dissolved in 50 mL of ether and stirred with 10 mL of saturated aqueous ferric chloride. TLC analysis showed the reaction to be complete within 10 min. The organic layer was removed, washed well with water, and dried. Removal of the solvent gave 85.5 mg (93%) of a yellow solid which was recrystallized from diisopropyl ether: mp 166.5–167.5 °C; NMR 6.50 (d of d, J = 13.0 Hz, J = 5.9 Hz), 6.01 (s, 1 H), 5.91 (s, 1 H), 5.21 (d of d, J = 13.0 Hz, J = 2.3 Hz, 1 H), 4.90 (d of d, J = 5.9 Hz, J = 2.3 Hz, 1 H), 3.86 (s, 3 H); IR 1673, 1601, 1195.

Anal. Calcd for $C_9H_8O_4$: C, 60.00; H, 4.48. Found: C, 60.30; H, 4.68.

2-Methoxy-5-phenoxy-1,4-benzoquinone (9). By a procedure analogous to that described above, 100 mg (0.406 mmol) of 4,5-dimethoxy-2-phenoxyphenol (**7**) gave 85 mg (91%) of a yellow solid which was recrystallized from diisopropyl ether: mp 139.5–140.5 °C; NMR 7.0–7.5 (m, 5 H), 5.95 (s, 1 H), 5.64 (s, 1 H), 3.86 (s, 3 H); IR 3070, 1680, 1613, 1597, 1212, 1199, 1187.

Anal. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 67.46; H, 4.51.

2-Morpholino-5-(vinyloxy)-1,4-benzoquinone (4b). By a procedure analogous to that described above 200 mg (0.652 mmol) of 4,5-dimorpholino-2-(vinyloxy)phenol (**2b**) was converted to 143 mg (93%) of **4b**: red-orange plates; mp 204–205 °C; NMR 6.49 (d of d, J = 13.0 Hz, J = 5.9 Hz, 1 H), 5.85 (s, 1 H) 5.65 (s, 1 H), 5.08 (d of d, J = 13.0 Hz, J = 2.3 Hz, 1 H), 4.78 (d of d, J = 5.9 Hz, J = 2.3 Hz, 1 H), 3.75 (s, 4 H), 3.50 (m, 4 H); IR 1665, 1624, 1578.

Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57. Found: C, 61.22; H, 5.54.

2-Ethoxy-5-methoxy-1,4-benzoquinone (10). A solution of 100 mg (0.555 mmol) of 2-methoxy-5-(vinyloxy)-1,4-benzoquinone (**4a**) in 100 mL of absolute ethanol was refluxed for 6 h. The solvent was removed in vacuo to give a yellow solid which was recrystallized from diisopropyl ether to give 95 mg (94%) of **10**: mp 197–198 °C (lit.[6] mp 197.5–198.5 °C); NMR 5.86 (s, 1 H), 5.84 (s, 1 H), 4.04 (q, J = 7 Hz, 2 H), 3.84 (s, 3 H), 1.49 (t, J = 7 Hz, 3 H).

2-Methoxy-5-morpholino-1,4-benzoquinone (11). A solution of 100 mg (0.426 mmol) of 2-morpholino-5-(vinyloxy)-1,4-benzoquinone (**4b**) in 100 mL of absolute methanol was refluxed for 6 h. Removal of the solvent in vacuo gave an orange red solid which was recrystallized from methanol to give 87.5 mg (92%) of **11**: mp 190–192 °C; NMR 5.69 (s, 1 H), 5.62 (s, 1 H), 3.80 (m, 7 H), 3.14 (m, 4 H); IR, 1668, 1620, 1580.

Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.18: H, 5.85. Found: C, 59.14; H, 5.58.

Acknowledgment. We thank the National Institutes of Health (CA 11890) for financial support of this work.

Registry No. **1a**, 21086-65-7; **1b**, 4608-10-0; **2a**, 90433-59-3; **2b**, 90433-60-6; **3a**, 90433-61-7; **3b**, 90433-62-8; **4a**, 90433-63-9; **4b**, 90433-64-0; **6**, 90433-65-1; **7**, 90433-66-2; **8**, 90433-67-3; **9**, 90433-68-4; **10**, 75080-61-4; **11**, 90433-69-5; Ag_2O, 20667-12-3; AgO, 1301-96-8; $FeCl_3$, 7705-08-0; $K_3Fe(CN)_6$, 13746-66-2; vinyl bromide, 593-60-2; phenyl bromide, 108-86-1.

(6) Cole, E. R.; Crank, G.; Hai Minh, H. T. *Aust. J. Chem.* **1980**, *33*, 527.

Benzopyrans. 17.[1] Triethylamine-Mediated Transformation of 4-Oxo-4*H*-1-benzopyran-3-carboxaldehyde[2]

Chandra Kanta Ghosh,* Chandrakanta Bandyopadhyay, and Nimai Tewari

Organic Chemistry Laboratory, Department of Biochemistry, Calcutta University, Calcutta 700 019, India

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So far as their reactions with a secondary aliphatic or aromatic amine are concerned, both the title aldehyde **1** and the corresponding acid **2** (Chart I) behave similarly to give the enamino ketone **9**.[3,4] The acid **2** on treatment

Scheme I

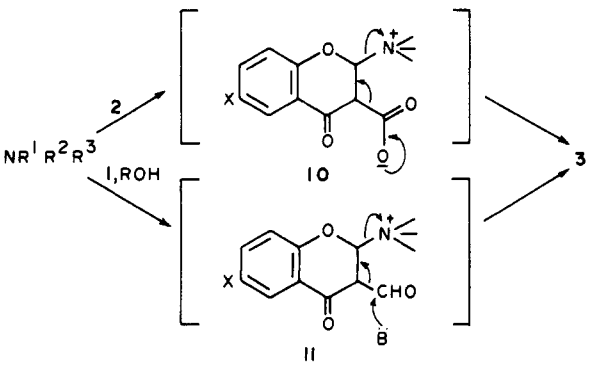


Table I. Triethylamine-Mediated Transformation Products of Chromone-3-carboxaldehyde (1)

X in 1/R of ROH	yield, % (mp, °C), of the products[a]			
	4	5	6	7
H/Me	*b*	10 (162)		7 (158)
Me/Et		8 (200)	6 (196)	
OMe/Me		15 (180)		
Cl/Me	30 (116)			
Br/Me	24 (108)		6 (210)	75 (280)[c]
Br/Et			56 (210)	80 (306)[c]
NO_2/Me	22 (142)			

[a] Only **3a** could be isolated in 2% yield by column chromatography, **3b,c** being detected by TLC; all the chromones **3** are known compounds (see ref 3 and references cited therein). Each of the products **8** obtained in 2–3% yield decomposed above 300 °C. [b] Detected by co-TLC with authentic sample. [c] Obtained by acid-catalyzed isomerization of **6** in the appropriate alcohol.

Table II. 3-(Dimethoxymethyl)-4-oxo-4*H*-1-benzopyrans 4 (R = Me)[a]

X	mp, °C	^{1}H NMR ($CDCl_3$), δ: H-5[b]	H-2[c]	other Ar H[b]	CH-$(OR)_2$[c]	$(OR)_2$
H	80	8.25	8.10	7.80–7.28	5.58	3.42 (s)
Cl	116	8.18	8.08	7.76–7.24	5.56	3.40 (s)
Br	108	8.32	8.08	7.84–7.28	5.56	3.40 (s)
NO_2	142	9.10	8.20	8.35–7.78	5.60	3.44 (s)

[a] Satisfactory analytical data (±0.4%) for C and H were obtained. [b] Aromatic protons show normal splitting. [c] Doublet due to allylic coupling, J = 0.8 Hz.

Table III. ^{1}H NMR, δ, for 2,3-Dihydro-2-(4-oxo-4*H*-1-benzopyran-3-yl)-4-oxo-4*H*-1-benzopyrans 5[a]

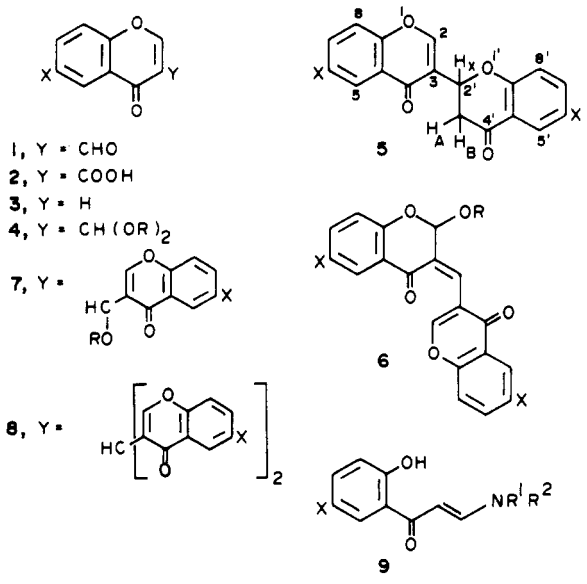
	vinyl H	Ar H (m)	Hx (m)	$H_A + H_B$[b]	X (s)
5a	8.72–7.00		5.72	3.00	
5b[c]	8.20[d]	8.04–6.92	5.72	3.00	2.46, 2.32
5c	8.24[d]	7.56–6.88	5.68	3.00	3.86, 3.78

[a] All the compounds gave satisfactory elemental analyses: C, ±0.36; H, ±0.37. [b] These two protons appear as dq, J_{AB} = 16 Hz, J_{AX} = 3 Hz, and J_{BX} = 14 Hz. [c] UV (EtOH) λ 220 (log ε 4.46) and 305 (4.07) nm; IR ($CHCl_3$) ν 1685 (4′-CO), 1635 (4-CO), 1610 (C=C) cm^{-1}; mass spectrum, m/e 320 (M^+), 303 (M – OH), 291 (M – H – CO), 275 (M – OH – CO), 213, 184. [d] Doublet due to allylic coupling, J = 0.8 Hz.

(1) Part 16: Ghosh, C. K.; Tewari, N.; Bhattacharyya, A. *Indian J. Chem.*, in press.
(2) For a preliminary account, see: Ghosh, C. K.; Bandyopadhya, C.; Tewari, N. "Proceedings of the Ninth International Congress of Heterocyclic Chemistry"; Tokyo, Aug 21–26, 1983; Abstr. No. G-100.
(3) Ghosh, C. K.; Khan, S. *Synthesis* **1981**, 719.

0022-3263/84/1949-2812$01.50/0

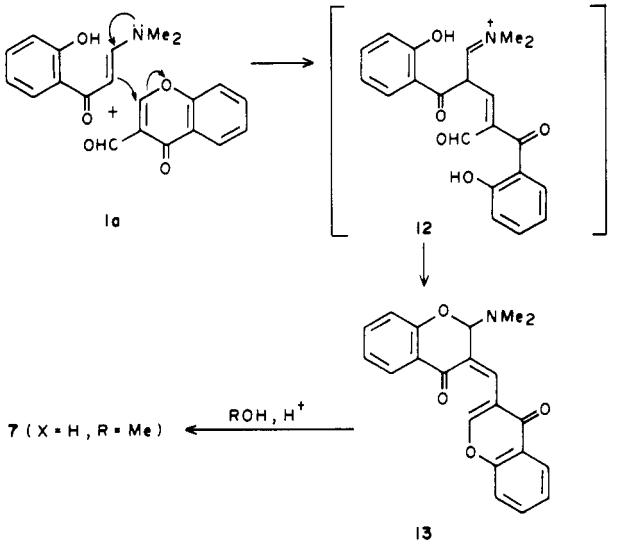
Chart I



with a tertiary aliphatic amine decarboxylates to chromone **3** via the zwitterionic intermediate **10** (Scheme I).[3] The aldehyde **1**, likewise its corresponding acid **2**, is also anticipated to undergo deformylation on treatment with an aliphatic tertiary amine[5] through a mechanism as depicted in Scheme I.

However, on refluxing **1** with an equimolar or catalytic amount of triethylamine in a protic solvent ROH, very little or no chromone **3** could be isolated; instead, varying amounts of the products **4**–**8** (Table I) were obtained. The structures of the products **3**, **4**, and **5** as established from analytical and spectral data (Tables II and III) had been further confirmed by independent syntheses. Thus, **3** was synthesized[3] by reflux the appropriate *o*-hydroxyacetophenone with dimethylformamide dimethyl acetal[6] and subsequent acid treatment of the resultant enamino ketone **9** ($R^1 = R^2 = Me$), **4** by acid catalyzed acetalization of **1**, and **5** by alkoxide-induced dimerization of **3**.[7] The product **7** could be isolated only in the transformation of **1a**, in other cases, e.g., **1b** and **1e**, **6** isomeric with **7** being obtained. An independent synthesis of **7** (X = H, R = Me) was achieved by condensing **1a** with **9** ($R^1 = R^2 = Me$) and subsequently refluxing the resultant condensate **13** arising through the intermediate **12** in methanol containing sulfuric acid as catalyst (Scheme II). The structure **6** was differentiated from that of **7** by their spectral data. Thus for **6**, the UV absorption at a relatively higher wave length (~355 nm) is compatible with its α-, β-, γ-, and δ-unsaturated ketone function; the IR spectrum (1675 and 1650 cm^{-1}) indicates the presence of two different ketone functions; in the ^1H NMR spectrum the multiplicity (qq) of the CH_2 protons of the ethoxy group confirms the linkage of the ethoxy group to a chiral centre as in **6** (X

Scheme II



= Br, R = Et). All these spectral data differ widely from those observed for **7** and several dichromonylmethane derivatives[5,8] allied to **7**. **6** on refluxing in alcohol in presence of an acid isomerized to **7**. Since the product **8** was insoluble in most organic solvents, its NMR spectrum could not be recorded. This structure has been assigned on the basis of elemental analysis, mass spectral fragmentation, and mechanistic consideration (vide infra). No transformation of **1** took place in an aprotic medium, and pyridine failed to bring about any change in **1**.

Though **3** dimerizes to **5** by treatment with sodium ethoxide,[7] it survived prolonged refluxing in ethanol containing triethylamine. So the isolation of **3** in extremely poor yield in the transformation reaction under consideration is due to less involvement of the reaction path as depicted in Scheme I and subsequent utilization of **3**, if any formed, in making the chromanone **5** by a process (vide infra) other than dimerization. A plausible mechanism accounting for all the transformation products **3**–**8** is depicted in Scheme III. Triethylamine undergoes 1,4-addition to **1**, giving the zwitterionic intermediate **14** that on protonation (→ **11**) and subsequent base-induced deformylative Hofmann elimination[3] gives **3**. An alternate reaction course of **14** is its solvolysis to **15** that rearranges by ring opening and ring closure to the keto enol ether **16**. The overall transformation process **1** → **16** is equivalent to an initially base catalyzed 1,4-addition of alcohol to **1** with concomitant rearrangement, the 1,4-addition sequence being very common for chromone having an electron-withdrawing functionality at 3-position.[9] Now, a base-catalyzed 1,4-addition of ROH[10] to **16** followed by water elimination results in 3-(dialkoxymethyl)chromone **4**. A 1,4-addition of **14** to **1** gives the intermediate **17** which on base-induced deformylation and deformylative Hofmann elimination forms the chromanone **5**. Similar 1,4-addition of **14** to **3** may also produce **5** via the intermediate **17** (H in place of CHO). Alcoholysis of **17** to **18**, subsequent base-catalyzed ring opening (→ **19**) and recyclization gives rise to **6**. Combination of the intermediates **14** and **16** gives **7** via **20**. Lastly, the trichromonylmethane **8** arises from

(4) For reviews on Chemistry of Chromone-3-Carboxaldehyde, see: Ellis, G. P. "Heterocyclic Compounds"; Weissberger, A., Ed.; Interscience: New York, 1977; Vol. 35, Chapter 19. Ghosh, C. K. *J. Heterocycl. Chem.* **1983**, *20*, 1437.

(5) 3-Formylchromone (**1**) behaves as an aromatic aldehyde in condensing with two molecules of *N,N*-diethylaniline in sulfuric acid to give a leuco base: Harnish, H. *Ann. Chem.* **1972**, *8*, 765.

(6) Eiden, F.; Schmiz, C. *Arch. Pharm. (Weinheim, Ger.)* **1980**, *313*, 120. Foehlisch, B. *Chem. Ber.* **1971**, *104*, 348. Gammill, R. B. *Synthesis* **1979**, 901.

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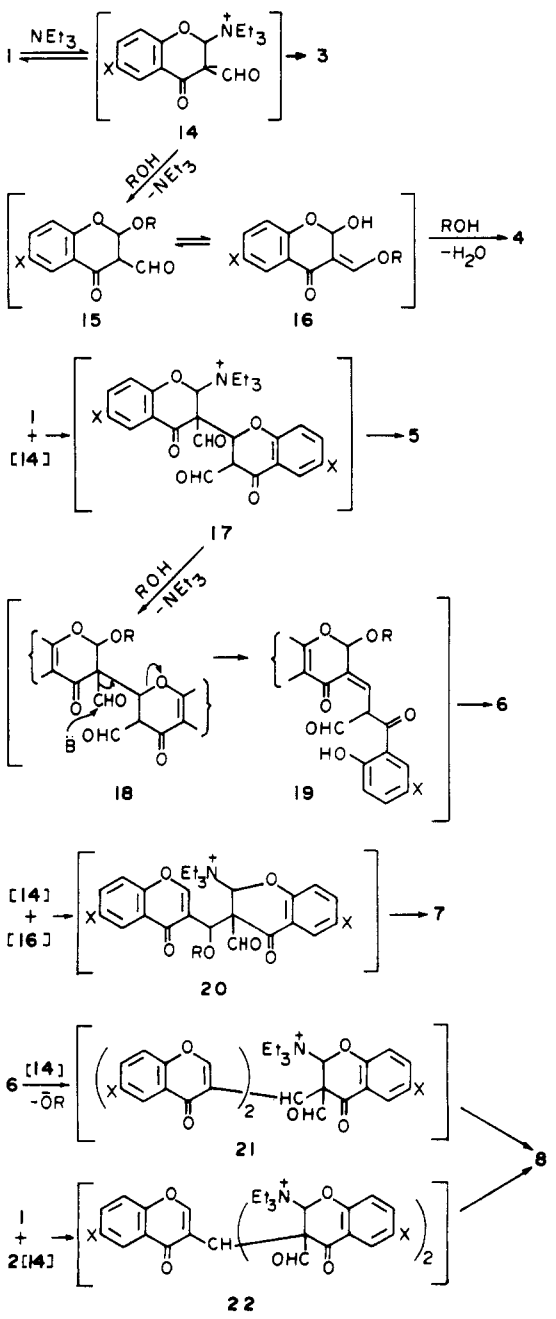
(9) Fitton, A. O.; Frost, J. R.; Suschitzky, H. *Tetrahedron Lett.* **1975**, 2099. Fitton, A. O.; Frost, J. R.; Hougton, P. G.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1691. Ghosh, C. K.; Bandyopadhyaya, C.; Morin, C. *Ibid.* **1983**, 1989.

(10) Yates, P.; Douglas, S. P. *Can. J. Chem.* **1982**, *60*, 2760.

Scheme III



the intermediate **21**, resulting from the reaction of **6** with **14**. **8** may also arise by double addition of **14** to **1** followed by usual elimination reaction of the intermediate **22**. This last reaction sequence finds an analogy in the formation of a trisubstituted methane derivative by base-catalyzed condensation of **1a** with two molecules of dimedone.[11]

Experimental Section

The reported melting points are uncorrected. The NMR spectra were recorded at 100 MHz in $CDCl_3$ solution with Me_4Si as internal standard.

Treatment of Chromone-3-carboxaldehyde (1) with Triethylamine in Alcohol. Typical Experiment. The aldehyde **1a** (1.74 g, 10 mmol) was refluxed in dry methanol (50 mL) containing triethylamine (1 mL) for 4 h. The precipitated solid was separated from the dark red reaction mixture by filtering the mixture while still hot, and then washing with hot methanol to give the trichromonylmethane (**8a**) as a white amorphous solid (28 mg, 2%). Since it was insoluble in most of the solvents **8a** could not by crystallized: mp 305 °C dec; ν_{max} (KBr) 1640 (CO), 1630 (CO), 1610 (C=C) cm^{-1}; MS, *m/e* (relative intensity) 448 (M^+, 100), 438 (13), 328 (87), 303 (9), 300 (9), 271 (16). Anal. Calcd for $C_{28}H_{16}O_6$: C, 74.99; H, 3.60. Found: C, 75.10; H, 3.21. The filtrate was concentrated and diluted with water when an oily mass appeared. It was extracted with chloroform, and the organic extract was dried, charcoalized, concentrated, charged over an alumina column, and eluted with ethyl acetate–light petroleum, bp 60–80 °C (1:4). The first two fractions (2 × 10 mL) of the eluate contained chromone (**3a**) (30 mg, 2%): mp and mmp[3] 61 °C (water). The middle fractions (4 × 15 mL) on evaporation of the solvent furnished the dichromonylmethane **7** (X = H, R = Me) (117 mg, 7%): mp and mmp 158 °C (chloroform–light petroleum). The latter fractions contained the chromanone **5a** (146 mg, 10%): mp and mmp[7] 162° (chloroform–light petroleum).

The other aldehydes (**1b–f**) were similarly refluxed in alcohol under the catalysis of triethylamine. After separation of the precipitated compound **8**, the reaction mixture was concentrated and diluted with water, and a solid mass was obtained; its fractional crystallization from chloroform–light petroleum afforded the compounds as listed in Table I. The spectral data of the compounds **4–6** are tabulated in Tables II–IV, respectively.

Authentic Sample of 3-(Dimethoxymethyl)chromone (4, R = Me). General Procedure. The aldehyde **1** (5 mmol) was refluxed in dry methanol (50 mL) containing *p*-toluenesulfonic acid (50 mg) for 12 h. A portion of the solvent (30 mL) was distilled, the residual solution was cooled and diluted with 5% sodium bicarbonate solution (25 mL), and the deposited solid was filtered, dried, and crystallized from benzene–light petroleum to afford the acetal **4** (Table II) in 70–90% yield.

Authentic Sample of the Ether 7 (X = H, R = Me). A solution containing **1a** (870 mg, 5 mmol) and 1-(dimethylamino)-2-(*o*-hydroxybenzoyl)ethylene (**9**, X = H, $R^1 = R^2$ = Me)[6] (955 mg, 5 mmol) in dry benzene (75 mL) was refluxed in a Dean–Stark apparatus for 20 h and then concentrated and diluted with light petroleum to yield the compound **13** (1.34 g, 74%): mp 217 °C (chloroform–light petroleum), λ_{max} (EtOH) 228 (log ϵ 4.31), 307 (3.87), and 370 (4.05) nm; δ 8.32–7.28 (8 H, m, Ar H + vinyl H), 7.16 (1 H, s, -$CHNMe_2$), 7.10–6.80 (2 H, m, H-8 and H-8′), and 3.16 [6 H, s, $N(CH_3)_2$]. Anal. Calcd for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03. Found: C, 72.88; H, 5.31; N, 4.27. The preceding compound **13** (173 mg, 0.5 mmol) was refluxed in methanol (15 mL) containing concentrated sulfuric acid (2 drops) for 8 h. Concentration of the reaction mixture followed by dilution with water afforded the ether **7** (X = H, R = Me) (100 mg, 60%): mp 158 °C (chloroform–light petroleum); λ_{max} (EtOH) 228 (log ϵ 4.41), 275 (4.20), and 307 (4.31) nm; δ 8.36–6.96 (10 H, m, Ar H + vinyl H), 5.84 (1 H, d, J = 0.7 Hz, CHOMe), and 3.56 (3 H, s, OCH_3); MS, *m/e* (relative intensity) 334 (M^+, 10), 319 (M – Me, 25), 303 (M – OMe, 27), 291 (319 – CO, 40), 275 (303 – CO, 10), 247 (275 – CO, 11), 199 (319 – $C_7H_4O_2$, 100), 171 (199 – CO, 88). Anal. Calcd for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22. Found: C, 71.68; H, 3.70.

Conversion of 6 to 7. The substrate **6** (X = Br, R = Et) (50 mg) was refluxed in ethanol (15 mL) containing sulfuric acid (2 drops) for 6 h. On concentration and subsequent dilution of the reaction mixture was precipitated the bischromone **7** (X = Br, R = Et) (40 mg, 80%): mp 306 °C (benzene); λ_{max} ($CHCl_3$) 247 (log ϵ 4.66) and 310 (4.08) nm; ν_{max} ($CHCl_3$) 1645 (CO), 1600 (C=C), 1560 cm^{-1}; δ 8.28 (2 H, d, J = 1 Hz, 2 × H-2), 7.72 (2 H,

Table IV. ^1H NMR, δ ($CDCl_3$), for 2,3-Dihydro-2-alkoxy-3-[4-oxo-4*H*-1-benzopyran-3-ylmethylene]-4-oxo-4*H*-1-benzopyrans 6[a]

substituents X	R	exocyclic vinyl H[b] (m)	cyclic vinyl H[b] + Ar H (m)	-CHOR (m)	OR
Me[c]	Et	8.20	8.00–6.92	5.92	3.86 (m), 1.24 (t)
Br	Me	8.34	8.12–6.86	5.80	3.54 (t)
Br	Et[d]	8.40	8.12–6.90	5.96	3.88 (m), 1.24 (t)

[a] All the compounds gave satisfactory (±0.4) C, H analyses. [b] Assignment may be interchangeable. [c] Two sets of methyl protons appearing at δ 2.44 do not perfectly overlap. [d] This compound shows: UV λ (EtOH) 225 (log ϵ 4.50), 319 (4.10), and 352 (4.02) nm; IR ν ($CHCl_3$) 1675 (CO), 1650 (CO), 1600 (C=C) cm^{-1}.

(11) Haas, G.; Stanton, J. L.; von Sprecher, A.; Wenk, P. *J. Heterocycl. Chem.* 1981, *18*, 607.

d, J = 2 Hz, 2 × H-5), 7.32 (4 H, m, Ar H), 5.60 (1 H, d, J = 1 Hz, CHOEt), 3.60 (2 H, q, OCH_2Me), 1.24 (3 H, t, CH_3). Anal. Calcd for $C_{21}H_{14}Br_2O_5$: C, 49.83; H, 2.79. Found: C, 49.48; H, 3.10. The compound **6** (X = Br, R = Me) was similarly converted to **7** (X = Br, R = Me); mp 280 °C, in 75% yield by refluxing it in methanol in the presence of sulfuric acid; δ 8.30 (2 H, d, J = 1 Hz, 2 × H-2), 7.70 (2 H, d, J = 2 Hz, 2 × H-5), 7.28 (4 H, m, Ar H), 5.78 (1 H, d, J = 1 Hz, CHOMe), 3.60 (3 H, s, OCH_3). Anal. Calcd for $C_{20}H_{12}Br_2O_5$: C, 48.81; H, 2.46. Found: C, 48.50; H, 2.12.

Acknowledgment. This research was supported by a grant from CSIR [Scheme No. 2(161)/81-EMR-II]. Help with spectral data from Dr. A. Chakravorty and Mr. P. Ghosh Dastidar of IICB, Calcutta, is duly acknowledged.

Registry No. **1a**, 17422-74-1; **1b**, 42059-81-4; **1c**, 42059-79-0; **1d**, 42248-31-7; **1e**, 52817-12-6; **1f**, 42059-80-3; **3a**, 491-38-3; **4d** (R = Me), 74729-96-7; **4e** (R = Me), 90368-62-0; **4f** (R = Me), 90368-63-1; **5a**, 52852-99-0; **5b**, 90368-64-2; **5c**, 90368-65-3; **6b** (R = Et), 90368-66-4; **6e** (R = Me), 90368-67-5; **6e** (R = Et), 90368-68-6; **7a** (R = Me), 90368-69-7; **7e** (R = Me), 90368-70-0; **7e** (R = Et), 90368-71-1; **8a**, 90368-72-2; **9a** (R^1 = R^2 = Me), 1776-08-5; triethylamine, 121-44-8.

Supplementary Material Available: Elemental analysis data for **4–6** (Table IIA–IVA) (3 pages). Ordering information is given on any current masthead page.

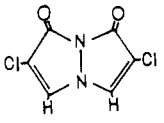
Bimanes. 20. Remarks on the Infrared Spectrum of 9,10-Dioxa-*syn*-(hydro,chloro)bimane (3,7-Dichloro-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione)

Victoria L. Shannon,† Herbert L. Strauss,*† and Edward M. Kosower*‡,[1]

Departments of Chemistry, University of California, Berkeley, California 94720, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, 69978 Israel, and State University of New York, Stony Brook, New York 11794

Received February 7, 1984

The bimanes are an interesting group of flexible bicyclic conjugated molecules.[2-9] Simple bimanes appear to be planar in the crystal. The crystal structure of *syn*-(H,Cl)B (**1**) [9,10-dioxa-*syn*-(hydro,chloro)bimane (3,7-dichloro-



1 *syn*-(H,Cl)B

1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione)] shows the molecules to be planar and tightly packed (d = 1.863 g cm^{-3}). However, high thermal parameters are found for the central nitrogens in the direction normal to the plane, and there are numerous bimanes with nonplanar structures in the crystal.[6,8] That bimanes equilibrate in solution between bent conformations is indicated by NMR spectra (averaging of different hydrogens on 4,6-bridging groups) and fluorescence spectra (bent and planar molecules have different absorption but similar emission spectra).[5]

Infrared spectra have been shown to be sensitive to intramolecular motion.[10] The effect of pressure (0–17 kbar) on the IR bands was studied to probe the influence

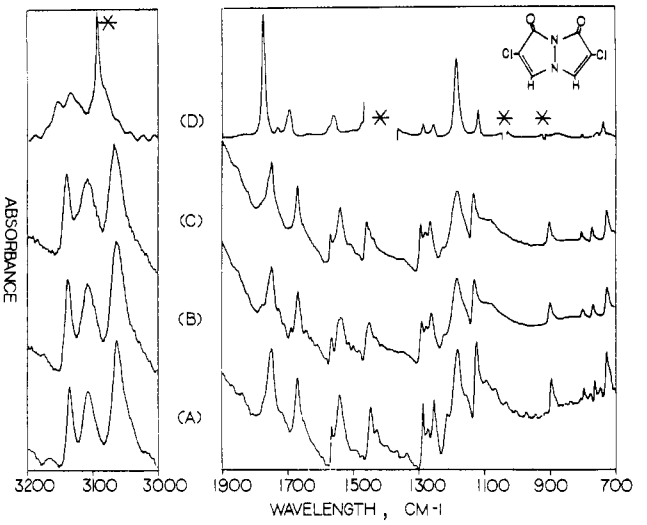


Figure 1. Infrared spectra of 9,10-dioxa-*syn*-(hydro,chloro)-bimane [syn-(H,Cl)B] (**1**). Sample ground with KBr as pellet in a diamond anvil cell (DAC) at (A) 1 bar (atmospheric pressure), (B) 11 kbar, (C) 17 kbar or (D) as saturated solution [0.028 M] in CH_3CN [1900–1700-cm^{-1} region] (or in CD_3CN (1% CD_2HCN) [3200–3000-cm^{-1} region]). The solvent spectrum was subtracted from the measured spectrum to give the spectrum from which the frequencies were obtained. Starred (*) bands are partially (C–H region) or wholly solvent bands.

of molecular motion within the crystalline environment of **1**. Restricting molecular motion of the bimane rings in the crystal should change the bands. It was also of interest to determine if pressure would induce a change in crystal structure.

Previous work[2] had revealed an unexpected set of C–H stretching bands in the infrared spectrum of a crystalline thin film of **1**. In place of, at most, two bands (a symmetric and an antisymmetric stretch), three main bands are observed, and at least two additional bands are resolvable by curve fitting. This prompted us to investigate the origin of the extra bands, using a comparison of solution spectra with those of the solid phase, to assess the contribution of interactions within the crystal.

Results

The three bands found previously in the crystalline thin film for the C–H stretching region are also found for **1** in a KBr pellet (Figure 1). (One or two additional small bands are resolvable by Lorentzian curve fitting.) The band positions are at 3135, 3107, and 3063 cm^{-1}. The unusually sharp and strong band at 3160 cm^{-1} found in the crystalline thin film is absent. Pressure has only a small effect on the C–H bands, the absorption at 3135 cm^{-1} shifting to 3138 cm^{-1} (11 kbar) or 3139 cm^{-1} (17 kbar). The other bands hardly change, except for a slight broadening.

† University of California, Berkeley.
‡ Tel-Aviv University and State University of New York. Address correspondence to Tel-Aviv University.

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