

The Reaction Between 3,3-Bis(methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran and 1,3-Bis(methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran, 2,2-Diphenyl-2*H*-chromen and 2,4-Diphenyl-4*H*-chromen, and Related Compounds

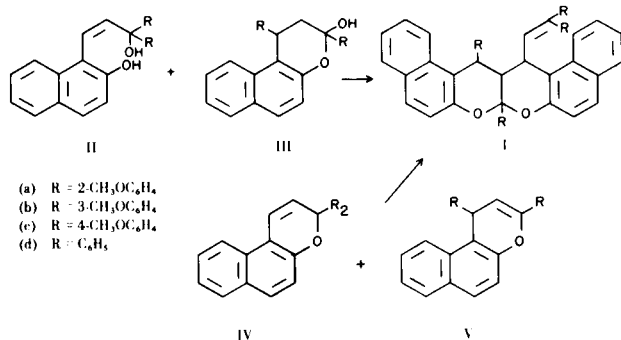
W. David Cotterill, Muhammad Iqbal, Robert Livingstone, and Maurice V. Walshaw

Department of Applied Chemical and Biological Sciences,  
The Polytechnic, Huddersfield HD1 3DH, England

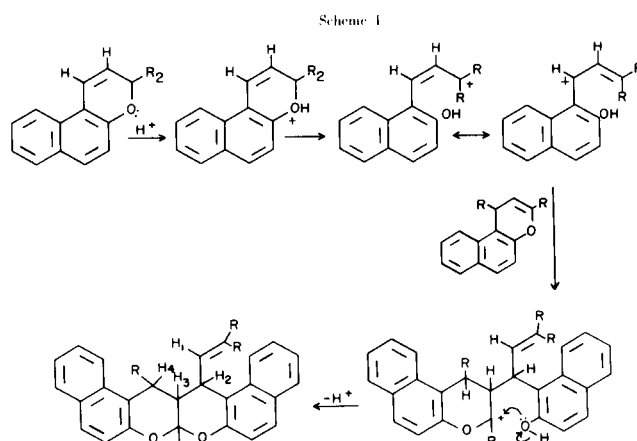
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The reaction between 3,3-bis(methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran and 1,3-bis(methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran under acid conditions gives a 7a,15a-dihydro-7a,15-bis(methoxyphenyl)-16-[2,2-bis(methoxyphenyl)-1-vinyl]dinaphtho-[2,1-*b*:2,1-*g*]-4*H*,5*H*-pyrano[2,3-*b*]pyran.

On occasions during the separation of the usual products obtained from the reaction between 5,6-benzocoumarin and 2-methoxyphenylmagnesium bromide (1) a solid (I), m.p. 276° was also isolated in low yield. The same compound (I) was formed in high yield by the interaction between equimolar proportions of either 3-(2-hydroxy-1-naphthyl)-1,1-bis(2-methoxyphenyl)prop-2-en-1-ol (II) and 2,3-dihydro-1,3-bis(2-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran-3-ol (III), or 3,3-bis(2-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (IVa) and 1,3-bis(2-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran (V) in boiling acetic acid.

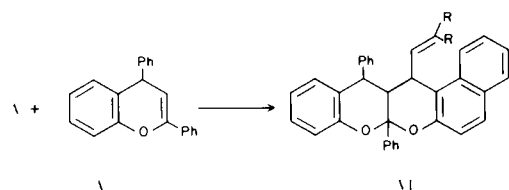


A mechanism for the acid-catalyzed formation of compound I is proposed which is similar to that previously suggested (2) for the formation of adducts from 1,1-diarylethylenes and 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans. The initial step involves the protonation of the ring oxygen atom of the 3,3-bis(2-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (IVa), followed by ring opening to give an allylic cation which reacts with the olefinic bond of 1,3-bis(2-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran (V) to give a further carbonium ion. The product is



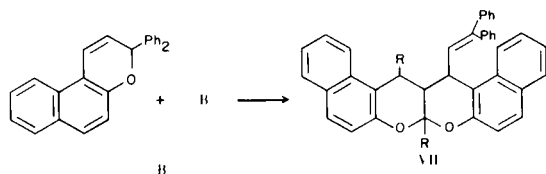
given by cyclisation and loss of a proton (Scheme 1).

All attempts to react 3,3-bis(3-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (IVb) with 1,3-bis(3-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran (Vb) were unsuccessful, but an adduct (Ic) was slowly deposited from a solution of 3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (IVc) and 1,3-bis(4-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran (Vc) in acetic acid saturated with dry hydrogen chloride. No reaction occurred between 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (IVd) and 1,3-diphenyl-1*H*-naphtho[2,1-*b*]pyran (Vd) in acetic acid, but an adduct Id was precipitated on warming the solution after saturating with dry hydrogen chloride. A number of related adducts VI and VII were obtained by reacting together the appropriate benzo- or naphthopyrans under acid conditions, but it was not possible to obtain adduct VIIc from 1,3-bis(3-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran. However, this compound combined with 3,3-bis(2-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran on warming in acetic acid saturated with dry hydrogen chloride.



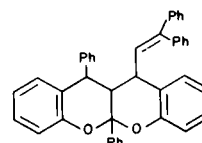
- (a) 3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran  
 (b) 3,3-Bis(2-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran  
 (c) 3,3-Bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran

- R Ph  
 R 2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
 R 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>



- (a) 1,3-Diphenyl-1*H*-naphtho[2,1-*b*]pyran  
 (b) 1,3-Bis(2-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran  
 (c) 1,3-Bis(3-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran  
 (d) 1,3-Bis(4-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran

- R Ph  
 R 2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
 R 3-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
 R 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>



VIII

The presence of a vinylic side chain in the adduct (VIc, R = 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) was proved by oxidative fission, 4,4'-dimethoxybenzophenone being isolated from the ozonolysis reaction.

The adduct VIII formed from 2,2-diphenyl-2*H*-benzo[*b*]pyran and 2,4-diphenyl-4*H*-benzo[*b*]pyran was assigned previously a different structure (3). Ozonolysis of adduct VIII afforded benzophenone, indicating the presence of a terminal pair of phenyl groups on a vinylic side chain.

A full analysis of the <sup>1</sup>H nmr spectra of the non-aromatic region of a number of the adducts was possible and the data is collected in Table I. The coupling constants, when fitted to the Karplus equation (4), yield approximate

TABLE I

## Nmr Spectroscopic Data

Compound	R	$\delta$ /ppm				J/Hz		
		H <sub>1</sub>	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	J <sub>1,2</sub>	J <sub>2,3</sub>	J <sub>3,4</sub>
VIa	Ph	5.28	4.52	3.47	4.27	9.5	3.0	8.0
VIb	2-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	4.77	4.17	3.22	3.88	8.1	1.9	11.2
VIc	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	4.85	4.20	3.20	3.86	9.0	2.0	11.2
VIIa	Ph	5.14	4.25	3.27	3.94	9.2	2.0	11.0
VIII <sup>3</sup>		5.80	4.21	3.22	3.72	10.0	4.0	10.5

TABLE II

## Mass Spectra (See Scheme II)

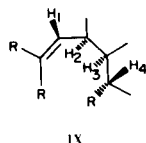
Adduct	R	R <sup>3</sup>	R <sup>1</sup>	R <sup>2</sup>	(X)		(XII)		(XI)	
					m/e	%	m/e	%	m/e	%
VIc	(Benzo)	H	4-MeOC <sub>6</sub> H <sub>4</sub>	Ph	678	0.68	394	100	284	8
VIIId	(Benzo)	(Benzo)	Ph	4-MeOC <sub>6</sub> H <sub>4</sub>	728	0.55	334	39	394	78
VIII	H	H	Ph	Ph	568	3.12	284	84.3	284	84.3

Adduct	(XIII)		(XIV)		(XV)		(XVI)		(XVII)	
	m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
VIc	*287	24	*207	23	283	13	496	1.2	495	1.9
VIIId	*257	86	*287	100	393	24	466	1.7	465	4.2
VIII	*207	100	207	100	*283	78.1	386	3.1	385	4.8

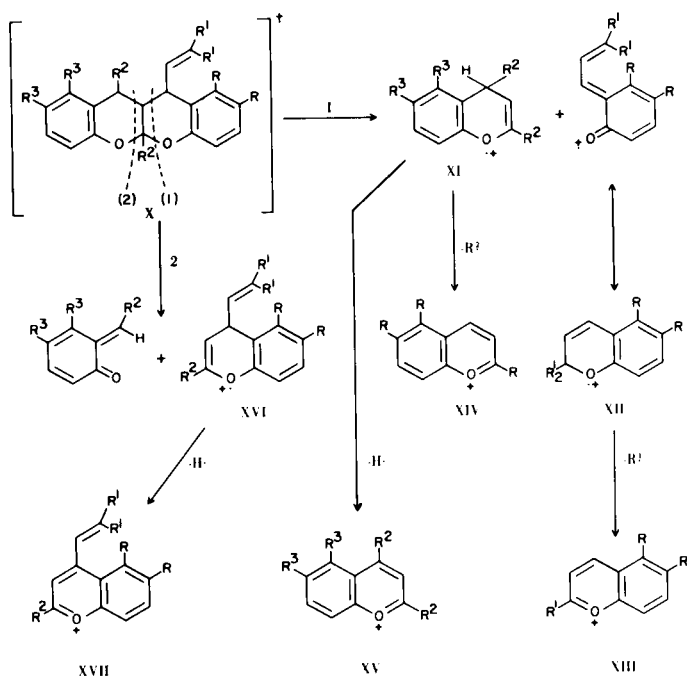
\*Supported by observation of metastable ions.

dihedral angles, which are in agreement with the stereochemistry indicated in the four-carbon fragment (IX). The coupling constant between  $H_1$  and  $H_2$  is large (9.0-10.0 Hz), which indicates that rotation about the C-C bond joining the vinylic side chain to the hetero ring is restricted by steric hindrance and the C- $H_1$  and C- $H_2$  bonds are locked in an antiperiplanar orientation (2). The low field doublet (e.g. VIc,  $\delta$  4.85) is assigned to the vinylic proton  $H_1$ ; the double-doublet ( $\delta$  4.20), and the other doublet ( $\delta$  3.86), to the benzylic protons  $H_2$  and  $H_4$ ; and the remaining double-doublet ( $\delta$  3.20) to proton  $H_3$ .



Mass spectrometry (5) provided further evidence for the proposed structure of the adducts and the major peaks (Table II) could be explained in terms of the fragmentations shown in Scheme II.

Scheme II



The molecular ion X undergoes a ready retro-Diels-Alder reaction by two routes 1 and 2 to give the ions XI, XII, and XVI, each of these may then lose either an aryl radical or a hydrogen atom to afford the stable naphtho- or benzopyrylium ions XIII, XIV, XV, and XVII. In all the adducts studied the fragments indicated in Table II were supported by observations of metastable ions.

## EXPERIMENTAL

The  $^1H$  nmr spectra were recorded with a Varian A60A spectrometer for saturated solutions in deuteriochloroform. Mass spectra were obtained with an A.E.I. MS902 instrument; compounds were introduced through the direct insertion probe. The electron beam energy was 70eV and the ion source was at ca. 200°.

M.p.'s were determined with a Kofler hot stage apparatus. 7a,15a-Dihydro-7a,15-bis(2-methoxyphenyl)-16-[2,2-bis(2-methoxyphenyl)-1-vinyl]dinaphtho[2,1-*b*:2,1-*g'*]-4*H*,5*H*-pyrano[2,3-*b*]pyran (Ia).

(i)

3-(2-Hydroxy-1-naphthyl)-1,1-bis(2-methoxyphenyl)prop-2-en-1-ol (2.06 g.) (1), 2,3-dihydro-1,3-bis(2-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran-3-ol (2.06 g.) (1), and acetic acid (14 ml.) were boiled for 0.17 hours and then cooled to yield a solid. Following filtration the solid was washed with methanol and recrystallized from benzene-light petroleum (b.p. 80-100°) to give the adduct Ia (3.36 g., 85.2%), m.p. 275-276°.

Anal. Calcd. for  $C_{54}H_{44}O_6$ : C, 82.2; H, 5.6. Found: C, 81.9; H, 5.6.

(ii)

3,3-Bis(2-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (1.97 g.), 1,3-bis(2-methoxyphenyl)-1*H*-naphtho[2,1-*b*]pyran (1.97 g.), and acetic acid (14 ml.) were boiled for 0.25 hour. The adduct Ia (3.79 g., 96%), m.p. and mixed m.p. 275-276° was obtained as above.

Preparation of Adducts from 3,3-Diaryl-3*H*-naphtho[2,1-*b*]pyran and 2,4-Diphenyl-3*H*-benzo[*b*]pyran.

The 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran (0.005 mole), 2,4-diphenyl-3*H*-benzo[*b*]pyran (1.42 g., 0.005 mole) and acetic acid or acetic acid saturated with dry hydrogen chloride were boiled for 0.5 hour and the mixture kept for several days to yield a solid. The solid was removed by filtration, washed with methanol, and recrystallized from benzene-light petroleum (b.p. 80-100°) to give the adduct. Data for adducts are shown in Table III.

Ozonolysis of 7a,13a-Dihydro-7a,13-diphenyl-14-[2,2-bis(4-methoxyphenyl)-1-vinyl]benzo[*b*]naphtho[2,1-*g'*]-4*H*,5*H*-pyrano[2,3-*b*]pyran (VIc).

Ozone was passed through a solution of the adduct (1.19 g.) in chloroform (125 ml.) at 0° for 6 hours. The solvent was removed at room temperature and the residue boiled with water (125 ml.) for 1 hour. Isolation with ether gave a gum which was chromatographed on alumina from light petroleum (b.p. 80-100°) solution to yield no products. Elution with benzene and then chloroform afforded gums, which on crystallization from ethanol gave 4,4'-dimethoxybenzophenone (0.22 g., 52.2%), m.p. and mixed m.p. 142-144°. Concentration of the mother-liquor gave a gum but no other products were isolated.

Ozonolysis of 5a,11a-Dihydro-5a,11-diphenyl-12-[2,2-diphenyl-1-vinyl]dibenzo[*b,g*]-4*H*,5*H*-pyrano[2,3-*b*]pyran (VIII).

Ozonolysis under the above conditions gave a gum from the adduct (0.879 g.), which was chromatographed on alumina from light petroleum (b.p. 40-60°) solution. Removal of the solvent gave benzophenone (0.205 g., 74%), as platelets, m.p. and mixed m.p. 48°, 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 238°.

TABLE III

Adduct	Reaction Solvent	Yield (%)	M.p., °C	Formula	Analysis				
					Calcd.		Found		
					C	H	C	H	
VIa	AcOH/HCl (30 ml.)	44	265-267	C <sub>46</sub> H <sub>34</sub> O <sub>2</sub>	89.1	5.5	89.0	5.4	
VIb	AcOH (35 ml.)	85.5	271-273	C <sub>48</sub> H <sub>38</sub> O <sub>4</sub>	84.9	5.6	85.5	5.7	
VIc	AcOH/HCl (40 ml.)	54.6	242-244	C <sub>48</sub> H <sub>38</sub> O <sub>4</sub>	84.9	5.6	84.4	5.8	
Adducts from 3,3-Diphenyl-3H-naphtho[2,1-b]pyran (0.005 mole) (1) and 1,3-Diaryl-1H-naphtho[2,1-b]pyran (0.005 mole) (1)									
VIIa	AcOH/HCl (30 ml.)	54.1	279-281	C <sub>50</sub> H <sub>36</sub> O <sub>2</sub>	89.8	5.4	89.8	5.4	
VIIb	AcOH/HCl (20 ml.)	45.9	265-267	C <sub>52</sub> H <sub>40</sub> O <sub>4</sub>	85.7	5.5	85.4	5.5	
VIIc	AcOH/HCl (40 ml.)	71.6	283-285	C <sub>52</sub> H <sub>40</sub> O <sub>4</sub>	85.7	5.5	85.9	5.7	
Adduct from 3,3-Bis(2-methoxyphenyl)-3H-naphtho[2,1-b]pyran and 1,3-Bis(3-methoxyphenyl)-1H-naphtho[2,1-b]pyran									
	AcOH/HCl	34.7	205-207	C <sub>54</sub> H <sub>44</sub> O <sub>6</sub>	82.2	5.6	82.4	5.7	

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## REFERENCES

- (1) W. D. Cotterill, R. Livingstone, and M. V. Walshaw, *J. Chem. Soc. C*, 1758 (1970).  
 (2) E. Bradley, W. D. Cotterill, R. Livingstone, and M. V. Walshaw, *ibid.*, 3028 (1971).  
 (3) J. Cottam, R. Livingstone, M. V. Walshaw, K. D. Bartle, and D. W. Jones, *ibid.*, 5261 (1965).  
 (4) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).  
 (5) C. S. Barnes and J. L. Occolowitz, *Aust. J. Chem.*, **17**, 975 (1964); B. Willhalm, A. F. Thomas, and F. Gautschi, *Tetrahedron*, **20**, 1185 (1964).