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Synthesis of 5-Styryltropolones

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5-Styryl-, 5-(*p*-bromostyryl)-, 5-(*p*-chlorostyryl)-, 5-(*p*-methoxystyryl)-, 5-(*p*-methylstyryl)-, 5-(*m*-chlorostyryl)- and 5-(*m*-methylstyryl)tropolone were synthesized by the Wittig reaction of 5-formyltropolone. Their UV and NMR spectra were determined.

In connection with the studies on syntheses and chemical properties of 4-styryltropolones(1) in our laboratory, we also investigated on the synthesis of 5-stytyltropolenes by means of the Wittig reaction with *p*- and *m*-substituted benzylidenetriphenylphosphorane on 5-formyltropolone (III). Seven 5-styryltropolones (IVa—g) have been synthesized and the results are described in this paper.

5-Styryltropolone (IVa) has firstly been synthesized by Matsumura(2) through the abnormal substitution reaction of 2-tosyloxy-4-styryltropolone. When this synthetic scheme was applied to *p*-methoxystyryl- and *p*-nitrostyryltropolone, we found that the separation of 2-tosyloxy-4-(substituted styryl)-tropolone from 2-tosyloxy-6-(substituted styryl)-tropolone was extremely difficult.

It would be expected that the Wittig reaction of substituted benzylidenetriphenylphosphorane with III, which has been obtained by the Reimer-Tiemann reaction of tropolone,(3) could introduce a styryl group at the position in tropolone nucleus. The Wittig reagents were formed with *m*- and *p*-substituted benzyltriphenylphosphonium halides(4—9) on treatment with sodium ethoxide in anhydrous ethanol. The Wittig reaction usually took 4 to 25 hr depending upon the nature of the substituent of the ylids used and gave 5-styryltropolones in excellent yield. It was strange, however, that *p*-nitrobenzylidenetriphenylphosphorane did not react with III.

Yields and melting points of the 5-styryltropolones are listed in Table 1.

UV spectra of the 5-styryltropolones are shown in Table 2. The absorption in the region of 380—405 mμ could be correlated to the electronic effects

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TABLE 1. THE WITTIG SYNTHESIS OF 5-STYRYLTROPOLONES

Reagent	Mp (°C)	Lit. mp	Reaction conditions			Product	Yield (%)	Mp (°C)	Lit. mp
			Mol ratio of I : III	Temp. (°C)	Time (hr)				
Ia	288	274—275[4]	3 : 1	50	18	IVa	68	132—133	131—133[2]
Ib	282—283	278 [5]	3 : 1	60	12	IVb*	80	239	—
Ic	289—290	[6]	2.9 : 1	50	22	IVc**	53	241—242	—
Id	241—242	236—238[7]	3.3 : 1	50	24	IVd**	88	198	—
Ie	262	267 [8]	2.9 : 1	30	24	IVe**	80	136	—
If	>300	310 [5]	3.5 : 1	50	25	IVf*	60	142—144	—
Ig	>300	[9]	3.3 : 1	47	6	IVg*	81	145—146	—

* Recrystallized from benzene-light petroleum.

** Recrystallized from benzene.

TABLE 2. UV ABSORPTION SPECTRAL DATA FOR 5-STYRYLTROPOLONES

Compound	λ_{max} mμ (ε)
IVa	235(30400), 260(20300), 270(23800), 277(inf.)(22000), 382(35000), 400(inf.)(34000)
IVb	237(26000), 262(16300), 274(21500), 281(20900), 384(36100), 405(35600)
IVc	237(28100), 261(inf.)(17600), 273(23300), 280(inf.)(23000), 384(38000), 405(inf.)(37200)
IVd	237(inf.)(26400), 261(inf.) (14500), 277(inf.)(11200), 390(inf.)(28000), 418(31200)
IVe	236(27200), 262(17300), 272(17800), 382(30200), 400(30000)
IVf	236(28600), 261(inf.)(19800), 271(24200), 278(inf.)(22200), 382(39800), 400(inf.)(37400)
IVg	236(28000), 261(inf.)(19000), 272(21000), 278(inf.)(19300), 382(36000), 400(inf.)(35500)

inf: inflection.

TABLE 3. NMR SPECTRAL DATA FOR 5-STYRYLTROPOLONES IN $CDCl_3$ AT 60 MHz

Compound	δ Value					
	OH	H_3,H_7*	H_4,H_6*	-CH=CH-	Phenyl or substituted phenyl	CH_3
IVa	7.9	7.40	7.60	7.06	7.45	
IVc	—	7.39	7.61	7.03	7.45	
IVe	8.1	7.33	7.61	7.04 7.36	7.25	2.43 2.35
IVf	7.9	7.36	7.61	7.00	7.32	
IVg	7.8	7.34	7.56	7.01	7.30	2.40

* $J_{3,4}=J_{6,7}=12$ Hz, analysed as an AB system.

TABLE 4. ANALYTICAL DATA FOR 5-STYRYLTROPOLONES

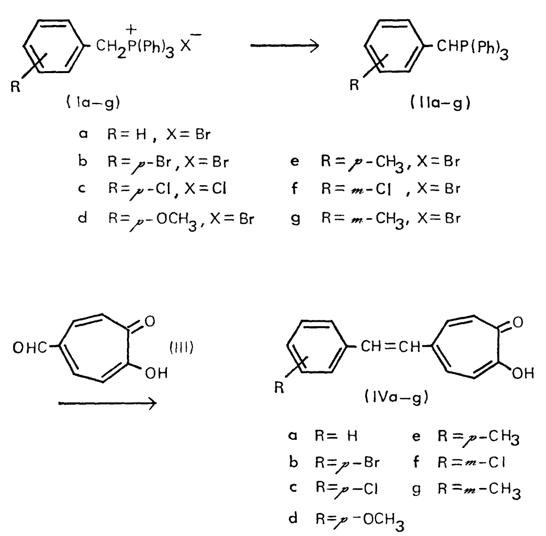
Compound	Formula	Found (%)		Calcd (%)	
		C	H	C	H
IVb	$C_{15}H_{11}O_2Br$	59.37	3.75	59.42	3.66
IVc	$C_{15}H_{11}O_2Cl$	69.31	4.27	69.64	4.29
IVd	$C_{16}H_{14}O_3$	75.36	5.69	75.57	5.55
IVe	$C_{16}H_{14}O_2$	80.47	6.29	80.64	5.92
IVf	$C_{15}H_{11}O_2Cl$	69.75	4.36	69.64	4.29
IVg	$C_{16}H_{14}O_2$	80.50	6.05	80.64	5.92

of *p*- and *m*-subtituents: *p*-CH_3O–, *p*-Br– and *p*-Cl– cause a bathochromic shift, while *m*-Cl– and *m*-CH_3– cause a little or none.

An absorption band at 950 cm^{-1} appeared in the IR spectra of all the 5-styryltropolones may indicate that the ethylenic double bond has a *trans* configuration.

NMR spectra of the 5-styryltropolones recorded in $CDCl_3$ are summarized in Table 3.

The ethylenic protons appeared as a sharp singlet and failed to show whether the configuration of the double bond is *trans* or *cis*. It was also observed that IVe showed two methyl protons and two



ethylenic protons, the intensities being 4 : 1. This indicates that the IVe is a mixture of *trans*- and *cis*-isomers. The presence of a band at 950 cm^{-1} in its IR spectrum is in favor of the *trans*-isomer being predominant.

pK_a measurements and a study of the correlation of pK_a values to the Hammett equation are now in progress.

Experimental

Measurements. IR spectra were determined in chloroform with a grating infrared spectrometer, Model DS 403G (Japan Spectroscopic Co. Ltd.). UV spectra were obtained in methanol with a recording spectrophotometer, Model EPS-2 (Hitachi Ltd.). NMR spectra were recorded in deuteriochloroform with TMS as an internal reference using a JNM C 60H (Japan Electron Optics Lab.). Melting points were determined with a Yanagimoto melting point apparatus.

5-Formyltropolone (III). 5-Formyltropolone was prepared according to the reference.[3] The work up procedure was, however, conveniently shortened by chloroform extraction of the products in place of continuous ether extraction and by chromatographic separation of III from the unchanged tropolone on silica (Wakogel C100) column.

Preparation of 5-Styryl- and 5-(*m*- and *p*-Substituted-styryl)tropolones (IVa—g). Phosphonium salt (I) (5.2 mmol) was treated with sodium ethoxide, prepared from metallic sodium (5.2 mmol) and anhydrous ethanol (13 m*l*). To the solution, there was added 5-formyltropolone (III) (1.67 mmol) and the mixture was stirred at a temperature between 30° and 60°C for a period of time shown in Table 1. The mixture was acidified with 2N sulfuric acid and extracted with chloroform. The chloroform was evaporated and the residue was chromatographed with chloroform on a silica column (Wakogel C100 (36 g) plus B10 (4 g)). The first fraction (100 m*l*) was taken and the chloroform was evaporated. The resulting solid was recrystallized from benzene or from a mixture of benzene and light petroleum (bp 30—70°C), giving 5-styryltropolone (IV) in 53—88% yield.

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