δ 0.7–1.0 (m, 3, diastereomeric $CHCH_3$), 1.05 (d, J = 6 Hz, 3, $CH_3CHCOOMe$), 1.3–2.1 (m, 7, ring CH_2, chain CH), 2.1–2.5 (m, 4, $CHC{=}O$, $CH_2C{=}O$), 3.66 (s, 3, OCH_3); IR (neat) 1733 (ester C=O), 1708 (ketone C=O) cm^{-1}. Anal. ($C_{12}H_{20}O_3$) C, H.

In addition, methyl γ-methyl-2-oxocyclohexanebutanoate (16 mg, 8%, t_R 13.3 min) was obtained: NMR ($CDCl_3$) δ 0.86 (br d, J = 6 Hz, 3, $CHCH_3$), 1.0–2.0 (m, 9, ring and chain CH's), 2.0–2.5 (m, 5, $CH_2C{=}O$), 3.64 (s, 3, OCH_3); IR (neat) 1738 (ester C=O), 1709 (ketone C=O) cm^{-1}. Anal. ($C_{12}H_{20}O_3$) C, H.

G. With *trans*-2-Butene. VPC analysis as above showed the crude material to be a 45:55 mixture of propanoic and butanoic esters as in F. Isolation as above gave 17 mg (8%) of methyl α,β-dimethyl-2-oxocyclohexanepropanoate and 19 mg (9%) of methyl γ-methyl-2-oxocyclohexanebutanoate, identical with the samples reported in F.

Reaction of 2-Lithioacetone with Propene. Purification by evaporative distillation (1 Torr, 100 °C) gave 65 mg (40%) of an inseparable mixture of methyl 3-methyl-5-oxohexanoate[19] (65%) and methyl 2-methyl-5-oxohexanoate (35%).[20] For the 3-methyl compound (isomer A): NMR ($CDCl_3$) δ 0.95 (d, J = 6 Hz, 3, $CHCH_3$), 2.09 (s, 3, CH_3CO), 2.16–2.7 (m, 5, $COCH_2CH(CH_3)CH_2COOMe$), 3.61 (s, 3, OCH_3). For the 2-methyl compound (isomer B): NMR ($CDCl_3$) δ 1.12 (d, J = 7 Hz, 3, $CH_3CHCOOMe$), 1.6-1.9 (m, 6 lines, 2, $CH_2CH(CH_3)COOMe$), 2.09 (s, 3, CH_3CO), 2.16–2.7 (m, 3, CHCO), 3.61 (s, 3, OCH_3). For the mixture: IR (neat) 1736 (ester C=O), 1715 (ketone C=O) cm^{-1}. Anal. ($C_8H_{14}O_3$) C, H.

Reaction of the Lithium Salt of Me_3Si-Protected Benzaldehyde Cyanohydrin with Ethene. The crude reaction solution (THF) was stirred with 30 mL of 2 N HCl for 0.75 h at 25 °C and extracted with ether (3 × 75 mL), and the combined extracts were washed with 2 N HCl (3 × 30 mL) and water (30 mL). Ice was added to the organic phase and the mixture was shaken with dilute NaOH (70 mL) for 0.1 h. (Care must be taken to avoid overhydrolysis to the carboxylic acid.) After washing with water and drying over anhydrous $MgSO_4$ the organic phase was concentrated under vacuum. Purification by medium-pressure liquid chromatography (SiO_2, 30:1 hexane–ether) gave 288 mg (50%) of methyl 3-benzoylpropionate:[21] NMR (CCl_4) δ A_2B_2 system δ_A = 2.55, δ_B = 3.16 (m, 4, $COCH_2CH_2COOMe$), 3.60 (s, 3, OCH_3), 7.4 (m, 3, ArH), 7.9 (m, 2, ArH); IR (CCl_4) 1740 (ester C=O), 1690 (Ar C=O), 1600 (Ar C=C) cm^{-1}. Anal. ($C_{11}H_{12}O_3$) C, H.

Reaction of Sodium Diethyl Acetamidomalonate with Ethene. The reaction was run in the usual fashion (Et_3N, HMPA) using carbanion prepared with LDA and 10% HMPA. Purification of the crude reaction mixture by medium-pressure liquid chromatography (SiO_2, 7:3 ethyl acetate–hexane) gave 240 mg of material. NMR ($CDCl_3$) showed this to be a 7:3 mixture of the desired product, 1-acetamidopropanetricarboxylic acid 1,1-diethyl-3-methyl esters (56%), identical in all respects with authentic material prepared by an alternate route,[22] and diethyl acetamidomalonate. This mixture resisted separation.

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Supplementary Material Available: ^{13}C NMR data (Table II) (8 pages). Ordering information is given on any current masthead page.

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Bimanes. 5. Synthesis and Properties of *syn*- and *anti*-1,5-Diazabicyclo[3.3.0]octadienediones (9,10-Dioxabimanes)

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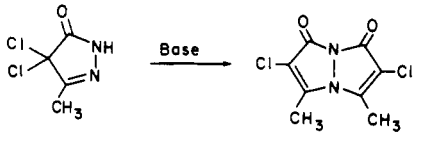
Contribution from the Department of Chemistry, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel, and the Department of Chemistry, State University of New York, Stony Brook, New York 11794. *Received December 17, 1979*

Abstract: A simple three-step synthesis of two essentially new classes of bicyclic heterocyclic compounds, the *syn*- and *anti*-1,5-diazabicyclo[3.3.0]octadienediones, from β-keto esters via the pyrazolinone and halopyrazolinone is described. The syn compounds (-3,6-diene-2,8-diones) are usually strongly fluorescent; the anti derivatives (-3,7-diene-2,6-diones) are normally nonfluorescent and very phosphorescent. A short form name, 9,10-dioxabimanes, is introduced (*bi*, two, and *manus*, hand), with substituents adjacent to the carbonyl designated R_1 (or α) and substituents at the second carbon being labeled R_2 (or β). "9,10-Dioxabimanes" may be described as *syn*-(or *anti*-)(R_2,R_1)B. 9,10-Dioxabimanes are relatively high-melting, sublimable, stable molecules with simple NMR and fairly characteristic IR spectra. The (R_2,Cl)B derivatives can be hydrogenated to (R_2,H)B compounds. Bromination of (CH_3,R_1)B produces useful monobromo and dibromo compounds. A plausible mechanism for the formation of both classes of 9,10-dioxabimanes is presented. The formation of mixed 9,10-dioxabimanes (e.g., (R_2,R_1)(R_2',R_1')B) from mixtures of halopyrazolinones is readily accounted for. The 9,10-dioxabimane rings are hydrogenated with some difficulty to a mixture of products, including some in which the N–N bond has been cleaved. *syn*-(CH_3,CH_3)B resists oxidation by a variety of agents but can be converted to an α-acetoxy derivative with ceric ion.

Introduction

In the course of attempts to prepare 2-octadecynoic acid via the treatment of the appropriate 4,4-dichloro-3-pyrazolin-5-one (the Carpino procedure[1c]) we noted the formation of a highly fluorescent compound in ca. 0.1% yield. The precursor for 2-butynoic acid yielded a similar fluorescent compound in 0.03% yield, and spectroscopic and analytical data suggested the possibility that the fluorescent compounds were derivatives of 1,5-diazabicyclo[3.3.0]octadienedione (eq 1).



(1)

Reasonably efficient and fairly general syntheses for the fluorescent compounds and the nonfluorescent isomers were de-

(1) (a) Tel-Aviv University and State University of New York. (b) Tel-Aviv University. (c) Carpino, L. A. *J. Am. Chem. Soc.* **1958**, *80*, 599.

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veloped on the basis of the unpromising results of the initial work. A literature search revealed that a small number of benzo derivatives analogous to the fluorescent compounds were prepared many years ago by Michaelis[2] via a condensation reaction which has been improved by Veibel[3] and now extended by ourselves. Our preliminary report[4] on the 1,5-diazabicyclo[3.3.0]octadienediones alluded briefly to their interesting chemical and photophysical properties. In the present paper, we shall describe the syntheses and some of the chemical and physical properties and suggest a mechanism of formation. In subsequent papers, the photophysical behavior, the crystal structure,[5] and many of the other useful and fascinating attributes of these molecules will be presented.

Results

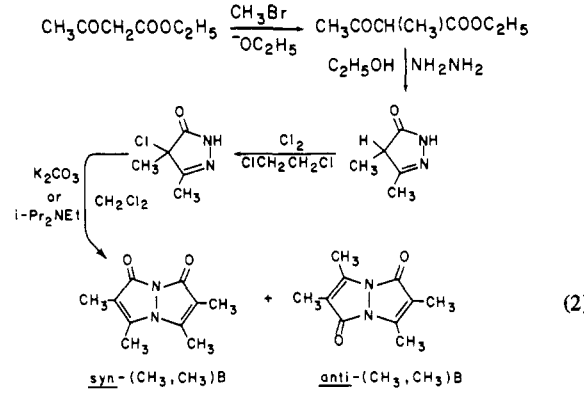
Syntheses. The logical intermediate in the conversion of a halopyrazolinone to a 1,5-diazabicyclo[3.3.0]octadienedione is a 2,3-diazacyclopentadienone, an intermediate which has been generated from the pyrazolinone by oxidation with $Pb(OAc)_4$. However, we noted that elimination of a hydrogen halide from the halopyrazolinone was much more effective in producing the desired compounds than oxidation of the pyrazolinone. After a number of trials, it was found that a heterogeneous base ($K_2CO_3 \cdot 1.5H_2O$) in a number of organic solvents gave the best yields of fluorescent bicyclic products. A soluble base, *N,N*-diisopropylethylamine, leads to good yields of bicyclic products, yielding mixtures in which the nonfluorescent product is predominant in a number of cases. Thus, by selecting the base used in the elimination step, it is possible to control the nature of the major product.

A typical sequence for the synthesis of the bicyclic compounds is as follows. Ethyl acetoacetate is alkylated in the presence of sodium ethoxide. Careful removal of unreacted ester by fractionation under reduced pressure is an absolute necessity to avoid product mixtures at a later stage. The β-keto ester is converted with hydrazine in ethanol to the pyrazolinone which is chlorinated by chlorine in 1,2-dichloroethane as described by Carpino.[1c] The chloropyrazolinone is purified whenever possible and then treated with hydrated potassium carbonate in dichloromethane by stirring (0–20 °C) for 3–12 h. A combination of crystallization and column chromatography usually affords both the fluorescent and nonfluorescent isomers of the 1,5-diazabicyclo[3.3.0]octadienediones. The execution of the elimination step in which a soluble base is used is equally simple, the base being added at a suitable rate to a solution of the chloropyrazolinone in dichloromethane cooled to a temperature at which the reaction proceeds at a reasonable rate (from 0 °C to room temperature for the examples described in this paper).

For the sake of brevity, the bicyclic products will be referred to as 9,10-dioxabimanes, the fluorescent isomer having the carbonyl groups in the proximal arrangement (syn) and the nonfluorescent isomer having carbonyl groups in the distal arrangement (anti). The nomenclature is explained fully in the Discussion. Equation 2 illustrates the formation of *syn*-(CH_3,CH_3)B (B = 9,10-dioxabimane) and *anti*-(CH_3,CH_3)B (B = 9,10-dioxabimane) from simple starting materials.

Separations of the 9,10-dioxabimanes by chromatography are relatively easy, since small changes in molecular structure produce significant changes in chromatographic behavior. Some 9,10-dioxabimanes are sensitive to base, and the chromatographic substrate may be varied according to need from alumina to silica to magnesium silicate.

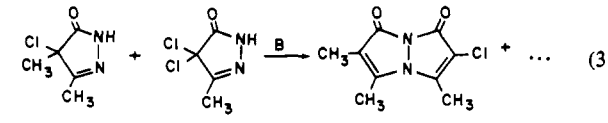
"Mixed" 9,10-dioxabimanes are easily made by the standard procedure by using a mixture of two different halopyrazolinones, the case of $(CH_3,CH_3)(CH_3,Cl)$B being illustrated in eq 3 (also



(2)

syn-(CH_3,CH_3)B anti-(CH_3,CH_3)B

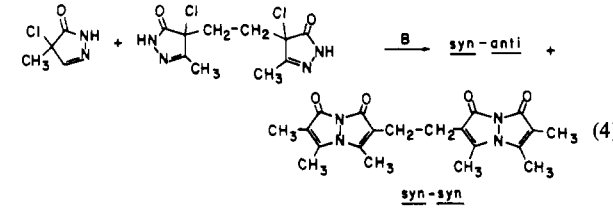
an example of the general formulation for 9,10-dioxabimanes, $(R_2,R_1)(R_2',R_1')$B).



(3)

syn-$(CH_3,CH_3)(CH_3,Cl)$B

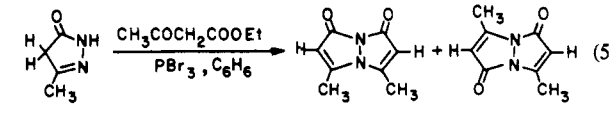
In a few cases, the 9,10-dioxabimane synthesis failed to give any product (e.g., from 3,4-trimethylenepyrazolin-5-one (see below)) or perhaps yielded only very small amounts of 9,10-dioxabimane. No single reason can be advanced for these failures. Attempts to produce a polymeric 9,10-dioxabimane from a dimethylene bis(halopyrazolinone) did not succeed, but "trapping" the intermediate(s) with the intermediate for (CH_3,CH_3)B led to small yields of mixed bis(9,10-dioxabimanes), as shown in eq 4. The diversity of compounds accessible through this very simple synthesis is clearly very large.



(4)

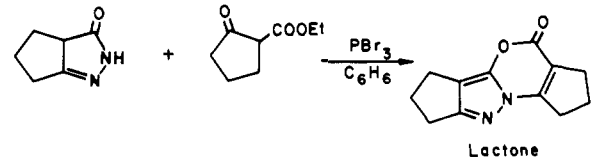
syn-syn

An alternative route to certain 9,10-dioxabimanes was first discovered by Michaelis[2] who heated *o*-carboxyphenylhydrazine with ethyl acetoacetate to produce a couple of *syn*- and *anti*-monobenzo-9,10-dioxabimanes along with a hydroxypyrazolyl acrylolactone which is encountered in a number of 9,10-dioxabimane preparations and transformations (see eq 6). Veibel[3] used PCl_3 as the condensing agent and we have found (a) that the reaction can be applied to the synthesis of 9,10-dioxabimanes with purely aliphatic substituents and (b) that the use of a solvent improves the procedure. The reaction of 3-methylpyrazolin-5-one with ethyl acetoacetate and PBr_3 in benzene is shown in eq 5. Both *syn*-(CH_3,H)B and *anti*-(CH_3,H)B are formed.



(5)

Only modest yields of lactone could be obtained from the application of this procedure to 3,4-trimethylenepyrazolin-5-one and 2-(carboethoxy)cyclopentanone (eq 6). 9,10-Dioxabimanes



(6)

Lactone

were not detected in the reaction product nor could they be produced in the halopyrazolinone reaction with base.

(2) Michaelis, A. *Justus Liebigs Ann. Chem.* **1910**, *373*, 148, 202.
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(4) Kosower, E. M.; Pazhenchevsky, B.; Hershkowitz, E. *J. Am. Chem. Soc.* **1978**, *100*, 6516.
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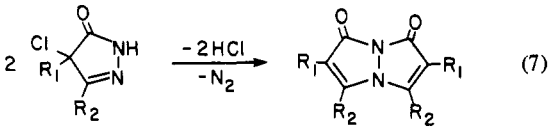
Structural Proof and Identification. A variety of data demonstrated that the fundamental conversion for the reaction of halopyrazolinones with base to yield a fluorescent product was that of the loss of two hydrogen halide molecules and one nitrogen molecule from two molecules of halopyrazolinone to give one molecule of product (eq 7). Mass spectra almost always showed



(7)

a parent peak, M^+ (EI), or M + 1 (CI). Chemical analyses showed that the molecules had the expected composition. In a number of CI mass spectra, peaks with the molecular weight 2M + 1 appeared. For this reason, the molecular weights were determined for a number of 9,10-dioxabimanes and revealed that they were monomeric in solution. The ^{13}C NMR spectra of several 9,10-dioxabimanes had the relatively simple pattern expected for a highly symmetrical molecule, with a single low-field peak for each of the three different ring carbons.

The ^1H NMR spectra of 9,10-dioxabimanes are usually quite simple and reflect the highly symmetrical nature of the structure carrying the protons, derivatives like the *syn*- and *anti*-$(CH_3,CH_3)B$ showing each only two different singlets. The infrared spectra of the *syn*- and *anti*-9,10-dioxabimanes are usually distinguishable from one another, especially in the carbonyl region, and are different from those of cyclic imides. The *syn*-9,10-dioxabimanes show three carbonyl bands, and the *anti*-9,10-dioxabimanes one band and a shoulder. These will be described in greater detail below.

The foregoing remarks indicate that the 9,10-dioxabimanes have the expected analytical composition, give mass spectra with parent peaks corresponding to the molecular weight, have ^{13}C and ^1H NMR spectra of appropriate character and simplicity, and exhibit infrared carbonyl bands different from those of related and precursor molecules. Final and unequivocal proof of molecular structure together with a definitive demonstration that the fluorescent molecules are syn and the nonfluorescent molecules anti came from X-ray crystallography.[5]

Physical Properties. The 9,10-dioxabimanes are crystalline solids which possess moderately high melting points. Their high thermal stability is reflected in the fact that many are unchanged if cooled immediately after melting, even from temperatures as high as 320 °C. Heating for longer periods produces chemical changes which are described in the following section. In many cases, the *syn*-9,10-dioxabimanes have higher melting points than the corresponding *anti*-isomers (*syn*-$(CH_3,CH_3)B$, mp 211–212 °C, *anti*-$(CH_3CH_3)B$, mp 174 °C; *syn*-$(C_6H_5,Cl)B$, mp 318–320 °C, *anti*-$(C_6H_5,Cl)B$, mp 236–237 °C), but this is not always true (*syn*-$(CH_3,Br)B$, mp 211–212 °C, *anti*-$(CH_3,Br)B$, mp 237–238 °C).

Many 9,10-dioxabimanes are quite volatile and can be sublimed readily at reduced pressure. *syn*-$(CH_3,CH_3)B$ sublimes unchanged at 200 °C (760 mm), *syn*-$(C_6H_5,Cl)B$ at 190 °C (0.1 mm), and *anti*-$(CH_3,CH_3)B$ at 120 °C (0.1 mm).

NMR Spectra. The ^{13}C NMR spectra of *syn*-$(CH_3,CH_3)B$ and *anti*-$(CH_3,CH_3)B$ reveal very little difference between the shifts of the carbons in the two isomers: syn 160.5, 146.1, 111.8, 11.9, 6.7 ppm vs. anti 161.6, 145.8, 112.1, 10.7, 6.3 ppm, with probable assignments (in the order shown) C=O, N—C=, C—C=, C(β), and C(α).

The ^1H NMR spectra of corresponding syn and anti isomers are quite similar, and the positions are similar to those of related α,β-unsaturated carbonyl compounds. For $(CH_3,CH_3)B$, the β-CH_3 signal for the syn isomer is found at 2.28 ppm, that for the anti isomer at 2.40 ppm. The α-CH_3 signals are found at 1.85 (syn) and 1.80 ppm (anti). The hydrogens attached directly to the rings (e.g., as in $(CH_3,H)B$) are found at 5.43 (syn) and 5.38 ppm (anti). The α hydrogens show allylic splitting from the β-methyl group, with J = 0.88 Hz (syn) or 1.18 Hz (anti), and the β-methyl groups show the corresponding splitting, with doublets centered at 2.38 ppm (J = 0.88 Hz) (syn) or 2.49 ppm (J = 1.18 Hz) (anti).

Table I. ^1H NMR Spectral Data for *syn*- and *anti*-Dioxabimanes (δ)[a]

(R_2,R_1)	$C_\alpha H$	$C_\alpha CH$	$C_\beta CH$
	syn-$(R_2,R_1)B$		
(CH_3,H)	5.42 (m)		2.42 (d)
(CH_3,CH_3)		1.85 (s)	2.28
(CH_3,Cl)			2.50 (s)
$(CH_3,Cl)(CH_3,H)$	5.48 (s)		2.42 (s)
$(CH_3,Cl)(CH_3,CH_3)$		1.81 (s)	2.32 (s), 2.41 (s)
(CH_2Br,CH_3)		1.98 (s)	4.55 (s)
	anti-$(R_2,R_1)B$		
(CH_3,H)	5.38 (m)		2.46 (d)
(CH_2Br,CH_3)		1.89 (s)	4.66 (s)
(CH_3,CH_3)		1.80 (s)	2.40 (s)
(CH_3,Cl)			2.65 (s)

[a] In $CDCl_3$ (s = singlet, d = doublet, br s = broad singlet, m = multiplet).

A β-substituent (i.e., X in XCH_2) shifts the α-CH_3 signal downfield by 0.04 ppm to 0.13 ppm, and is useful for analysis. Some selected ^1H NMR data are shown in Table I.

IR Spectra. One of the best methods for characterizing 9,10-dioxabimanes is that of infrared spectroscopy. Three bands are usually observed for *syn*-9,10-dioxabimanes in the carbonyl region (1760–1790, 1735–1750, 1660–1690 cm^{-1}) whereas *anti*-9,10-dioxabimanes show one strong band (1680–1715 cm^{-1}) often accompanied by a shoulder at 1735–1755 cm^{-1}. A survey of the infrared data is presented in Tables II (syn compounds) and III (anti derivatives).

UV Spectra. *syn*-9,10-Dioxabimanes have absorption spectra indicating three electronic transitions in the ultraviolet region, with either two bands and a shoulder or three bands. The longest wavelength absorption varies between 354 and 409 nm, with absorption coefficients between 5500 and 12000 for dioxane solutions. *anti*-9,10-Dioxabimanes without conjugating substituents show only one absorption band in the ultraviolet range. However, a conjugating group leads to at least one and sometimes two additional bands. The absorption maxima of the anti derivatives are more intense and invariably at considerably shorter wavelengths than those of the corresponding syn compounds, with positions ranging from 317 to 354 nm and absorption coefficients between 11000 and 18800. Some typical absorption maxima are listed in Table IV.

Fluorescence Spectra. *syn*-9,10-Dioxabimanes exhibit a striking and strong fluorescence in solution. In dioxane, the positions of the fluorescence maxima vary between 388 and 495 nm, accompanied by shoulders at 20-nm longer wavelength. The quantum yields of fluorescence of many of the compounds range between 0.6 and 0.9. In contrast, the fluorescence of the *anti*-9,10-dioxabimanes is very weak, with quantum yields between 0.001 and 0.002 for maxima between 440 and 500 nm. Some typical fluorescence data are included in Table IV.

Phosphorescence Spectra. *syn*-9,10-Dioxabimanes are often phosphorescent at 77 K with maxima ranging between 450 and 600 nm and quantum yields less than 0.009. *anti*-9,10-Dioxabimanes are much more strongly phosphorescent than *syn*-9,10-dioxabimanes with maxima between 445 and 525 nm and quantum yields up to about 0.45.

The photophysical properties of the 9,10-dioxabimanes will be reported in much more detail elsewhere.[6,7]

Chemical Properties. The reactions of 9,10-dioxabimanes may be divided into three general groups for the purpose of gaining an overall view of the chemical behavior, namely, substitution, rearrangement, and ring opening. A number of electrophilic agents lead to very useful substitution products, as does catalytic reduction with hydrogen in certain cases. High temperatures lead to thermal

(6) Huppert, D.; Dodiuk, H.; Kanety, H.; Kosower, E. M. *Chem. Phys. Lett.* **1979**, *65*, 164–168.
(7) Kosower, E. M.; Dodiuk, H.; Kanety, H., in preparation.

Table II. Infrared Spectral Data for *syn*-Dioxabimanes (cm^{-1})

						3500–1415-cm^{-1} range								
(CH_3,H)	3130	3020				1765	1740	1660	1640 (s)	1600	1570	1485 (s)	1465	1415
(CH_3,CH_3)				2920			1745	1680		1610				
(CH_3,Cl)			2980	2930		1760		1690 1670 (s)		1600	1565 1545		1455	
(C_6H_5,CH_3)		3060		2920		1780	1740	1700	1630	1590		1500	1450	1430 1415
(C_6H_5,Cl)		3060		2930		1770		1690	1620	1590	1560	1495	1450	1420
(CH_3,C_6H_5)		3040	2980	2920		1760 (s)	1735	1700 (s) 1665		1605	1580 1570		1460 1450	1420
$(CH_3,H)(CH_3,Cl)$	3110					1765		1685	1615	1600	1575 1560		1450	1415
$(CH_3,CH_3)(CH_3,Cl)$				2930			1745	1675	1625		1575		1450	1415
(CH_2Br,CH_3)		3070	3000	2920		1755		1680 1665	1625	1600			1460	1415
						1400–690-cm^{-1} range								
(CH_3,H)	1400	1320	1290	1265	1205	1155		1070	1045	995	810	790	730	715
(CH_3,CH_3)	1405								1030					
(CH_3,Cl)	1405	1340	1290	1260		1170		1070	1040				740	
(C_6H_5,CH_3)	1390	1375		1240	1225 1190	1160		1095	1030	935		790	755 740	700
(C_6H_5,Cl)		1375	1300	1250	1200		1145	1080	1035	930		770	730	700
(CH_3,C_6H_5)	1390	1340	1275	1260		1150	1135	1090 1070		920	840	775	730	705 695
$(CH_3,H)(CH_3,Cl)$	1400	1360	1280		1215	1165	1135		1040		820	780	740	720
$(CH_3,CH_3)(CH_3,Cl)$	1385	1370	1300 1270		1210	1160	1120	1060	1035	985			730	
(CH_2Br,CH_3)	1390			1250	1235		1120		1000	970			750	

Table III. Infrared Spectral Data for *anti*-Dioxabimanes (cm^{-1})

						3500–1300-cm^{-1} range								
(CH_3,H)	3120	3110		1730 (s)	1680		1590			1445	1400		1350	
(CH_3,CH_3)	3370	2930	1825	1750 (s)	1695	1630					1415		1365	
(CH_3,C_6H_5)	3055				1675					1450	1410		1365	1330	1310
(CH_3,Cl)	3460			1725	1700	1600					1400		1355	1335	
(C_6H_5,Cl)	3065	2930		1730	1715	1605	1590	1575	1490	1450			1365		
(CH_2Br,CH_3)	3400	2985		1755 (s)	1680					1450	1410	1390			
						127–650-cm^{-1} range								
(CH_3,H)			1215	1170	1095		1015	880	820					
(CH_3,CH_3)		1275		1170	1105		995					735	705	
(CH_3,C_6H_5)		1265			1085	1040			805	770		735	705	
(CH_3,Cl)				1190	1150	1035				785		720		
(C_6H_5,Cl)			1205	1175		1040			820	775	740		690	
(CH_2Br,CH_3)				1185		1050		895	800			730	705	650

Table IV. Absorption and Emission Data for *syn*- and *anti*-Dioxabimanes in Dioxane

	absorption[a]			fluorescence	
(R_2,R_1)	λ_1 max (ϵ)	λ_2 max (ϵ)	λ_3 max (ϵ)	λ_{max}	ϕ_F[b]
		syn-$(R_2,R_1)B$			
(CH_3,H)	354 (8600)	250 (sh, 4500)	225 (12 000)	388, 405 (sh)	0.76
(CH_3,CH_3)	359 (6500)	255 (sh, 5200)	235 (14 600)	420, 440 (sh)	0.72
(C_6H_5,CH_3)	358 (7000)	265 (16 000)	220 (13 600)	447, 475 (sh)	0.67
(CH_3,C_6H_5)	395 (8000)	262 (10 200)	220 (7600)	470, 500 (sh)	0.72
(C_6H_5,C_6H_5)	409 (10 000)	305 (sh, 8800)	225 (22 500)	495, 525 (sh)	0.75
(C_6H_5,Cl)	369 (6700)	270 (15 500)	235 (sh, 10 600)	457, 480 (sh)	0.62
(CH_3,Cl)	364 (7100)	255 (sh, 7000)	235 (14 300)	429, 455 (sh)	0.79
(CH_2Br,CH_3)	390 (6600)	266 (11 000)			
		anti-$(R_2R_1)B$			
(CH_3,H)	325 (14 600)			440	0.001
(CH_3,CH_3)	322 (15 100)			463	0.001
(CH_3Cl)	325 (15 500)			463	0.001
(CH_3,C_6H_5)	344 (18 800)	248 (22 100)		476	0.002
(C_6H_5,Cl)	354 (11 750)	288 (22 700)	275 (20 000)	500	0.002
(CH_2Br,CH_3)	349 (11 500)				

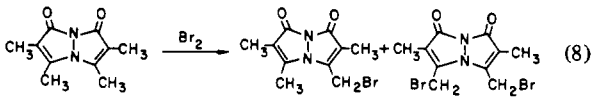
[a] sh = shoulder. [b] Uncorrected for refractive index. Referred to quinine sulfate 0.1 N H_2SO_4, $\phi_F = 0.55$.

rearrangements of both *syn*- and *anti*-9,10-dioxabimanes. In both electrophilic reactions and thermal rearrangements, many of the products contain the bimane ring, which thus *persists* through these chemical transformations. Basic nucleophiles (methoxide or hydroxide ions or amines) cause ring opening. However, the ring-opened products readily return to 9,10-dioxabimanes when treated with electrophilic agents.

Electrophilic Agents H^+. 9,10-Dioxabimanes change very little in absorption spectrum on solution in acids such as moderately concentrated H_2SO_4, concentrated HCl, or 1 M HCl. A solution

of *syn*-(CH_3,CH_3)B in 6 N H_2SO_4 has an absorption spectrum in which the longest wavelength maximum shifts slightly (386 nm (H_2O) to 392 nm (H_2SO_4)) without intensity change, and the rest of the spectrum is almost unchanged in intensity or position; such solutions are quite stable, with spectra indicating that 40% of the syn compound is still present after 4 months at room temperature. *anti*-(CH_3,CH_3)B in 6 N H_2SO_4 shows even less change in absorption spectrum (316 nm (H_2O) to 318 nm (H_2SO_4)) and 90% of the original compound is still present after 4 months at room temperature. The decrease in bimane absorption in acid is, in both cases, accompanied by an increase in absorption near 210 nm, implying breakdown to very small molecules. A solution of *syn*-(CH_3,CH_3)B in 10% HCl is stable at room temperature, but 15 h of reflux leads to the formation of 3,4-dimethyl-2-pyrazolin-5-one (45%) and 2-butanone (54%). *anti*-(CH_3,CH_3)B was recovered in 90% yield after 24 h of reflux in 10% HCl.

Electrophilic X_2. Depending upon the substrate, two types of products (substitution of α-H (ring) or substitution of β-alkyl H) may be isolated for the reaction of 9,10-dioxabimanes with bromine. *syn*-(CH_3,H)B is converted into *syn*-(CH_3,Br), a synthesis which gives better yields than base treatment of a bromopyrazolinone. A more important bromination reaction is that which occurs with *syn*-(CH_3,CH_3)B, in which 1 equiv of bromine leads to a mixture dominated by a monobromo compound, and 2 equiv of bromine give a good yield of a dibromo derivative. The bromo compounds are photosensitive, and it is best to carry out the procedure and the chromatographic separation required to obtain pure monobromo compound in red light or in apparatus protected from light. The conversion is illustrated in eq 8.

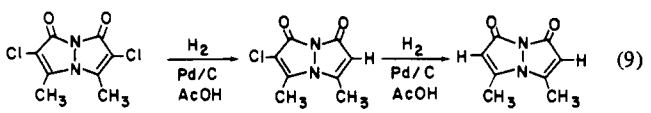


(8)

anti-(CH_3,CH_3)B also yields monobromo and dibromo derivatives, the proportion again depending upon the amount of bromine used. Neither *syn*- nor *anti*-($BrCH_2$,CH_3)B reacts further with bromine to any appreciable extent, a circumstance which makes the bromination reactions very simple.

Iodine monochloride reacts with *syn*-(CH_3,H)B to give *syn*-(CH_3,I)B, a compound which could not be made by the usual route because of the instability of the iodopyrazolinone. Bromination of *syn*-(CH_3,CH_3)(CH_3,C_6H_5)B yields only a monobromo derivative, *syn*-($BrCH_2$,CH_3)(CH_3,C_6H_5)B, even in the presence of excess bromine. The great variation in the reactivity of the 9,10-dioxabimanes with the nature of substituents on the bimane ring is shown by the unreactivity of *syn*-(CH_3,Cl)B, which gave only a monobromo derivative in the presence of 2 equiv of bromine for several months. Chlorination does not lead to substitution products even in the case of *syn*-(CH_3,C_6H_5)B and the products, which are complex mixtures of polychloro compounds, have not been examined further.

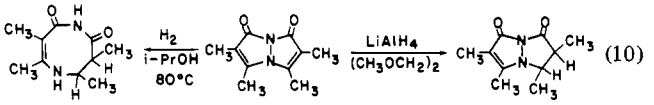
Hydrogen. Reaction of hydrogen with *syn*-(CH_3Cl)B over platinum or palladium in acetic acid proceeds easily in two stages, the first leading to the mixed bimane, *syn*-(CH_3,Cl)(CH_3,H)B, and the second yielding *syn*-(CH_3,H)B (eq 9). The anti isomer behaves in a parallel fashion on hydrogenation.



(9)

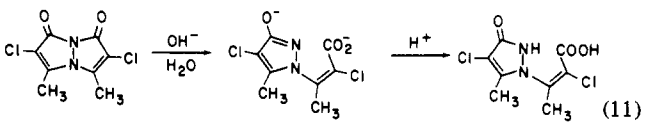
Catalytic hydrogenation of *syn*-(CH_3,CH_3)B proceeds much more slowly than the reaction with *syn*-(CH_3,Cl)B, using 3 atm of H_2 at 80 °C in isopropyl alcohol. After 48 h, a 10% yield of a product was isolated and characterized by NMR, IR, and mass spectra as a cyclic compound in which the N–N bond had been cleaved. *syn*-(CH_3,CH_3)B also reacted relatively slowly with $LiAlH_4$, and a dihydro derivative could be isolated in only 14% yield (eq 10).

Nucleophiles. Bases. The sensitivity of many 9,10-dioxabimanes to bases was readily noted during their syntheses (which require

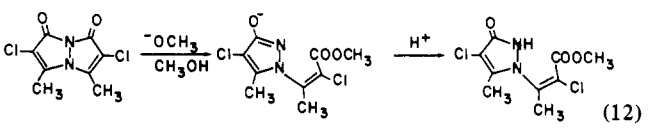


(10)

basic conditions) and purification (certain 9,10-dioxabimanes cannot be chromatographed on basic alumina). The absorption and fluorescence of *syn*-(CH_3,Cl)B disappeared quickly on mixing with 5% aqueous K_2CO_3, a new absorption band appearing at 291 nm in place of 388 nm. Acidification and extraction with CH_3CN gave a 70% yield of 3-(4′-chloro-3′-methyl-3′-pyrazolin-5′-on-1′-yl)-2-chlorocrotonic acid, for which the possibility that the product might be simply an adduct of hydroxide ion and the *syn*-(CH_3,Cl)B could be excluded by isolation and identification of the corresponding methyl ester from the reaction of methoxide ion. The methyl ester was unequivocally identified by its similarity to the methyl ester isolated from the reaction of methoxide ion with *syn*-(CH_3,H)B, the product having the requisite vinyl hydrogen. These reactions are shown in eq 11 and 12, the absorption maxima for the various species also being indicated.

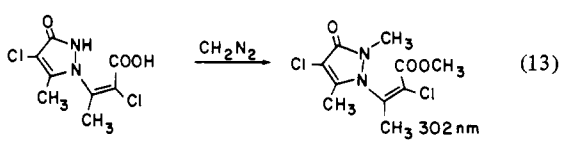


(11)



(12)

The reaction of the acid shown in eq 11 with CH_2N_2 yields only a dimethylated product, the *N*-methyl ester shown in eq 13, rather than the possible enol ether ester.



(13)

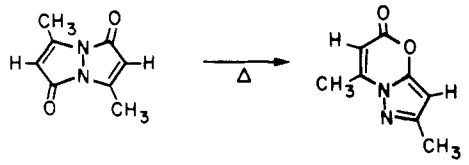
Both ester and acid are readily converted back to the 9,10-dioxabimanes from which they were obtained through the use of the appropriate electrophilic agents. For example, the acid (eq 11) is converted back to *syn*-(CH_3,Cl)B in over 90% yield on treatment with acetic anhydride.

The rate of the reaction of both *syn*- and *anti*-9,10-dioxabimanes with hydroxide ion varies considerably with the structure of the bimane. The details will be reported separately.[8]

Thermal Rearrangements. Although the 9,10-dioxabimanes are very stable compounds, prolonged heating at high temperatures does lead to chemical changes. The half-life of *syn*-(CH_3,CH_3)B in the absence of oxygen at 280 °C is about 10 h. Surprisingly, the major transformation product is *anti*-(CH_3,CH_3)B, and a preparative-scale experiment yielded 63% of the anti derivative along with 23% recovered *syn*-(CH_3,CH_3)B and a small amount of unidentifiable black residue. Heating *anti*-(CH_3,CH_3)B at 280 °C for 9 h led to 92% recovery of unchanged anti compound, a small amount of black residue, and no detectable *syn*-(CH_3,CH_3)B. *syn*-(CH_3,H)B was completely decomposed after 20 h at 280 °C (black insoluble solid), but after 6 h at 250 °C yielded 8% starting material, 43% *anti*-(CH_3,H)B, and 23% of a hydroxypyrazolyl acrylic acid lactone. Heating *anti*-(CH_3,H)B for 6 h at 250 °C gave 63% starting material, 10% lactone, and a trace of syn compound, detectable only by its fluorescence on a thin-layer chromatogram (eq 14).

syn-(–(CH_2)$_4$–)B was unchanged after heating for 20 h at 280 °C, 85% starting material being recovered with no trace of anti

(8) Kanety, H.; Kosower, E. M., unpublished results.



(14)

compound found by chromatography. Under similar conditions, *syn*-(CH_3,C_6H_5)(CH_3,CH_3)B gave a tarry mixture from which *anti*-(CH_3,C_6H_5)(CH_3,CH_3)B (10%) and *anti*-(CH_3,C_6H_5)B (13%) could be isolated along with traces of *anti*-(CH_3,CH_3)B and the syn starting material. Certain 9,10-dioxabimanes were unusually stable. *syn*-(C_6H_5,Cl)B and and *syn*-(C_6H_5,C_6H_5)B were unchanged after 4 h at 310 °C, but decomposed completely after 18 h at 350 °C.

Oxidation. Our experience in working with many 9,10-dioxabimanes suggests that these molecules are not reactive toward oxygen, since we have not noted any air sensitivity. Indeed, *syn*-(CH_3,CH_3)B resisted oxidation by either selenium dioxide or chromium trioxide under a variety of conditions. However, conversion to the potentially useful α-acetoxy compound *syn*-(CH_3,CH_2OOCCH_3)(CH_3,CH_3)B was achieved in modest yield with ceric ammonium nitrate in acetic acid.

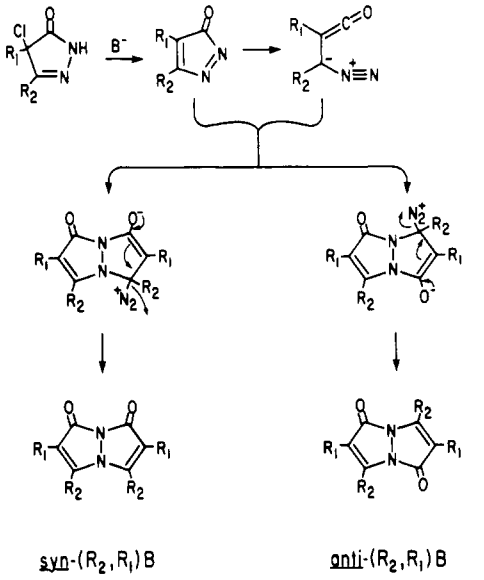
Photochemical Reactivity. *syn*-9,10-Dioxabimanes without halogens on the alkyl substituents are surprisingly stable toward irradiation in the region of the longest wavelength absorption. Some changes, which have not been further investigated, take place after long exposure at 254 nm. For example, long irradiation of *syn*-(CH_3,CH_3)B at 360 nm led to almost complete recovery of starting material, whereas similar irradiation at 254 nm gave only 60% recovery. However, an interesting photochemical rearrangement occurs upon irradiation of anti compounds, with the formation of the hydroxypyrazolylacrylolactone observed in thermal rearrangements (eq 14). Further information on the scope and mechanism of the rearrangement will be given elsewhere[9] (see brief comment in the Discussion).

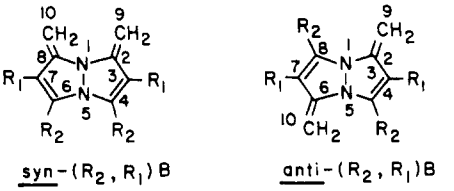
Discussion

The 1,5-diazabicyclo[3.3.0]octadienediones which are the subject of the present paper represent two essentially new classes of compounds. The term "essentially" is used because the few examples made previously[10] were *sui generis*, from synthetic routes of limited generality, and with little recognition of the physical and chemical potential inherent in such simple bicyclic ring systems.

The scope of the new synthesis of the 1,5-diazabicyclo-[3.3.0]octadienediones became clear soon after an effective procedure was developed. It was obvious that both written and verbal discussion would be hindered without some brief notation for referring to the individual compounds. The shape and relationship of the two five-membered rings suggested a name based on "two hands" and led us to the general name, bimane, from the Latin *bi*, two, and *manus*, hand. However, the basic structure chosen included exocyclic carbons so as to resemble as much as possible a hydrocarbon. There are two possible arrangements for the exocyclic methylene groups, one in which the methylene groups are on the same side (syn) of the ring system and a second in which the groups are on the opposite side (anti) of the bicyclic ring system. The basic ring systems, 2,8-bis(methylene)-1,5-diazabicyclo[3.3.0]octa-3,6-diene, or *syn*-bimane, and 2,6-bis(methylene)-1,5-diaza[3.3.0]octa-3,7-diene, or *anti*-bimane, are illustrated below. If the methylene carbons are numbered 9 and 10, the dione derivatives are then *syn*-9,10-dioxabimane and *anti*-9,10-dioxabimane. *syn*-Dioxabimane or *anti*-dioxabimane could then be used to refer to the compounds. Two examples of the application of these simple rules are as follows: *syn*-(C_6H_5,Cl)B = *syn*-(phenyl,chloro)dioxabimane = 3,7-dichloro-4,6-diphenyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione; *anti*-(CH_3,CH_3)B = *anti*-(methyl,methyl)dioxabimane = 2,3,6,7-tetramethyl-1,5-diazabicyclo[3.3.0]octa-3,7-diene-2,6-dione. The classical name for these systems, pyrazolo[1,2-*a*]pyrazole, does not seem brief or clear enough for our purposes.

Scheme I. Suggested Mechanism for Formation of *syn*- and *anti*-9,10-Dioxabimanes





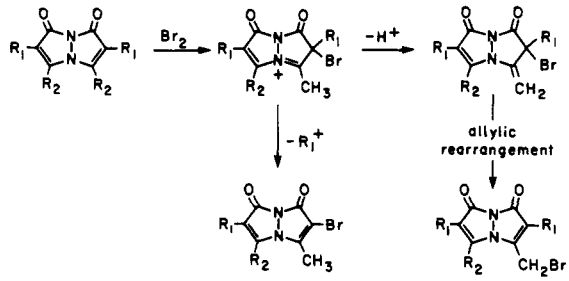
Mechanism of Formation of Dioxabimanes. We are able to write a plausible scheme for the formation of dioxabimanes on the basis of our observations and information from the literature. First, the initial reaction of base with a halopyrazolinone leads to a 2,3-diazacyclopentadienone. The latter has been trapped by reactive dienes to yield the expected adducts.[11,19] Colored intermediates have been noted in the reaction mixtures;[20] we have been able to observe the spectrum of the probable intermediate (λ_{max} 475 nm) and follow in a qualitative way its rise and fall in concentration in the course of a synthetic procedure.[21] Second, two products are formed, suggesting that a second intermediate, which can react in two ways, is involved. Furthermore, in at least one case, the reaction is accelerated by light without any apparent change in the overall results, implying that the first intermediate, the diazacyclopentadienone, must be in part converted into another

(9) Kosower, E. M.; Kanety, H.; Dodiuk, H. *Eur. Cong. Org. Chem.*, abstracts, August 1979, and manuscript in preparation.

(10) Carpino[1c] noted the formation of a yellow compound, almost certainly *syn*-(C_6H_5,Cl)B, but never published the promised structure. Only four examples of *syn*-9,10-dioxabimanes have appeared previously in the literature. Two were characterized by Michaelis[2] and two were described by Veibel and Lillelund[3] (*syn*-(benzo)(CH_3,H)B, *syn*-(benzo)(CH_3,Br)B, *syn*-(benzo)-(CH_3,CH_3CH_2)B, and *syn*-(benzo)(C_6H_5,H)B). A small number of *anti*-9,10-dioxabimanes have been reported by Rees[11] (*anti*-(C_6H_5,C_6H_5)B), Mosby,[12] Gibson and Lindsey[13] (*anti*-(benzo,benzo)B), and Søtofte[14] (*anti*-(benzo)(CH_3,Br)B). Some *anti*-bimanes had also been isolated by Michaelis[15,16] and investigated by Veibel.[17] It is also likely that *syn*- and *anti*-(CH_3,CH_3)B were obtained by Hüttel[18] but assigned different structures.

(11) Rees, C. W.; Yelland, M. *J. Chem. Soc., Perkin Trans. 1* **1973**, 221.
(12) Mosby, W. L. *Chem. Ind. (London)* **1957**, 17.
(13) Gibson, G. K, J.; Lindsey, A. S. *J. Chem. Soc. C* **1967**, 1792.
(14) Søtofte, I. *Acta Chem. Scand.* **1973**, *27*, 661.
(15) Michaelis, A.; Eisenschmidt, C. *Ber.* **1904**, *37*, 2228.
(16) Michaelis, A. *Justus Liebigs Ann. Chem.* **1910**, *373*, 129.
(17) Veibel, S. et al. *Acta Chem. Scand.* **1948**, *2*, 914, 921.
(18) Hüttel, R.; Wagner, E.; Sickenburger, B. *Justus Liebigs Ann. Chem.* **1957**, *607*, 109.
(19) Carpino, L. A.; Terry, P. H.; Thatte, S. D. *J. Org. Chem.* **1966**, *31*, 1025.
(20) Gillis, B. T.; Weinkam, R. *J. Org. Chem.* **1967**, *32*, 3321.
(21) Ben-Shoshan, M.; Faust, D.; Iny, G., unpublished results.

Scheme II. Suggested Mechanism for Formation of Bromoalkyl *syn*- and *anti*-9,10-Dioxabimanes (The Case of a 9,10-Dioxa-*syn*-bimane Is Illustrated)



intermediate.[21] Third, the second intermediate must be reasonably reactive since what might appear to be the least stable isomer is usually formed in highest yield (i.e., syn rather than anti), at least on the surface of the potassium carbonate. In homogeneous reactions the predominant product in many cases is the anti isomer, presumably the most stable product.

We propose that the second intermediate is a diazoalkylketene, which reacts with the diazacyclopentadienone in a 1,4- or 1,6-addition reaction. The 1,4-addition leads to the *syn*-dioxabimane and the 1,6-addition gives rise to the *anti*-dioxabimane. Scheme I sets forth the proposed mechanism.

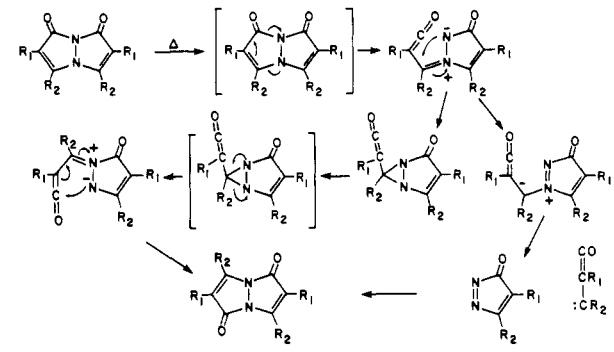
Physical Properties. The substantial thermal stability of 9,10-dioxabimane derivatives, especially in the anti series, remains to be explored for possible applications. The photostability and generally strong fluorescence of the *syn*-dioxabimanes also promise to be of considerable utility and have already found application in the form of fading-resistant fluorescent labels in biological systems.[22-24]

The photophysical properties of the dioxabimanes require a more extensive discussion than would be possible in the present article.[6,7]

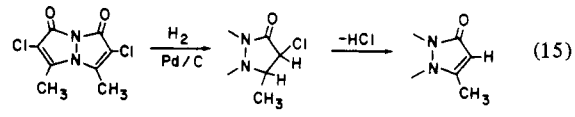
Chemical Properties. Although the stability of the dioxobimanes is certainly worthy of attention, we do not mean to imply in any way that they have "aromatic character". The chemical reactivity, the "normal" positions of the NMR signals, and the fact that the molecules in the crystal can be either planar or nonplanar all point to the idea that the dioxabimanes behave in the manner expected for α,β-unsaturated amide systems, with their stability somewhat enhanced because of the mutual electrical influence of the two rings and possibly some steric effects. The special and somewhat unique features of the 9,10-dioxabimane system are under study.

The chemical reactions of the dioxabimanes are most conveniently divided into three groups, as already mentioned in the Results section. These are substitution, rearrangement, and ring opening. The substitution reactions which we have examined are mainly those involving electrophilic reagents, and the chief one among these is the reaction with bromine. It is necessary to explain the rather facile substitution of Br for H which takes place upon reaction of bromine with many dioxabimanes. Addition of the bromine electrophile to the α position leads to a stabilized carbonium ion (adjacent nitrogen), and the intermediate can then lose a proton. In the case of *syn*-(CH_3,CH_3)B, the proton can only come from the β-methyl group, leading to an allylic bromide which can then rearrange to the product actually isolated. In the case of *syn*-(CH_3,H)B, the proton is more easily lost from the α position and the product is then *syn*-$(CH_3,Br)(CH_3,H)$B. During bromination of *syn*-(CH_3,CH_3)B, the bromine can be seen to disappear extremely rapidly, followed by the appearance of a white precipitate which then redissolves to give a solution containing (by thin-layer chromatography) the product bromide(s). The bromination mechanism is shown in Scheme II.

Scheme III. Suggested Mechanism for Formation of 9,10-Dioxa-*anti*-bimanes from 9,10-Dioxa-*syn*-bimanes through Thermal Rearrangement (The Intramolecular Pathway Appears to be the Dominant One in Most Cases, but a Formal Route for Formation of the Product via Intermolecular Reaction Is Indicated)



Hydrogen reacts with (R,X)B (X = Cl, Br, etc.) probably via an addition–elimination pathway to yield first the mixed bimane (R,H)(R,X)B and finally (R,H)B. The course of the reaction is indicated in eq 15.



(15)

The thermal rearrangement of *syn*-9,10-dioxabimanes to *anti*-9,10-dioxabimanes is rather interesting and may be rationalized by the mechanism shown in Scheme III. The rearrangement of the anti compound to the lactone, which may proceed by either thermal or photochemical routes, probably involves a biradical route, since present indications are that the photochemical reaction goes by way of the triplet.[9]

The ring-opening reactions of the dioxabimanes which we have studied are mainly those of basic nucleophiles, and attack on the carbonyl group is the most reasonable first step which may be written to explain the course of the reaction. The products of the ring-opening reaction, quite apart from their considerable propensity to reform the dioxabimane system on treatment with electrophilic agents, would appear to be an interesting group of polyfunctional heterocyclic molecules.

Experimental Section

Among the instruments used in the research were the following: Cary Model 17 (UV, vis), JEOL 60 MHz, Varian EM-360, and Bruker WH90 spectrometers (^1H and ^{13}C NMR), a Hitachi Perkin-Elmer MPF-4 fluorescence spectrometer, Perkin-Elmer Models 337, 257 (IR) spectrometers, a Du Pont 21-491B mass spectrometer, Cahn Electrobalance Model G-2 (<2-mg weighings), and Hewlett-Packard gas chromatograph, Model 5831.

Synthesis of 1,5-Diaza[3.3.0]bicyclooctadienediones (9,10-Dioxabimanes). Detailed procedures will be given for several compounds, followed by brief descriptions for the other compounds included in the present article. The procedures appear to be applicable to a substantial number of cases with only minor modifications, as expected, in the workup and purification of mixtures of compounds with different chromatographic and solubility properties.

syn- and anti-(methyl,methyl)bimanes (3,4,5,7-tetramethyl-1,5-diazabicyclo[3.3.0]octa-3,5-diene-2,8-dione [*syn*-(CH_3,CH_3)B] and 3,4,7,8-tetramethyl-1,5-diazabicyclo[3.3.0]octa-3,7-diene-2,6-dione [*anti*-(CH_3,CH_3)B]. Ethyl acetoacetate was converted into ethyl α-methylacetoacetate[25a] with sodium ethoxide and methyl bromide in ethanol. The product mixture was carefully fractionated through a 1-m glass helices packed column under vacuum so as to remove ethyl acetoacetate, the

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purity of the fractions being checked by gas chromatography (SE-30 column, temperature programmed: 50 °C, 5 min to 200 °C, 25 min). [The products will be contaminated with (methyl,chloro)bimanes if purification is not rigorous at this point; most other keto esters can be purified by simple vacuum distillation or crystallization since the physical properties are usually different from those of the starting ester.] The pure ethyl α-methylacetoacetate was converted into 3,4-dimethyl-2-pyrazolin-5-one by heating with a small excess of hydrazine in ethanol for 1 h. The 3,4-dimethyl-2-pyrazolin-5-one (137.8 g, 1.23 mol) was mixed with 1,2-dichloroethane (1.2 L), and chlorine was introduced at a rate such that the mixture refluxed gently until all the solid had dissolved and the solution had a yellow green color. The solution was cooled, the chlorine was removed with a stream of air, and the solution was filtered. The solvent was removed, the oily residue was dissolved in benzene–petroleum ether (bp 60–80 °C) (1:1, 300 mL), and the solution was cooled to yield 3,4-dimethyl-4-chloro-2-pyrazolin-5-one (110.7 g) to which was added a further 21.0 g from the filtrate after concentration and cooling (total yield 131.7 g (73.1%), mp 56 °C). The procedure is slightly more convenient than that previously described (lit.[25] mp 57–59 °C, 63%).

Heterogeneous Base Procedure. 3,4-Dimethyl-4-chloro-2-pyrazolin-5-one (70 g, 0.48 mol) in dichloromethane (500 mL) was added over 2 min to a vigorously stirred mixture of potassium carbonate hydrate, potassium carbonate ($K_2CO_3 \cdot 1.5H_2O$, 150 g; K_2CO_3, 50 g), and dichloromethane (250 mL) cooled in an ice bath. The ice bath was removed after 1 h and stirring continued at room temperature for 18 h. The course of the reaction may be followed by using thin-layer chromatography to watch the disappearance of the starting chloropyrazolinone. The appearance of the solid changes during this time. Celite (50 g) was added and the solution was filtered through a thick Celite layer, yielding, after evaporation, a yellow solid which was dissolved in the minimum volume of boiling acetonitrile. After the solution was cooled, yellowish crystals of *syn*-(CH_3,CH_3)B (27.5 g) were deposited. Further cooling of the filtrate yielded, after recrystallization from acetonitrile, another 2.5 g of *syn*-(CH_3,CH_3)B. All filtrates were evaporated and the residue was chromatographed on alumina (150 g, activity II or III) with dichloromethane as eluant. The first material eluted is *anti*-(CH_3,CH_3)B (2.10 g) followed by *syn*-(CH_3,CH_3)B (1.60 g).

Products. 9,10-Dioxa-*syn*-(methyl,methyl)bimane: 31.6 g (68.9%); yellowish crystals from CH_3CN; mp 211–212 °C; IR ($CHCl_3$) 2890, 1745, 1670, 1610, 1400, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) 1.85 (s), 2.28 (s) ppm; ^{13}C NMR ($CDCl_3$) 160.5 (C=O), 146.1 (=C—N), 112.0 (CO—C=), 11.9 (CH_3), 6.7 (CH_3) ppm; UV (dioxane) max 359 nm (ε 6500), 255 (5200, sh), 235 (14 600); fluorescence (dioxane) max (ϕ_F) 420 nm, 440 sh, 0.72; mass spectrum, *m/e* 192 (M^+). Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.57. Found: C, 62.53; H, 6.16; N, 14.91.

9,10-Dioxa-*anti*-(methyl,methyl)bimane: 2.10 g (4.6%); white needles from EtOAc; mp 174 °C; IR (KBr) 2930, 1750 (sh), 1695, 1630, 1415, 1275, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) 1.80 (s), 2.40 (s) ppm; ^{13}C NMR ($CDCl_3$) 161.6 (C=O), 145.8 (=C—N), 112.1 (CO—C=), 10.7 (CH_3), 6.3 (CH_3) ppm; UV (dioxane) max 322 nm (ε 15 100); mass spectrum, *m/e* 192 (M^+). Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.57. Found: C, 62.64; H, 6.24; N, 14.83.

Homogeneous Base Procedure. A number of tertiary amines proved to be active in promoting the formation of 9,10-dioxabimanes from chloropyrazolinones, but the most satisfactory base (yield, workup) is *N,N*-diisopropylethylamine, $(i\text{-Pr})_2NEt$, or "Hünig base", for which we give a typical procedure using the same chloropyrazolinone to which the heterogeneous base procedure described above was applied. The homogeneous base procedure leads, in many cases, to a mixture of bimanes in which the *anti*-bimane is the dominant product, whereas the heterogeneous base procedure produces a mixture in which the *syn*-bimane predominates. Since the total yield of bimanes and the ratio of *syn*- to *anti*-bimanes vary with the substrate used, no detailed generalizations about the synthesis can be put forward at this time.

Both heterogeneous and homogeneous base procedures were applied to 3-methyl-4,4-dichloro-2-pyrazolin-5-one (via chlorination in 65% yield, mp 111–112 °C (lit.[1c] 76%, mp 112 °C)). Reaction with $K_2CO_3 \cdot 1.5H_2O$ (1.1 mol/mol of dichloropyrazolinone) in dichloromethane required 4–6 h at 0 °C (deep yellow to pale orange reaction mixture) and yielded a mixture of bimanes from which a substantial fraction of *syn*-(CH_3,Cl)B could be isolated in pure form by crystallization. Chromatography on silica yielded further *anti*-(CH_3,Cl)B, 0.25 g (4%), and additional *syn*-(CH_3,Cl)B (total of 2.5 g (39%) from 9.0 g of starting material).

N,N-Diisopropylethylamine (7 g, 60 mmol) was added dropwise to a solution of 3-methyl-4,4-dichloro-2-pyrazolin-5-one (10 g, 60 mmol) in CH_2Cl_2 cooled in an ice bath. The mixture was stirred for 4 h, the solvent was evaporated, and the residue was chromatographed on silica gel (CH_2Cl_2–petroleum ether (1:1), then CH_2Cl_2) to yield *anti*-(CH_3,Cl)B, 3.0 g (43%), and *syn*-(CH_3Cl)B, 1.7 g (25%).

9,10-Dioxa-*syn*-(methyl,chloro)bimane: yellow crystals from CH_3CN; mp 253 °C; IR (KBr) 2930, 1820 (sh), 1760, 1690, 1600, 1455, 1405, 1290 cm^{-1}; ^1H NMR ($CDCl_3$) 2.50 (s) ppm; UV (dioxane) max 364 nm (ε 7100), 255 (7000, sh), 235 (14 300); fluorescence (dioxane) max (ϕ_F) 429 nm, 455 sh, 0.79; mass spectrum, *m/e* 232, 234, 236 (M^+). Anal. Calcd for $C_8H_6Cl_2N_2O_2$: C, 41.23; H, 2.60; N, 12.02. Found: C, 41.50; H, 2.69; N, 12.30.

9,10-Dioxa-*anti*-(methyl,chloro)bimane: white crystals from CH_3CN; mp 195 °C; IR (KBr) 1695, 1600, 1400, 1335, 1150, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) 2.65 (s) ppm; UV (dioxane) max 325 nm (ε 15 500); mass spectrum, *m/e* 232, 234, 236 (M^+). Anal. Calcd for $C_8H_6Cl_2N_2O_2$: C, 41.23; H, 2.60; N, 12.02. Found: C, 41.24; H, 2.78; N, 11.88.

The homogeneous base procedure was also utilized in the preparation of (methyl,methyl)bimanes. Addition of *N,N*-diisopropylethylamine (4.65 g, 36 mmol) to 3,4-dimethyl-4-chloro-2-pyrazolin-5-one (5.0 g, 34 mmol) in CH_2Cl_2 at room temperature led to a dark mixture from which, after standing overnight, could be isolated through chromatography on alumina *anti*-(CH_3,CH_3)B, 1.7 g (52%), and *syn*-(CH_3,CH_3)B, 35 mg (1%).

3-Methyl-4,4-dibromo-2-pyrazolin-5-one (35% yield, mp 130 °C (lit.[26] mp 132 °C)) is reacted with 2 equiv of $K_2CO_3 \cdot 1.5H_2O$ in dichloromethane, leading to 8% *syn*-(CH_3,Br)B and 0.1% *anti*-(CH_3,Br)B. A variant of the homogeneous base procedure, using 1.1 equiv of K_2CO_3 in 1:1 water–dimethylformamide, led to a 21% yield of *anti*-(CH_3,Br)B after extraction with dichloromethane.

9,10-Dioxa-*syn*-(methyl,bromo)bimane: yellow crystals from CH_3CN; mp 211–212 °C dec; IR (KBr) 1760, 1690, 1600, 1455, 1415, 1295, 1160, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) 2.60 (s) ppm; UV (dioxane) max 368 nm (ε 7100), 255 (7500, sh), 235 (14 000); fluorescence (dioxane) max (ϕ_F) 429 nm, 455 sh, 0.59; mass spectrum, *m/e* 320, 322, 324 (M^+). Anal. Calcd for $C_8H_6Br_2N_2O_2$: C, 29.84; H, 1.88; N, 8.70. Found: C, 30.09; H, 1.95; N, 8.84.

9,10-Dioxa-*anti*-(methyl,bromo)bimane: white crystals from CH_3CN; mp 237–238 °C; IR (KBr) 1790 (sh), 1690, 1590, 1395, 1370, 1265 cm^{-1}; ^1H NMR ($CDCl_3$) 2.66 (s) ppm; UV (dioxane) max 325 nm (ε 14 800); mass spectrum, *m/e* 320, 322, 324 (M^+).

3-Phenyl-4,4-dichloro-2-pyrazolin-5-one (40% yield, mp 173–175 °C (lit.[1c] 78%, mp 173–175 °C)) gave an intensely red reaction mixture with hydrated potassium carbonate, a color that changed to brownish yellow after 30 min. Crystallization and chromatography gave *syn*-(C_6H_5,Cl)B (26%) and *anti*-(C_6H_5,Cl)B (5%), respectively, the syn compound disappearing during chromatography on alumina using dichloromethane–petroleum ether (bp 40–60 °C) as eluant. A variation of the homogeneous base procedure using 0.2 N NaOH in slight deficiency gave 10% *anti*-(C_6H_5,Cl)B and 10% *syn*-(C_6H_5,Cl)B after extraction and chromatography on silica gel.

9,10-Dioxa-*syn*-(phenyl,chloro)bimane: yellow needles or rods from CH_3CN; mp 318–320 °C; IR (KBr) 3060, 1770, 1690, 1620, 1495, 1420, 1200, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) 7.13 (br s), 7.24 (br s) ppm; UV (dioxane) max 369 nm (ε 6400), 270 (15 500), 235 (10 600, sh); fluorescence (dioxane) max (ϕ_F) 457 nm, 480 sh, 0.62; mass spectrum (CI), *m/e* 357, 359 (M + 1)$^+$ alike. Anal. Calcd for $C_{18}H_{10}Cl_2N_2O_2$: C, 60.53; H, 2.82; N, 7.84. Found: C, 60.57; H, 2.95; N, 7.58.

9,10-Dioxa-*anti*-(phenyl,chloro)bimane: yellow crystals from CH_3CN; mp 236–237 °C; IR (KBr) 1730, 1715, 1605, 1450, 1350, 1175 cm^{-1}; UV (dioxane) max 325 nm (ε 15 500); mass spectrum (CI), *m/e* 357 (M + 1)$^+$ alike. Anal. Calcd for $C_{18}H_{10}Cl_2N_2O_2$: C, 60.53; H, 2.82; N, 7.84. Found: C, 60.78; H, 3.01; N, 7.48.

3,4-Tetramethylene-4-chloro-2-pyrazolin-5-one (85% yield, mp 110–112 °C (lit.[27] 58%, mp 113 °C)) was reacted with hydrated potassium carbonate in dichloromethane to give a 54% yield of *syn*-(-$(CH_2)_4$-)B and no *anti*-bimane. Reaction with base in a two-phase system (benzene and 5% aqueous KOH; after mixing at 0 °C, stirred 18 h) gave 27.4% *anti*-(-$(CH_2)_4$-)B and 8.5% of the *syn*-isomer.

9,10-Dioxa-*syn*-(tetramethylene)bimane: bluish white crystals from CH_3CN; mp 258–260 °C; IR (KBr) 2970, 1735, 1665, 1660, 1440, 1240, 1210, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) 1.85 (m, 4 H), 2.2–2.6 (m, 2 H) ppm; UV (dioxane) max 354 nm (ε 6500), 255 (6500, sh), 232 (18 700); fluorescence (dioxane) max (ϕ_F) 418 nm, 440 sh, 0.80; mass spectrum, *m/e* 244 (M^+). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.50; H, 6.50; N, 11.30.

9,10-Dioxa-*anti*-(tetramethylene)bimane: white needles from CH_3CN–*i*-PrOH (1:1); mp 309 °C; IR (KBr) 2940, 1680, 1625, 1430, 1410, 1300, 1260, 1175, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) 1.8 (m, 4 H), 2.25–2.6 (m, 4 H) ppm; UV (dioxane) max 317 nm (ε 14 400), 254

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(3200); mass spectrum, *m/e* 244 (M^+). Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.77; H, 6.72; N, 11.52.

3-Methyl-4-phenyl-4-chloro-2-pyrazolin-5-one (yield 50%, mp 82 °C (lit.[28] 67%, mp 81–82 °C), 2.7 mmol) was reacted with hydrated potassium carbonate in dichloromethane, yielding 20% *syn*-(CH_3,C_6H_5)B and 3.2% *anti*-(CH_3,C_6H_5)B after chromatography.

9,10-Dioxa-*syn*-(methyl,phenyl)bimane: yellow crystals from CH_3CN; mp 284 °C; IR (KBr) 2980, 1760 (sh), 1735, 1660, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) 2.52 (s, 3 H), 7.41 (br s, 5 H) ppm; UV (dioxane) max 395 nm (ε 8000), 262 (10 200), 220 (7600); fluorescence (dioxane) max (ϕ_F) 470 nm, 500 sh, 0.72; mass spectrum, *m/e* 316 (M^+). Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.95; H, 5.06; N, 8.86. Found: C, 75.88; H, 5.16; N, 9.08.

9,10-Dioxa-*anti*-(methyl,phenyl)bimane: yellow solid from CH_3CN; mp 265 °C; IR (KBr) 3055, 1675, 1450, 1410, 1365 cm^{-1}; ^1H NMR ($CDCl_3$) 2.65 (s, 3 H), 7.48 (br s, 5 H) ppm; UV (dioxane) max 344 nm (ε 18 800), 248 (22 100); mass spectrum, *m/e* 316 (M^+). Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.95; H, 5.06; N, 8.86. Found: C, 76.09; H, 5.27; N, 9.09.

3,4-Diphenyl-4-chloro-2-pyrazolin-5-one (yield 66%, mp 168 °C dec (lit.[28] 67%, mp 172–174 °C)) yielded only 7% *syn*-(C_6H_5,C_6H_5)B upon reaction with hydrated potassium carbonate in dichloromethane.

9,10-Dioxa-*syn*-(phenyl,phenyl)bimane: bright yellow crystals from CH_3CN; mp 312 °C; IR (KBr) 1750, 1740, 1680, 1610, 1565, 1450, 1340, 1240, 1070 cm^{-1}; ^1H NMR (Me_2SO-d_6) 7.08 (s), 7.18 (s) ppm; UV (dioxane) max 409 nm (ε 10 000), 350 (8800, sh), 255 (22 500); fluorescence (dioxane) max (ϕ_F) 495 nm, 525 sh, 0.75; mass spectrum, *m/e* 440 (M^+). Anal. Calcd for $C_{30}H_{20}N_2O_2$: C, 81.80; H, 4.58; N, 6.36. Found: C, 81.62; H, 4.54; N, 6.04.

"Mixed" 9,10-Dioxabimanes. If two different chloropyrazolinones are used in the bimane synthesis, "mixed" bimanes are formed along with the bimanes formed from the individual precursors separately. Either an excess of the less reactive precursor is used or the reactive precursor is added at a controlled rate to the less reactive chloropyrazolinone. "Reactivity" in this case is judged by how fast the chloropyrazolinone disappears in a typical bimane synthesis. Careful chromatographic separation is generally required to separate the individual components of a product mixture. The reaction itself is generally carried out by the heterogeneous base procedure and worked up by removal of the reaction solvent after filtration followed by chromatography.

9,10-Dioxa-*syn*-(methyl,phenyl)(methyl,methyl)bimane. 3-Methyl-4-phenyl-4-chloro-2-pyrazolin-5-one (1.67 g, 8 mmol) and hydrated potassium carbonate (3.0 g, 18 mmol) were mixed in dichloromethane (60 mL), and a solution of 3,4-dimethyl-4-chloro-2-pyrazolin-5-one (1.20 g, 8.1 mmol) in dichloromethane (30 mL) was added over 20 min. After 12 h of being stirred at room temperature, the mixture was filtered, the solvent evaporated, and the product mixture chromatographed on silica gel, using CH_2Cl_2–petroleum ether (bp 60–80 °C) as eluant. In order of elution, the compounds isolated were *syn*-(CH_3,C_6H_5)B (60 mg, 4.8%), *syn*-$(CH_3,C_6H_5)(CH_3,CH_3)$B (1.05 g, 52%), and *syn*-(CH_3,CH_3)B (95 mg, 12.5%).

***syn*-$(CH_3,C_6H_5)(CH_3,CH_3)$B**: bright yellow crystals from CH_3CN; mp 227 °C; IR (KBr) 1735, 1665, 1605, 1570, 1415, 1250, 1200 cm^{-1}; ^1H NMR ($CDCl_3$) 1.85 (s, 3 H), 2.40 (s), 2.48 (s, 6 H), 7.48 (s, 5 H) ppm; UV (dioxane) max 380 nm (ε 11 000), 255 (15 000), 223 (27 700); fluorescence (dioxane) max (ϕ_F) 452 nm, 490 sh, 0.68; mass spectrum, *m/e* 254 (M^+).

3-Methyl-4,4-dichloro-2-pyrazolin-5-one (4.2 g, 25 mmol) in CH_2Cl_2 (30 mL) was added dropwise to a vigorously stirred mixture of 3,4-dimethyl-4-chloro-2-pyrazolin-5-one (3.8 g, 25 mmol) and *N,N*-diisopropylethylamine (6.5 g, 50 mmol) in CH_2Cl_2 (30 mL) cooled in an ice bath. After 1 h, the bath was removed, stirring was continued for 2 h, the solvent was evaporated, and the residue was chromatographed on silica gel (0.06–0.2-mm mesh, elution with $CHCl_3$–petroleum ether (1:1)). Multiple chromatographies were required to purify all six bimane components of the product mixture, which were, in the order of elution, *anti*-(CH_3,Cl)B (660 mg, 13%), *anti*-$(CH_3,CH_3)(CH_3,Cl)$B (850 mg, 17%), *anti*-(CH_3,CH_3)B (160 mg, 3%), *syn*-(CH_3,Cl)B (370 mg, 7.8%), *syn*-$(CH_3,CH_3)(CH_3,Cl)$B (410 mg, 8%), and *syn*-(CH_3,CH_3)B (100 mg, 2%) (total *anti*-bimanes, 33%, total *syn*-bimanes, 17.8%, total bimanes, 50.8%).

***syn*-$(CH_3,CH_3)(CH_3,Cl)$B**: yellowish solid from EtOAc; mp 242–244 °C; IR (KBr) 2930, 1745, 1675, 1625, 1570, 1415, 1210 cm^{-1}; ^1H NMR ($CDCl_3$) 1.81 (s, 3 H), 2.32 (s), 2.40 (s, 6 H) ppm; UV (dioxane) max 365 nm (ε 8000), 252 (5900); fluorescence (dioxane) max (ϕ_F) 423 nm, 445 sh, 0.76; mass spectrum, *m/e* 212, 214 (M^+).

***anti*-$(CH_3,CH_3)(CH_3,Cl)$B**: white solid; mp 134 °C; IR (KBr) 3420, 2940, 1725 (s), 1695, 1645, 1620, 1400, 1355, 1310, 1220, 1160, 1085, 1040, 980, 800, 735 cm^{-1}; ^1H NMR ($CDCl_3$) 1.85 (s), 2.45 (s), 2.52 (s) ppm; UV (dioxane) max 323 nm (ε 15 100); mass spectrum, *m/e* 212, 214 (M^+).

1,2-Dimethylene-4,4′-bis(3-methyl-4-chloro-2-pyrazolin-5-one). Diethyl 2,5-bis(2-iminoethyl)hexanedioate was synthesized according to Perkin.[29a] Ethyl acetoacetate (260 g, 2 mol) was added to sodium ethoxide (2 mol, from Na) in ethanol (1.5 L) over 30 min, followed by 1,2-dibromoethane (190 g, 1 mol). The mixture was refluxed overnight, cooled, and filtered, the solvent was evaporated, steam was passed through the oily residue until most of the volatile material had been removed, and the oil was separated and dissolved in ethanol (300 mL). Ammonia was passed through the solution for 1.5 h. After 32 h, the yellow crystalline precipitate was filtered off, yielding 7.0 g (2.5%) of product after trituration with methanol; mp 172–174 °C (lit.[29a] 173–174 °C). The bis(pyrazolinone) was produced by refluxing a suspension of the above product (1.0 g, 3.5 mmol) with hydrazine hydrate (400 mg, 8 mmol) in ethanol (4 mL) overnight (ammonia evolution, change in nature of solid) and was isolated by filtering and washing with ethanol to yield a white crystalline solid: mp >280 °C (lit.[29b] 250 °C); IR (KBr) 3400, 2700 (br), 1620, 1585 cm^{-1}. Chlorination of the bis(pyrazolinone) (0.50 g, 2.3 mmol) was effected by introducing chlorine into a hot nitromethane suspension until the solid dissolved and the solution became greenish. After 1 h, the chlorine was removed, the solution was filtered hot, most of the solvent was removed, and ether (10 mL) was added to the 5–6 mL of residual solution. The dimethylenebis(chloropyrazolinone) separated as a yellowish solid: 0.59 g (88%); mp 220 °C dec; IR (KBr) 3220, 1745, 1710, 1615 cm^{-1}.

Bis(9,10-dioxa-*syn*-(methyl,methyleno)(methyl,methyl)bimane) and 9,10-Dioxa-*syn*-(methyl,methyleno)(methyl,methyl)bimane-9,10-dioxa-*anti*-(methyl,methyleno)(methyl,methyl)bimane. 1,2-Dimethylene-4,4′-bis(3-methyl-4-chloro-2-pyrazolin-5-one) (0.50 g, 1.73 mmol) and 3,4-dimethyl-4-chloro-2-pyrazolin-5-one (0.82 g, 5.56 mmol) were stirred at room temperature with hydrated potassium carbonate (1.50 g, 9.1 mmol) for 3 days, the mixture was filtered, the solvent was removed, and the residue was chromatographed on alumina (activity II). Elution was begun with dichloromethane and completed with dichloromethane containing 10% methanol, yielding (in order of elution) *syn*-(CH_3,CH_3)B (110 mg, 10.3%), *syn*-$(CH_3,CH_2–)(CH_3,CH_3)$B-*anti*-$(CH_3,CH_2–)$-(CH_3,CH_3)B (5.0 mg, 0.7%), and bis(*syn*-$(CH_3,CH_2–)(CH_3,CH_3)$B (14.1 mg, 2.1%).

Bis(*syn*-$(CH_3,CH_2–)(CH_3CH_3)$B): yellow solid from CH_3CN; mp >320 °C; IR (KBr) 2920, 1755 (sh), 1730, 1680, 1620, 1590, 1440, 1410, 1365, 1265, 1225, 1165, 1090, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) 1.80 (s, 3 H), 2.26 (s), 2.30 (s), 2.35 (s), 2.45 (s, 8 H) ppm; UV (CH_3CN) max 372 nm (ε 3900), 336 (3700), 256 (6400), 228 (8500); fluorescence (CH_3CN) max (ϕ_F) 440 nm, 465 sh, 0.55; mass spectrum (CI), *m/e* 383 $(M + 1)^+$.

***syn*-$(CH_3,CH_2–)(CH_3,CH_3)$B-*anti*-$(CH_3,CH_2–)(CH_3,CH_3)$B**: yellow solid from CH_3CN; mp >320 °C; IR (KBr) 2920, 1740, 1730, 1725, 1680, 1625, 1590, 1440 (sh), 1410, 1350, 1270, 1240, 1185, 1020 cm^{-1}; UV (dioxane) max 375 nm (ε 5600), 327 (11 500), 260 (6300), 232 (14 000); fluorescence (dioxane) max (ϕ_F) 420 nm (0.37); mass spectrum (CI), *m/e* 383 $(M + 1)^+$.

Other Procedures. A modification of the Michaelis–Veibel condensation procedure may be utilized to synthesize 9,10-dioxobimanes in cases for which the precursor may not be accessible (i.e., benzobimanes) or in which the usual procedure is not effective. No attempt has been made to optimize the synthetic conditions, since it is unlikely that the procedure will be as generally useful as those which involve base treatment of halopyrazolinones.

3-Methyl-2-pyrazolin-5-one (4.9 g, 50 mmol), ethyl acetoacetate (5.0 g, 39.4 mmol), and phosphorus tribromide (3.0 g, 11 mmol) were refluxed in benzene (50 mL) overnight. Water (50 mL) was added, the organic phase was separated, and the aqueous phase was extracted repeatedly with dichloromethane. The combined organic phases were dried and evaporated, and the residue was chromatographed on alumina, using dichloromethane–petroleum ether (bp 40–60 °C) to yield *anti*-(CH_3,H)B, 645 mg (8%). An experiment carried out in the absence of benzene gave 1.9% *syn*-(CH_3,H)B and 0.8% *anti*-(CH_3,H)B.

9,10-Dioxa-*syn*-(methyl,hydrogen)bimane: pale yellow crystals from EtOAc–CH_3CN; mp 249–250 °C; IR (KBr) 3130, 3020, 1765, 1740, 1660, 1465, 1400, 1265 cm^{-1}; ^1H NMR ($CDCl_3$) 2.38 (d, 3 H), 5.42 (m, 1 H) ppm; ^{13}C NMR ($CDCl_3$) 160.0 (C=O), 151.5 (=C—N), 103.8 (CO—C=), 12.5 (CH_3) ppm; UV (dioxane) max 354 nm (ε 4500), 250 (4500, sh), 225 (12 000); fluorescence (dioxane) max (ϕ_F) 388 nm, 405 sh, 0.76; mass spectrum, *m/e* 164 (M^+). Anal. Calcd for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.06. Found: C, 58.50; H, 4.99; N, 17.24.

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9,10-Dioxa-*anti*-(methyl,hydrogen)bimane: white crystals from CH_3CN; mp 178 °C; IR (KBr) 3120, 1730 (sh), 1680, 1590, 1445, 1400, 1355, 1215, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) 2.49 (d, 3H), 5.38 (m, 1 H) ppm; ^{13}C NMR ($CDCl_3$) 159.2 (C=O), 149.6 (=C—N), 105.3 (CO—C=), 13.4 (CH_3) ppm; UV (dioxane) max 325 nm (ϵ 14 600); mass spectrum, *m/e* 164 (M^+).

Reaction of indazolinone (1.0 g, 7.6 mmol), ethyl acetoacetate (3.0 g, 23 mmol), and PBr_3 (3.5 g, 13 mmol) in benzene as described above yielded *syn*-(benzo)(CH_3,H)B, 40 mg (2.7%), and *anti*-(benzo)(CH_3,H)B, 230 mg (16%).

9,10-Dioxa-*syn*-(benzo)(methyl,hydrogen)bimane: yellow solid from EtOAc; mp 266 °C (lit.[2] 267 °C); IR (KBr) 1790, 1745, 1670, 1610, 1545, 1430, 1325, 1230, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) 2.55 (s, 3 H), 5.42 (br s, 1 H), 7.35–8.0 (m, 4 H) ppm; UV (dioxane) max 376 nm (ϵ 5400), 293 (7000), 258 (6600); fluorescence (dioxane) max (ϕ_F) 426 nm (0.55); mass spectrum, *m/e* 200 (M^+).

9,10-Dioxa-*anti*-(benzo)(methyl,hydrogen)bimane: yellow solid from EtOAc; mp 166 °C (lit.[16] mp 166–168 °C); IR (KBr) 3105, 1720, 1690, 1615, 1480, 1400, 1235 cm^{-1}; ^1H NMR ($CDCl_3$) 2.57 (d, 3 H), 5.54 (m, 1 H), 7.04–7.09 (m, 4 H) ppm; UV (dioxane) max 349 nm (ϵ 10 900), 278 (4800), 267 (5400); mass spectrum, *m/e* 200 (M^+).

Reaction of 3,4-trimethylene-2-pyrazolin-5-one (2.48 g, 20 mmol), 2-(carboethoxy)cyclopentanone (6.24 g, 40 mmol), and PBr_3 in benzene gave, after workup, an oil, which, after dissolution in EtOAc–petroleum ether (bp 40–60 °C), precipitated a white solid, which was purified by sublimation at 100 °C (0.02 mm) to yield a material identified as 2,3-trimethylene-3-(5-hydroxy-3,4-trimethylenepyrazol-1-yl)propenoic acid lactone: yield 0.69 g (16%); mp 111–112 °C; IR (KBr) 2970, 1765, 1740 (sh), 1690, 1650, 1610, 1515, 1465, 1440, 1425 cm^{-1}; ^1H NMR ($CDCl_3$) 2.6 (unresolved m) ppm; UV (dioxane) max 299 nm (ϵ 5500); mass spectrum, *m/e* 216 (M^+).

Electrophilic Reactions of 9,10-Dioxabimanes. H⁺. *syn*-(CH_3,CH_3)B (192 mg, 1 mmol) was refluxed for 15 h with 10% HCl. Half of the solution was treated with 2,4-dinitrophenylhydrazine to yield 60 mg (54%) of 2-butanone 2,4-dinitrophenylhydrazone, mp 115 °C (lit.[30] 116–117 °C); the other half was evaporated and neutralized with $NaHCO_3/H_2O$, and the precipitate was recrystallized from *i*-PrOH to give 25 mg (45%) of 3,4-dimethyl-2-pyrazolin-5-one, mp 267–268 °C (lit.[31] mp 269 °C), with mass spectrum, *m/e* 112 (M^+).

ICl. Iodine monochloride (300 mg, 1.85 mmol) was added over 10 min to *syn*-(CH_3,H)B (100 mg, 0.61 mmol) in dichloromethane. After 1 h, the solid was filtered off and recrystallized to yield 120 mg (42%) of *syn*-(CH_3,I)B.

9,10-Dioxa-*syn*-(methyl,iodo)bimane: yellow solid from CH_3CN–DMF (1:1); mp 215–220 °C dec; turns brown on exposure to light; IR (KBr) 1760, 1675, 1575, 1465, 1450, 1400, 1040, 730 cm^{-1}; UV (dioxane) max 384 nm (ϵ 7600), 265 (4500), 232 (5200); fluorescence (dioxane) max (ϕ_F) 440 nm, 460 sh, 0.21; mass spectrum (CI), *m/e* 417 ($M + 1)^+$. Anal. Calcd for $C_8H_6I_2N_2O_2$: C, 23.66; H, 1.60; N, 7.04. Found: C, 23.08; H, 1.44; N, 6.73.

Br_2. Bromine (160 mg, 1 mmol) in dichloromethane (2 mL) reacted rapidly with *syn*-(CH_3,H)B (70 mg, 0.43 mmol) in dichloromethane (3 mL) to yield a precipitate of *syn*-(CH_3,Br)B, 110 mg (79%) after recrystallization from CH_3CN, identical with that obtained through base treatment of the dibromopyrazolinone.

Bromine (2.56 g, 21 mmol) in CH_2Cl_2 (25 mL) was added over 1 h to *syn*-(CH_3,CH_3)B (1.92 g, 10 mmol) in CH_2Cl_2 (50 mL) at room temperature. A white precipitate formed and then redissolved during addition. After 30 min, solvent was removed from the orange solution, and the solid was dissolved in EtOAc (20 mL). Large block-like, yellow crystals of *syn*-($BrCH_2$,CH_3)B separated on standing, 2.65 g (76%).

9,10-Dioxa-*syn*-(bromomethyl,methyl)bimane: mp 176–177 °C; IR (KBr) 1760, 1685, 1670, 1600, 1410, 1390, 1250, 745 cm^{-1}; ^1H NMR ($CDCl_3$) 1.98 (s, 3 H), 4.55 (s, 2 H) ppm; UV (dioxane) max 390 nm (ϵ 6600), 266 (11 000). Anal. Calcd for $C_{10}H_{10}Br_2N_2O_2$: C, 34.32; H, 2.88; N, 8.00. Found: C, 34.55; H, 2.84; N, 8.13.

Bromine (0.79 g, 4.9 mmol) was reacted as above with *syn*-(CH_3,CH_3)B (1.0 g, 5.2 mmol). After standing overnight, the solution was washed with water, the CH_2Cl_2 evaporated, and the residue chromatographed on a silica column protected from light. (Thin-layer chromatography is useful for following the course of bromination reactions; the bromo compounds are nonfluorescent but become fluorescent after some time on the TLC plate. The starting material and the two bromination products are readily resolved by TLC.) Elution (30% petroleum ether–CH_2Cl_2 to CH_2Cl_2 over 10–30 h, depending on the scale of preparation) gave, in order, *syn*-($BrCH_2$,CH_3)B (40 mg, 2.2%) and *syn*-($BrCH_2$,CH_3)(CH_3,CH_3)B (790 mg, 49%).

9,10-Dioxa-*syn*-(bromomethyl,methyl)(methyl,methyl)bimane: yellow crystals from EtOAc; mp 142 °C; IR (KBr) 1745, 1675, 1625, 1600, 1435, 1240, 1085, 740 cm^{-1}; ^1H NMR ($CDCl_3$) 1.82 (s), 1.87 (s, 6 H), 2.46 (s, 3 H), 4.35 (s, 2 H) ppm; UV (dioxane) max 377 nm (ϵ 7000), 248 (13 500). Anal. Calcd for $C_{10}H_{11}BrN_2O_2$: C, 44.28; H, 4.06; N, 10.33. Found: C, 44.37; H, 4.14; N, 10.18.

Caution: Bromo- and iodomethyl derivatives of bimanes appear to be fairly photosensitive, at least in solution, and their preparation and use are best carried out in red light (or dim light). The photosensitivity is clearly related to the longest wavelength absorption band, and thus the syn derivatives are much more sensitive than the anti derivatives.

Monobromo (58% yield) and dibromo (84% yield) derivatives of *anti*-(CH_3,CH_3)B are obtained in the same way as described for the syn compounds, except that the chromatographic separation of the monobromo compound in this case is easy, chromatography on silica (eluant CH_2Cl_2) being effected in 1 h, with the monobromo derivative the first material eluted.

9,10-Dioxa-*anti*-(bromomethyl,methyl)bimane: yellowish white solid from EtOAc; mp 150 °C; IR (KBr) 1675, 1450, 1410, 1390, 1230, 1050, 895, 730 cm^{-1}; ^1H NMR ($CDCl_3$) 1.89 (s, 3 H), 4.66 (s, 2 H) ppm; UV (dioxane) max 349 nm (ϵ 11 500). Anal. Calcd for $C_{10}H_{10}Br_2N_2O_2$: C, 34.32; H, 2.88; N, 8.00. Found: C, 34.16; H, 2.88; N, 7.88.

9,10-Dioxa-*anti*-(bromomethyl,methyl)(methyl,methyl)bimane: yellow crystals from EtOAc; mp 110 °C; IR (KBr) 1740 (sh), 1690, 1630, 1410, 1365, 1280, 1220, 1175 cm^{-1}; ^1H NMR ($CDCl_3$) 1.74 (s), 1.80 (s, 6 H), 2.40 (s, 3 H), 4.49 (s, 2 H); UV (dioxane) max 336 nm (ϵ 11 300).

syn-(CH_3,Cl)B (110 mg, 0.4 mmol) and bromine (150 mg, 0.94 mmol) were mixed in CH_2Cl_2 (9 mL) and left at room temperature for 7 weeks. Crystallization of the residue from EtOAc after removal of the solvent yielded *syn*-($BrCH_2$,Cl)(CH_3,Cl)B, 45 mg (31%). The monobromide (20 mg) was converted into the corresponding monoacetate by treatment with fused KOAc in refluxing acetone for 24 h, obtaining the pure product (6 mg (32%)) after chromatography on silica gel and elution with CH_2Cl_2–petroleum ether (bp 40–60 °C).

9,10-Dioxa-*syn*-(bromomethyl,chloro)(methyl,chloro)bimane: yellow powder; mp 181–182 °C; IR (KBr) 1760, 1690, 1595, 1425, 1280, 1170, 725 cm^{-1}; ^1H NMR ($CDCl_3$) 2.63 (s, 3 H), 4.45 (s, 2 H) ppm; UV (dioxane) max 383 nm (ϵ 7100), 250 (12 200).

9,10-Dioxa-*syn*-(acetoxymethyl,chloro)(methyl,chloro)bimane: yellow solid; mp 162 °C; IR (KBr) 1765, 1690, 1605, 1450, 1215, 1170, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) 2.20 (s, 3 H), 2.50 (s, 3 H), 5.23 (s, 2 H) ppm; mass spectrum, *m/e* 290 (M^+).

syn-(CH_3,C_6H_5)(CH_3,CH_3)B (300 mg, 1.2 mmol) and bromine (200 mg, 1.25 mmol) were allowed to react in CH_2Cl_2 (10 mL) for 1 h, yielding, after evaporation of the solvent and crystallization from ether, 360 mg (91%) of *syn*-($BrCH_2$,CH_3)(CH_3,C_6H_5)B.

9,10-Dioxa-*syn*-(bromomethyl,methyl)(methyl,phenyl)bimane: yellow needles; mp 204 °C; IR (KBr) 1740 (sh), 1730, 1665, 1465, 1430, 1255, 1115, 775, 740 cm^{-1}; ^1H NMR ($CDCl_3$) 1.92 (s, 3 H), 2.61 (s, 3 H), 4.43 (s, 2 H), 7.55 (s, 5 H); UV (dioxane) max 391 nm (ϵ 7100), 254 (15 000), 226 (12 700, sh).

Reduction and Oxidation of *syn*-Dioxabimanes. *syn*-(CH_3,Cl)B (1.0 g, 4.3 mmol) was reduced with hydrogen over 10% palladium/charcoal (0.10 g) in acetic acid (80 mL) containing potassium acetate (21 mmol) over 4 h at 70–80 °C. CH_2Cl_2 (50 mL) was added, the solution filtered, the solvent evaporated, more CH_2Cl_2 added, the solution washed with $NaHCO_3/H_2O$ and water, dried (Na_2SO_4), and evaporated, and the residue crystallized from EtOAc–CH_3CN to yield 390 mg of *syn*-(CH_3,H)B (55%). Interrupting the reduction after 2 h gave a product mixture from which chromatography on silica (elution with CH_2Cl_2–petroleum ether (bp 60–80 °C)) yielded, in order, *syn*-(CH_3,Cl)B (90 mg, 9%), *syn*-(CH_3,Cl)(CH_3,H)B (310 mg, 36%), and *syn*-(CH_3,H)B (240 mg, 34%).

9,10-Dioxa-*syn*-(methyl,chloro)(methyl,hydrogen)bimane: yellow crystals from EtOAc; mp 210 °C; IR (KBr) 1765, 1685, 1615, 1600, 1575, 1450, 1400, 1280, 1215, 1165, 1135, 820, 740 cm^{-1}; ^1H NMR ($CDCl_3$) 2.42 (s, 6 H), 5.48 (s, 1 H) ppm; UV (dioxane) max 362 nm (ϵ 6600), 250 (4300, sh); fluorescence (dioxane) max (ϕ_F) 410 nm, 430 sh, 0.76; mass spectrum, *m/e* 198, 200 (M^+). Anal. Calcd for $C_8H_7ClN_2O_2$: C, 48.38; H, 3.55; N, 14.10. Found: C, 48.60; H, 3.58; N, 14.30.

syn-(CH_3,CH_3)B (0.50 g, 2.6 mmol) in *i*-PrOH (80 mL) was hydrogenated over platinum oxide (50 mg) at 70 °C and 60 psi. After 15 h, workup and chromatography on alumina (eluant CH_2Cl_2–CH_3OH (3%)) gave one oily fraction which was crystallized from diethyl ether–acetonitrile and identified as 3,4,6,7-tetramethyl-1,5-diaza-3-cyclooctene-2,8-dione: 50 mg (10%); mp 143 °C; IR (KBr) 3000–2750 (br), 1595, 1510, 1455, 1440, 1340, 1290, 1240, 1180, 1140, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) 1.25 (t, 6 H), 1.85 (s, 3 H), 2.20 (s, 3 H), 2.85 (m, 1 H), 4.30 (m, 1 H),

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6.00 (br s, 1 H), 7.8 (br s, 1 H) ppm; UV (CH_3CN) max 268 nm (ϵ 8750); mass spectrum, *m/e* 196 (M^+).

Hydrogenation of *syn*-(C_6H_5,CH_3)B under the same conditions gave a 14% yield of the analogous 3,7-dimethyl-4,6-diphenyl-1,5-diaza-3-cyclooctene-2,8-dione as needles, mp 171 °C.

syn-(CH_3,CH_3)B (200 mg, 1.04 mmol) was added in one portion to lithium aluminum hydride (70 mg, 1.84 mmol) in 1,2-dimethoxyethane (10 mL). After 10 min, water was added, the solution filtered, the solvent evaporated, and the residue triturated with *i*-PrOH–ether (1:1) to yield white crystals (from *i*-PrOH), mp 157 °C, identified as 3,4,6,7-tetramethyl-1,5-diazabicyclo[3.3.0]oct-3-ene-2,8-dione: 35 mg (14%); IR (KBr) 1765, 1650, 1580, 1460, 1435, 1380, 1360, 1310, 1275, 1185 cm^{-1}; ^1H NMR ($CDCl_3$) 1.35 (d, 3 H), 1.54 (d, 3 H), 1.82 (s, 3 H), 2.20 (s, 3 H), 2.86 (1 H), 3.70 (m, 1 H) ppm; UV (CH_3OH) max 306 (ϵ 7000); mass spectrum, *m/e* 194 (M^+).

Ceric ammonium nitrate (1.0 g, 1.82 mmol) in 90% acetic acid (20 mL) was added dropwise over 1 h to *syn*-(CH_3CH_3)B (192 mg, 1.0 mmol) in acetic acid (5 mL), the mixture stirred for 2 h, most of the solvent evaporated, CH_2Cl_2 (30 mL) added, the solution washed with H_2O, dried ($MgSO_4$), and evaporated, and the residue crystallized twice from *i*-PrOH to yield *syn*-(CH_3,CH_2OAc)(CH_3CH_3)B, 74 mg (30%).

9,10-Dioxa-*syn*-(methyl,acetoxymethyl)(methyl,methyl)bimane: yellow needles; mp 156–157 °C; IR (KBr) 1750, 1730, 1660, 1630, 1590, 1445, 1415, 1390, 1255 (sh), 1220, 1190 (sh), 1120, 1020, 970, 935, 920 cm^{-1}; ^1H NMR ($CDCl_3$) 1.88 (s, 3 H), 2.08 (s, 3 H), 2.37 (s, 3 H), 2.50 (s, 3 H), 4.85 (2 H) ppm; UV (dioxane) max 367 nm (ϵ 8400), 246 (6000, sh), 229 (12 400); fluorescence (dioxane) max (ϕ_F) 410 nm, 440 sh, 0.68; mass spectrum, *m/e* 250 (M^+).

Reactions of 9,10-Dioxabimanes with Bases. *syn*-(CH_3,Cl)B (120 mg, 0.52 mmol) in CH_3CN (5 mL) was mixed with 5% aqueous K_2CO_3 (20 mL) and the mixture stirred for 15 h [UV max 291 nm (ϵ 5100)], brought to pH 2 with 2% H_2SO_4 [UV max 256 nm (ϵ 6000)], evaporated, and extracted with CH_3CN to yield 2-(2-carboxy-2-chloro-1-methyl-1-vinyl)-3-methyl-4-chloro-3-pyrazolin-5-one: 91 mg (70%); white crystals from $CHCl_3$; mp 240 °C dec; IR (KBr) 3200–2500 (br), 1690, 1615, 1545 cm^{-1}; ^1H NMR (CD_3CN) 2.26 (s), 2.40 (s) ppm; UV max (pH 6.6) 260 nm (ϵ 5800), 222 (6000); UV max (pH 10.8) 294 nm (ϵ 5000), 242 (6200); UV max (CH_3CN) 286 nm (ϵ 3700), 224 (7800); mass spectrum, *m/e* 250 (M^+). Reaction of the carboxy compound (40 mg, 0.16 mmol) in *i*-PrOH with excess CH_2N_2 in ether for 3 h followed by removal of the solvent after treatment with HOAc and crystallization from *i*-PrOH yielded 15 mg of material for which data are consistent with a structural assignment as 2-(2-(carbomethoxy)-2-chloro-1-vinyl)-1,3-dimethyl-4-chloro-3-pyrazolin-5-one: IR (KBr) 1730, 1695, 1620, 1550, 1340, 1265, 1145, 1100, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) 2.10 (s), 2.25 (s), 3.25 (s), 3.65 (s) ppm; UV (CH_3CN) max 288 nm, 224; UV (pH 10.15) max 301 nm, 238; UV (3 N H_2SO_4) max 285 nm (sh), 228; mass spectrum, *m/e* 278, 280 (M^+).

Reaction of *syn*-(CH_3,Cl)B (50 mg, 0.215 mmol) with aqueous K_2CO_3 as described above was treated with acetic anhydride (5 mL) rather than being extracted with CH_3CN. After 24 h, workup yielded *syn*-(CH_3,Cl)B, 45 mg (90%), identical with the original (mp, TLC, and IR).

syn-(CH_3,Cl)B (200 mg, 0,86 mmol) was added to $NaOCH_3$ in CH_3OH (1.5 M, 5 mL), yielding an orange solution [UV max 340 nm, 237] which was brought to pH 2 with 2% H_2SO_4/CH_3OH [UV max 290 nm]. The solution was filtered and the solvent evaporated to yield 2-(2-(carbomethoxy)-2-chloro-1-methyl-1-vinyl)-3-methyl-4-chloro-3-pyrazolin-5-one: colorless crystals from *i*-PrOH; mp 220 °C dec; 100 mg (44%); IR (KBr) 2950 (br), 2600 (br), 1730, 1620, 1555, 1440, 1320, 1280, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) 2.07 (s, 3 H), 2.29 (s, 3 H), 3.59 (s, 3 H), 5.30 (br s, 1 H) ppm; UV (CH_3CN) max 289 nm (ϵ 3000), 225 (5000); mass spectrum, *m/e* 265 (M^+).

syn-(CH_3,Cl)B (100 mg, 0.43 mmol) was treated with $NaOCH_3$ as above, and the orange solution was added to 0.2 M phosphate buffer, pH 6.7 (120 mL); the mixture was allowed to stand overnight and was worked up to yield *syn*-(CH_3,Cl)B, 78 mg (78%). The reappearance of *syn*-(CH_3,Cl)B was also followed spectroscopically at 388 nm. The final absorption corresponded to 93% regeneration of *syn*-(CH_3,Cl)B.

Thermal Conversions of 9,10-Dioxabimanes. Samples of bimanes were sealed off in heavy-walled glass tubes under high vacuum and then heated to the designated temperature (±5 °C) in an oven.

***syn*-(CH_3,CH_3)B**: A series of samples were heated between 38 and 280 min at 280 °C. Absorption spectra suggested (a) the conversion to product to be reasonably "clean" and (b) that the half-life was 2–4 h. A sample of 75 mg on heating for 20 h at 280 °C yielded 23% recovered *syn*-(CH_3,CH_3)B and 63% *anti*-(CH_3,CH_3)B.

***anti*-(CH_3,CH_3)B**: A sample (45 mg) was heated at 280 °C for 9 h. After sublimation [100 °C (0.01 mm)], 40.1 mg (89%) of starting material was recovered. No syn isomer was detected by TLC.

***syn*-(CH_3,H)B**: After 35 mg of the bimane was heated at 250 °C for 6 h, thick-layer chromatographic separation yielded a lactone (8 mg, 23%), *anti*-(CH_3,H)B (15 mg, 43%), and the starting material (3 mg, 8%).

3-(5-Hydroxy-3-methylpyrazol-1-yl)-2-butenoic acid lactone: colorless crystals from *i*-PrOH; mp 123 °C; IR (KBr) 3120, 3090, 1740, 1630, 1570, 1480, 1460, 1410, 1375, 1365, 1200, 1180, 1070, 905, 830, 800 cm^{-1}; ^1H NMR ($CDCl_3$) 2.27 (s, 3 H), 2.50 (d, 3 H), 5.50 (m, 1 H), 5.68 (s, 1 H) ppm; UV (dioxane) max 286 nm (ϵ 11 800); mass spectrum, *m/e* 164 (M^+).

***anti*-(CH_3,H)B**: After 40 mg of the bimane was heated at 250 °C for 6 h, chromatography yielded only the lactone cited above (4 mg, 10%) and the starting material (25 mg, 63%). A trace of *syn*-(CH_3,H)B was detected through its fluorescence on TLC.

***syn*-(–(CH_2)4–)B**: The bimane (66.0 mg) was heated to 280 °C for 20 h. Crystallization from EtOAc gave 85% recovery of starting material.

***syn*-(CH_3,CH_3)(CH_3,C_6H_5)B**: The bimane (67 mg) was heated for 20 h at 280 °C and a bimane fraction was isolated by rapid chromatography, followed by thick-layer chromatography, yielding *anti*-(CH_3,C_6H_5)B (5.2 mg, 12.6%) and *anti*-(CH_3,CH_3)(CH_3,C_6H_5)B (6.9 mg, 10.3%). Small amounts of *syn*-(CH_3,CH_3)B and starting material were detected through their fluorescence on TLC but were not isolated.

9,10-Dioxa-*anti*-(methyl,methyl)(methyl,phenyl)bimane: yellow crystals from *i*-PrOH; mp 140 °C; IR (KBr) 1680, 1410, 1360, 1280, 1145, 1080, 1045, 1030, 795 cm^{-1}; ^1H NMR ($CDCl_3$) 1.83 (s, 3 H), 2.50 (s, 3 H), 2.62 (s, 3 H), 7.55 (br s, 5 H) ppm; UV (dioxane) max 332 nm (ϵ 14 500), 234 (10 100); mass spectrum, *m/e* 254 (M^+).

Molecular-weight determinations were made by the Signer method,[32,33] using CH_2Cl_2 as solvent and azobenzene (*trans*-1,2-diphenyldiazene) as reference substance. Three syn and anti pairs [(CH_3,CH_3)B, (CH_3,Cl)B, and (C_6H_5,Cl)B] were examined; all of these substances gave molecular weights (at ca. 0.1 M concentrations) within 2% of those calculated for the monomer.

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