhodamines obtained are of the following types:



(IV) : $R^1=R^2=R^4=H$; $R^3=-OH$.

(V) : $R^1=Me$; $R^2=R^4=H$; $R^3=-OH$.

(VI) : $R^1=R^3=-OH$; $R^2=R^4=H$.

(VII) : $R^1=R^2=R^4=H$; $R^3=NEt_2$.

(VIII) : $R^1=H$; $R^2=R^4=Br$; $R^3=-OH$.

(IX) : $R^1=R^2=R^4=H$; $R^3=-OCOMe$.

(X) : $R^1=-OH$; $R^2=Me$.

1. Loiwai and Jain, *this Journal*, 1962, 39, 251, 285.

2. Cope, "Organic Syntheses", Vol. 30, John Wiley & Sons, New York, 1956, p. 23.

EXPERIMENTAL

1,3-Butadiene (from a butadiene cylinder) was passed into dry benzene (500 ml) and maleic anhydride (196 g.), taken in a 2-litre three-necked flask fitted with an efficient stirrer, a gas inlet tube, a thermometer, and a reflux condenser, to obtain *cis*- Δ^4 -tetrahydrophthalic anhydride (III). The product, when recrystallised from ligroin, melted at 103-104°. The anhydride (III) on hydrolysis gave the corresponding acid, m.p. 163-64°. The preparation of phthaleins and rhodamines, given below, were carried out using the anhydride (III) by methods described earlier¹.

Resorcinol- Δ^4 -*tetrahydrophthalein* (IV) was obtained by condensation of a mixture of anhydride (III) (2.5 g.) and resorcinol (4.0 g.) at 160-80° for 3 hrs. in presence of 4-5 drops of H₂SO₄ (conc.).

Orcinol- Δ^4 -*tetrahydrophthalein* (V) was obtained as in (IV) from a mixture of anhydride (III, 2.5 g.) and orcinol (4.5 g.) by heating at 140-60° for 4 hrs. in presence of H₂SO₄ (conc., 3 to 4 drops).

Phloroglucinol- Δ^4 -*tetrahydrophthalein* (VI) was obtained like the compound (IV) by heating a mixture of anhydride (III, 2.5 g.) and phloroglucinol (4.5 g.) at 180-200° for 3 hrs. in presence of H₂SO₄ (conc., 4 drops).

m-*Diethylaminophenol*- Δ^4 -*tetrahydrophthalein* (VII) was obtained by condensation of a mixture of anhydride (III, 2.5 g.) and *m*-diethylaminophenol (5.6g.) at 100 to 105° for 3 hours in presence of H₂SO₄ (conc., 3-4 drops).

Tetrabromoresorcinol- Δ^4 -*tetrahydrophthalein* (VIII) was obtained by brominating compound (IV) by the method of Baeyer².

Resorcinol- Δ^4 -*tetrahydrophthalein diacetate* (IX) was obtained by acetylating compound (IV) with acetic anhydride in presence of fused sodium acetate.

o-*Cresol*- Δ^4 -*tetrahydrophthalein* (X) was obtained by heating a mixture of anhydride (III, 2.5 g.) and *o*-cresol (6g.) at 110-15° for 14 hrs. in presence of H₂SO₄ (conc., 8 drops). The excess of *o*-cresol was removed from the phthalein, as usual.

The characteristic properties and the analytical data of the above compounds are recorded in Table I.

The absorption maxima (λ_{max}) of the compounds prepared were determined using "Hilger" Uvispek spectrophotometer. The maxima for phthalein type of compounds were taken in neutral and alkaline (a drop of 5% NaOH) ethanolic solutions (Table II) and the maxima for the rhodamine type of compounds were determined in neutral and acidic (a drop of 5*N*-HCl) ethanolic solutions (Table III). The maxima for phthaleins and rhodamines from phthalic anhydride were also determined under similar conditions.

TABLE I

Dyes.	M.P.	Colour of the crystals.	Colour in		Formula.	Found.	Reqd.
			EtOH soln.	Alkaline EtOH soln.			
IV	245° (d)**	Reddish brown	Orange	Pink with green fluorescence	C ₂₀ H ₁₆ O ₃	C : 71.20% H : 4.80	71.43% 4.78
V	220° (d)	Brown-red	Yellow	Light pink with green fluorescence	C ₂₂ H ₂₀ O ₅	C : 72.49 H : 5.50	72.53 5.49
VI	280°	Red	Orange	Orange-red	C ₂₀ H ₁₆ O ₇	C : 65.01 H : 4.38	65.22 4.35
VII	118°	Pink	Pink	*Intense pink	C ₂₈ H ₃₄ O ₃ N ₂	C : 75.24 H : 7.66 N : 6.26	75.34 7.62 6.28
VIII	200° (d)	Pink-red	Blood-red	Deep pink	C ₂₀ H ₁₂ O ₅ Br ₄	Br : 49.8	49.08
IX.	190°	Yellowish brown	Yellow	Yellow	C ₂₄ H ₂₀ O ₇	C : 68.20 H : 4.79	68.57 4.76
X	165° (d)	Whitish brown	Yellow	Purple-pink	C ₂₂ H ₂₂ O ₄	C : 75.13 H : 6.31	75.43 6.29

* Colour in EtOH soln. containing HCl.
** (d) decomposes.

TABLE II

Phenols.	Phthaleins. EtOH solution.		<i>cis</i> - Δ^4 -Tetrahydrophthaleins. EtOH solution.	
	Neutral.	Alkaline.	Neutral.	Alkaline.
Resorcinol	450 m μ	490 m μ	455 m μ	495 m μ
Orcinol	445	490	440	505
Phloroglucinol	440	460	440	480
Tetrabromoresorcinol	525	515	530	520
<i>o</i> -Cresol	..	560	..	550

TABLE III

From phthalic anhydride.		From <i>cis</i> - Δ^4 -tetrahydrophthalic anhydride.	
<i>m</i> -Diethylaminophenolphthalein (Rhodamine B).		<i>m</i> -Diethylaminophenol- Δ^4 -tetrahydrophthalein.	
Neutral EtOH.	Acidic EtOH.	Neutral EtOH.	Acidic EtOH.
535 m μ	545 m μ	535 m μ	545 m μ

DISCUSSION

A comparative study of the absorption maxima (λ_{\max}) of the dyestuffs (phthaleins and rhodamines) shows that the change in the lower portion of the phthalein dyes (decreasing unsaturation in the phthalic acid portion) has no appreciable effect on the light absorption, except in cases of *o*-cresol and orcinol and to some extent in the cases of resorcinol and tetrabromoresorcinol compounds. In the case of *o*-cresol compound of the anhydride (III), maximum absorption takes place at 550 $m\mu$ as compared with *o*-cresolphthalein, which absorbs at 560 $m\mu$, whereas in the case of orcinol compound of the anhydride (III), the maximum absorption takes place at 440 (neutral alc.) and 505 $m\mu$ (alk. alc.) when compared with orcinolphthalein (Orcein) which absorbs at 445 and 490 $m\mu$ respectively.

These slight variations may be due to the decreasing unsaturation in the phthalic acid portion, but these are not consistent with the other phenolic compounds (phloroglucinol and *m*-diethylaminophenol), which show maximum absorption in the same region as the phthaleins from phthalic anhydride.

Therefore, as observed earlier¹, these variations could only be accounted for if correct correlation between electronic oscillations and atomic vibrations is established.

The authors express their sincere thanks to Dr. S. M. Mitra, Principal, Birla College, and to Dr. R. D. Gupta, Head of the Department of Chemistry, Birla College, Pilani, for providing necessary facilities.

One of the authors (N. C. Jain) also expresses his gratitude to the Government of India for granting him a research fellowship.