BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3265—3267 (1970)

Syntheses of 4-Styryltropolones

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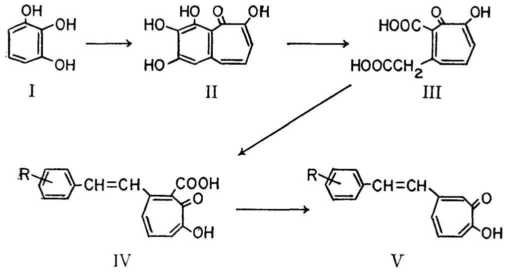
(Received October 25, 1969)

The syntheses of colchicine and its derivatives led to the syntheses of many derivatives of 4-styryltropolone.[1–4] In order to examine the chemical reactivities of 4-styryltropolone, one of us (H. M.) investigated its reactions with various nucleophilic reagents.[5]

It was reported that the substituent on the tropolone ring affects the dissociation of tropolone derivatives.[6] It is of interest to know the extent of the effect of the substituent in the benzene ring of styryltropolones.

The present communication deals with the syntheses of 4-styryltropolones having *p*-methyl, *p*-chloro, *m*-chloro and *m*-nitro groups in the benzene ring.



IVa R=H Va R=H
IVb R=*p*-CH_3 Vb R=*p*-CH_3
IVc R=*p*-Cl Vc R=*p*-Cl
IVd R=*m*-Cl Vd R=*m*-Cl
IVe R=*m*-NO_2 Ve R=*m*-NO_2

Scheme 1

Syntheses

The starting material, 3-carboxy-4-carboxymethyltropolone (III), was prepared from pyrogallol (I) *via* purpurogallin (II).[7] Condensation of *p*-methyl-, *p*-chloro-, *m*-chloro- and *m*-nitrobenzaldehydes with III under a similar condition used for the synthesis of 4-styryltropolone[3] gave the substituted 3-carboxy-4-styryltropolones, IVb, IVc, IVd and IVe, respectively. 3-Carboxy-4-styryltropolones were heated under reduced pressure to afford the corresponding 4-styryltropolones, Vb, Vc, Vd and Ve, respectively.

Properties

Ultraviolet Absorption Spectra. The ultraviolet absorption spectra of 4-styryltropolones are shown in Fig. 1. The positions and molecular extinction coefficients of the maximum absorptions are listed in Table 1.

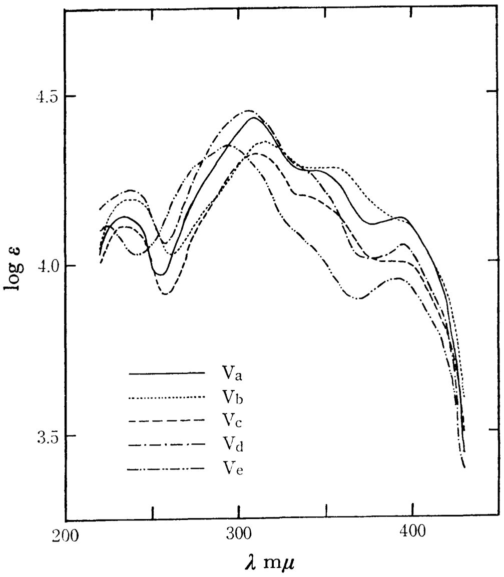


Fig. 1. Ultraviolet absorption spectra of 4-styryltropolones in methanol solution.
Va ———, Vb ---------, Vc -----, Vd — - —, Ve —-—

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7) R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, **1951**, 561.

Table 1. UV Data of 4-styryltropolones: $\lambda_{\max}^{\text{MeOH}}$ mμ (log ε)

Va	236(4.14)	308(4.43)	338(sh.)	395(4.13)
Vb	239(4.19)	314(4.36)	352(sh.)	—
Vc	232(4.14)	310(4.33)	340(sh.)	390(4.00)
Vd	236(4.22)	306(4.45)	—	396(4.05)
Ve	223(4.11)	295(4.35)	—	394(3.95)

The pattern of all the absorption bands is very similar to that of 4-styryltropolone.[3,5] The absorption maxima in the 280—330 mμ region shift toward the long and short wavelengths with the presence of electron-donating and electron-attracting substituents, compared with that of 4-styryltropolone (308 mμ).

Infrared Absorption Spectra. The infrared spectral data of 4-styryltropolones are summarized in Table 2. As characteristic absorption bands, there are the $\nu_{C=O}$ and δ_{CH} (in *trans* –CH=CH–) absorption bands in 1610—1595 and 960—955 cm^{-1}, respectively.

Table 2. IR Data of 4-styryltropolones (in cm^{-1}; chloroform solution)

Va	Vb	Vc	Vd	Ve
3200(w)	3200(w)	3200(w)	3200(w)	3200(w)
3000(m)	3000(m)	3000(m)	3000(m)	3000(m)
1609(s)	—	1609(s)	1610(s)	1609(s)
1598(s)	1599(s)	1595(s)	1600(s)	1599(s)
1547(m)	—	1545(m)	1549(m)	—
—	—	—	—	1529(s)
—	1512(s)	—	1512(s)	—
1488(s)	1485(s)	1492(s)	1482(s)	1483(s)
1472(s)	1471(m)	1471(s)	1474(s)	1470(sh)
1401(m)	—	1405(m)	—	—
—	—	1350(s)	—	—
1260(s)	—	1262(s)	1260(s)	1261(m)
—	1251(s)	1251(s)	1255(s)	1251(m)
1205(s)	—	1202(m)	1204(m)	1200(s)
—	1172(s)	—	—	—
1148(w)	1146(m)	1145(w)	1148(s)	—
—	1030(m)	1090(m)	—	—
959(s)	958(s)	959(m)	959(s)	957(m)
816(m)	827(m)	822(m)	815(w)	—
688(s)	—	—	680(m)	—
—	658(w)	569(m)	661(m)	659(m)

The ethylenic linkage which connects benzene ring with tropolone ring is found to be a *trans* configuration, because there is a very sharp absorption band in the 960—955 cm^{-1} region. This is also found in 3-carboxy-4-styryltropolones. It is found that the $\nu_{C=O}$ values are little affected by the substituents in the benzene ring.

Dissociation Constants. The dissociation constants were measured in 50% aqueous methanol. These values are listed in Table 3, and give the Hammett equation:

$$pK_a = 7.83 - 0.13\sigma$$

The details are described in another paper.[8]

Table 3. Dissociation constants of 4-styryltropolones

Compound	R	pK_a
Va	H	7.83
Vb	p-CH$_3$	7.85
Vc	p-Cl	7.81
Vd	m-Cl	7.76
Ve	m-NO$_2$	7.74

Experimental

Elementary analyses were performed in the Elementary Analyses Center of Kyushu University. All the melting points were measured on a Yanagimoto micro-melting point apparatus and are uncorrected. The infrared absorption spectra were taken on a JASCO DS-403G grating spectrophotometer in chloroform, and the ultraviolet absorption spectra on a Hitachi EPS-2 spectrophotometer in methanol.

3-Carboxy-4-styryltropolones (IVb—e). 3-Carboxy-4-carboxymethyltropolone (III) (10 mmol) was dissolved in acetic acid (30 m*l*) on gentle heating, and acetic anhydride (1.5 m*l*) was added to the solution at 50°C. After the solution was maintained at 80°C for 30 min, the solution was cooled down to 40°C, substituted benzaldehydes (10 mmol) and pyridine (0.7 m*l*) were added, and the mixture was kept at 40—45°C for 1 hr. The mixture was further heated up to 60°C, and stirring was continued for 3 hr after removal of the source of heat. The reaction mixture was poured into 10% hydrochloric acid (50 m*l*) which was cooled with ice to afford IVb—e. The yields and melting points are listed in Table 4.

Table 4. 3-Carboxy-4-styryltropolones

Compound	R	Yield (%)	Mp* (°C)
IVb	p-CH$_3$	83.1	196—199
IVc	p-Cl	85.5	204—206
IVd	m-Cl	81.5	169—172
IVe	m-NO$_2$	53.7	215—218

* Decomposition points.

4-Styryltropolones (Vb—e). 4-(Substituted styryl)-tropolones were obtained from IVb—e (5 mmol) by decarboxylation at 160—200°C/5 mmHg in a sublimation flask. The substances obtained were recrystallized from methanol. The yields, melting points and data of analyses are shown in Table 5.

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8) K. Imafuku, S. Nakama and H. Matsumura, *Tetrahedron*, **26**, 1821 (1970).

TABLE 5. 4-STYRYLTROPOLONES

Compound	R	Yield (%)	Mp (°C)	Elementary analyses (%) Found C	Found H	Found N	Calcd C	Calcd H	Calcd N
Vb	*p*-CH_3	37.8	156—156.5	80.34	5.90	—	80.64	5.92	—
Vc	*p*-Cl	31.6	151—151.5	69.57	4.28	—	69.62	4.26	—
Vd	*m*-Cl	44.5	138.5—139	68.98	4.27	—	69.62	4.26	—
Ve	*m*-NO_2	34.9	142—143	66.74	4.07	5.19	66.91	4.12	5.20

The authors wish to express their gratitude to Professor Emeritus Tetsuo Nozoe for his kind encouragement and to Dr. Kazu Kurosawa of Kumamoto University for his helpful suggestions. The authors' thanks are due to the Ministry of Education for financial support.