Bimanes. 10. Photochemical Rearrangement of 1,5-Diazabicyclo[3.3.0]octa-3,7-diene-2,6-diones (9,10-Dioxa-*anti*-bimanes)

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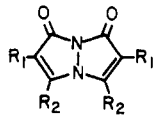
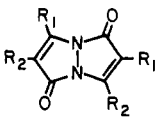
1,5-Diazabicyclo[3.3.0]octa-3,7-diene-2,6-diones (9,10-dioxa-*anti*-bimanes) rearrange quantitatively on irradiation in the 320-nm absorption band to isomeric lactones, one from symmetrical bimanes and two from unsymmetrical bimanes ("mixed" bimanes). The quantum yield of lactone is often high and depends upon bimane substitution and solvent viscosity. Fast intersystem crossing (Huppert et al.[4]), oxygen inhibition of lactone formation, and efficient formation of lactone via a triplet sensitizer implicate the triplet as a key intermediate. The suggested mechanism of lactone formation involves a twisted π-π^* triplet.

We have recently described two large classes of compounds, the *syn*- and *anti*-1,5-diazabicyclo[3.3.0]octadienediones (1 and 2) with the short form names 9,10-dioxa-*syn*-bimanes [*syn*-(R_2,R_1)B (1)] and 9,10-dioxa-*anti*-bimanes [*anti*-(R_2,R_1)B, 2].[2,3]



syn-(R_2,R_1)B

1



anti-(R_2,R_1)B

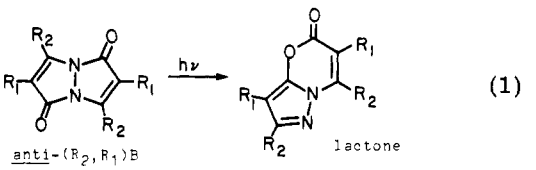
2

The *syn*-bimanes (1) are strongly fluorescent. In contrast, the *anti*-bimanes (2) are weakly fluorescent and, at 77 K, strongly phosphorescent. Very fast intersystem crossing ($k > 10^{11}$ s^{-1}) is observed for the anti-bimanes.[4] The photophysical properties are discussed elsewhere.[5,6] The bromo derivatives of the *syn*-bimanes have found considerable use as fluorescent thiol labeling agents in biological and biochemical systems.[7-10]

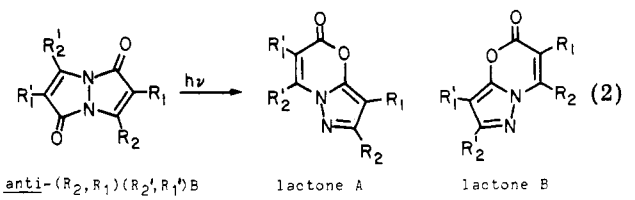
syn-Bimanes are quite stable to irradiation in the longest wavelength absorption band (however, bromobimanes isomerize reversibly).[11] The present paper describes the smooth photoisomerization of *anti*-bimanes to lactones[12] and sets forth a mechanism for the conversion.

Results

Photoisomerization. Irradiation of *anti*-(CH_3,CH_3)B (3; 2 with $R_1 = R_2 = CH_3$) in degassed CH_3CN produces an isomeric lactone (eq 1). The reaction can be followed



anti-(R_2,R_1)B — lactone (1)



anti-(R_2,R_1)(R_2',R_1')B — lactone A — lactone B (2)

spectrophotometrically, the absorption maximum of 3 [322 nm (ϵ 15 100)] differing from that for the lactone 4 [λ_{max} 294 nm (ϵ 11 200)]. An isosbestic point in the spectra indicates that the starting material is cleanly converted to one absorbing product (Figure 1). Many *anti*-bimanes behave in a similar way.

Some physical properties of the *anti*-bimanes and the photoisomerization products are compared in Table I. "Mixed" *anti*-bimanes (i.e., compounds with $R_2 \neq R_2'$ or $R_1 \neq R_1'$) yield two different lactones on photoisomerization (eq 2). The lactone ratios and NMR data are present in Table II.

Characterization of the Product. The product (hydroxypyrazolyl)acrylolactones are identified through spectroscopic (NMR, UV, IR, mass) and chemical means. The same products are formed in a number of solvents, but the ratio of the two lactones derived from "mixed" bimanes varies with solvent, as noted in Table II.

The infrared spectra of the photoproducts exhibit strong carbonyl bands between 1735 and 1740 cm^{-1}, typical for six-membered-ring lactones[13] and readily distinguished from the carbonyl bands of the *anti*-bimanes (1680–1690 cm^{-1}). The ^1H NMR spectra of the photoproducts are different from those of the *anti*-bimanes; *anti*-(CH_3,CH_3)B (3) shows two singlets while the photoproduct (4) has four singlets, all at positions different from those of the starting material. As expected, the parent peaks in the mass spectrum of the photoproducts have the same mass as those of the starting material, and the spectra show very similar fragmentation patterns. Chemical analyses are consistent with the lactone structure. Thermal rearrangement of *anti*-(CH_3,H)B (5) forms a lactone (6) which is identical (by melting point TLC, NMR, UV, IR) to that formed in the photochemical rearrangement.[14]

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(14) The thermal rearrangements of the *syn*- and *anti*-bimanes are described in ref 3.

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Table I. Physical Properties of 9,10-Dioxa-*anti*-bimanes (B) and Their Photoisomerization Products, Hydroxypyrazolylacrylolactones (L)

substituent R_2	substituent R_1		mp, °C	^{1}H NMR ($CDCl_3$), ppm	UV (CH_3CN) λ_{max}, nm (ϵ)	IR (KBr), cm^{-1}
CH_3	CH_3	B	174	1.80 (s, 3 H), 2.40 (s, 3 H)	322 (15 100)	1750 sh, 1695
		L	112	1.94 (s, 3 H), 2.06 (s, 3 H), 2.26 (s, 3 H), 2.54 (s, 3 H)	294 (11 200)	1735
CH_3	Cl	B	195	2.65 (s)	325 (15 500)	1725, 1700
		L	144	2.35 (s, 3 H), 2.72 (s, 3 H)	300 (12 500)	1740
CH_3	H	B	178	2.46 (d, 3 H), 5.35 (q, 1 H)	325 (14 600)	1730 sh, 1680
		L	123	2.27 (s, 3 H), 2.50 (d, 3 H), 5.50 (q, 1 H), 5.68 (s, 1 H)	286 (11 800)	1740
	$(CH_2)_4$	B	309	1.80 (m, 4 H), 2.25-2.60 (m, 4 H)	317 (14 400)	1680
		L	135	1.82 (m, 4 H), 2.40-3.00 (m, 4 H)	296 (12 400)	1735
C_2H_5	CH_3	B	109	1.30 (t, 3 H), 1.80 (s, 3 H), 2.75 (q, 2 H)	322 (15 000)	1690
		L	47	1.24 (t, 3 H), 1.30 (t, 3 H), 1.99 (s, 3 H), 2.06 (s, 3 H), 2.64 (q, 2 H), 2.98 (q, 2 H)	295 (10 900)	1735
CH_3	D	B	178	2.48 (s)	325(14 600)	1730 sh, 1680
		L	123	2.334 (s, 3 H), 2.543 (s, 3 H)	286 (11 900)	1740
CH_3	$CH_2COOC_2H_5$	B	180	1.281 (t, 3 H), 2.475 (s, 3 H), 3.283 (s, 2 H), 4.183 (q, 2 H)	325 (16 000)	1725, 1690
		L	88	1.275 (t, 6 H), 2.289 (s, 3 H), 2.559 (s, 3 H), 3.459 (s, 2 H), 3.525 (s, 2 H), 4.173 (q, 2 H), 4.188 (q, 2 H)	294 (12 700)	1745, 1725

Table II. ^{1}H Nuclear Magnetic Resonance Data for "Mixed" 9,10-Dioxa-*anti*-bimanes and the Lactone Mixtures Resulting from Photoisomerization (See Eq 2)

substituents R_2	R_1	R_2'	R_1'	compd	product ratio (A/B)	^{1}H NMR ($CDCl_3$), ppm
CH_3	CH_3	CH_3	Cl	bimane		1.85 (s, 3 H), 2.45 (s, 3 H), 2.52 (s, 3 H)
				lactone A	1.7[a,b]	2.00 (s, 3 H), 2.28 (s, 3 H), 2.72 (s, 3 H)
				lactone B		2.10 (s, 3 H), 2.32 (s, 3 H), 2.58 (s, 3 H)
CH_3	CH_3	CH_3	H	bimane		1.80 (s, 3 H), 2.40 (s, 3 H), 2.44 (d, 3 H), 5.25 (q, 1 H)
				lactone A	~12[a,c]	1.98 (s, 3 H), 2.27 (s, 3 H), 2.51 (d, 3 H), 5.54 (q, 1 H)
				lactone B		2.04 (s, 3 H), 2.24 (s, 3 H), 2.45 (s, 3 H), 5.70 (s, 1 H)
CH_3	H	CH_3	Cl	bimane		2.47 (s, 3 H), 2.52 (d, 3 H), 5.35 (q, 1 H)
				lactone A	very low[a,d]	
				lactone B		2.32 (s, 3 H), 2.52 (d, 3 H), 5.64 (q, 1 H)
CH_3	H	CH_3	D	bimane		2.438 (s, 6 H), 5.389 (d, 1 H)
				lactone A	1[a]	2.335 (s, 3 H), 2.540 (s, 3 H), 5.788 (s, 1 H)
				lactone B		2.335 (s, 3 H), 2.540 (s, 3 H), 5.595 (s, 1 H)
CH_3	CH_3	CH_3	Br	bimane		1.825 (q, 3 H), 2.460 (q, 3 H), 2.524 (s, 3 H)
				lactone A	1.8[a,e]	1.982 (s, 3 H), 2.266 (s, 3 H), 2.739 (s, 3 H)
				lactone B		2.083 (q, 3 H), 2.315 (s, 3 H), 2.546 (q, 3 H)
CH_3	H	CH_3	Br	bimane		2.51 (d, 3 H), 2.53 (s, 3 H), 5.46 (q, 1 H)
				lactone A	very low[a]	
				lactone B		2.33 (s, 3 H), 2.53 (d, 3 H), 5.64 (q, 1 H)
benzo		CH_3	H	bimane		2.58 (d, 3 H), 5.51 (q, 1 H), 7.15-7.80 (m, 4 H)
				lactone A		2.380 (s, 3 H), 5.70 (s, 1 H)
				lactone B		7.38-8.24 (m, 4 H)

[a] In N_2-purged CH_3CN. [b] In N_2-purged *i*-PrOH, the ratio is 2.1-2.2; in N_2-purged CH_3OH, it is 3.1. [c] In N_2-purged CH_3OH, only lactone A is observed. [d] In N_2-purged CH_3OH, only lactone B is observed. [e] In N_2-purged *i*-PrOH, the ratio is 2.2; in N_2-purged CH_3OH, it is 3.3.

The lactone (7) formed by photoisomerization of *anti*-(benzo)(CH_3,H)B (8) appears to be the same (melting point, solubility) as that reported by Michaelis[15] and Viebel.[16] The structures of the lactones formed from the "mixed" bimanes were assigned on the basis of NMR spectra and, if necessary, rate constants for the reaction

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Table III. Photochemical Quantum Yields (ϕ_{ph}) of Lactone from *anti*-Bimanes[a,b]

R_2, R_1 for *anti*-(R_2,R_1)B	solvent			
	CH_3CN	1,2-ED[c]	glycerol	other
CH_3, CH_3	0.34, 0.40 (sens),[d] 0.03 (air), 0 (O_2)	0.20	0.18	0.38 (CH_3OH), 0.03 (CH_3OH, air)
CH_3, Cl	0.38	0.10		
CH_3, Br	0.37			
CH_3, H	0.014, 0.052 (3 °C), 0.35 (sens)[d]	0.23	0.28	0.22 (CH_3OH), 0.31 (H_2O)
CH_3, D	0.017	0.23, 0.18 (50 °C), 0.27 (15 °C)	0.28	0.31 (H_2O)
CH_2OH, CH_3	0.06			
CH_3, CH_3; CH_3, H	0.004, 0.22 (sens)[d]	0.065	0.028	0.022 (CH_3OH)
CH_3, Cl; CH_3, H	0.005, 0.20 (sens)[d]	0.054	0.028	
CH_3, H; CH_3, D	0.013		0.36	
CH_3, CH_3; CH_3, Cl	0.38			

[a] Unless purging with air or O_2 is indicated, all solutions [$(1-2) \times 10^{-4}$ M] were degassed on a vacuum line and irradiated at 320 or 330 nm (solutions containing sensitizer were irradiated at 390 nm, a wavelength at which $I_0 = 2.20 \times 10^{-8}$ einstein/cm²/s) at 25 °C, except for the instances noted. [b] ±10% variation for the average of at least two measurements. [c] 1,2-ethanediol. [d] sensitizer: thiaxanthene-9-one (E_T = 65 kcal/mol, concn = 3×10^{-4} M).

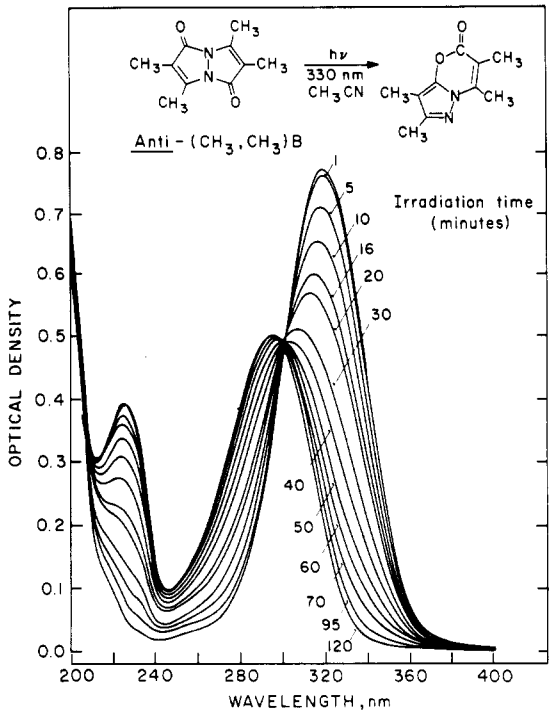
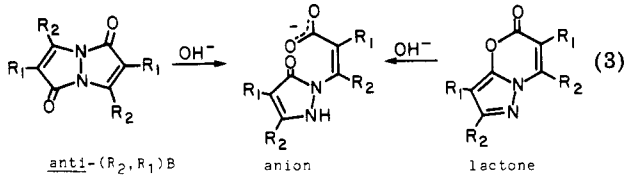


Figure 1. Series of spectra taken during irradiation of a N_2-purged solution of *anti*-(CH_3,CH_3)B (5.2×10^{-5} M) in CH_3CN with a flux of 6.35×10^{-9} einstein/cm²/s at 320 nm. The isosbestic point is clearly shown. The times of irradiation are indicated on the spectrum. (Only 20 min would be required under these conditions for complete isomerization of a thoroughly degassed solution of the same anti-bimane).

with hydroxide ion (see below). "Mixed" bimanes carrying one hydrogen at the R_1 position yield mostly one isomer, that in which the hydrogen-carrying three-carbon chain has moved to form the lactone ring.

Lactone Hydrolysis. Hydroxide ion reacts with *anti*-bimane to yield the same compound as does hydrolysis of the lactone (eq 3). In the case of *anti*-



(3)

(CH_3,Cl)B (**9**) and the corresponding lactone (**10**), the products (**11**) from the reaction of each with hydroxide ion have been isolated and proven to be identical by NMR, UV, IR, and mass spectrometry and melting point.[17]

The UV spectra of the hydrolysis products differed from those of the lactones and *anti*-bimanes. The rates of reaction of *anti*- and *syn*-bimanes with hydroxide ion vary considerably with the substituent.[17] The lactones also vary in their rate of reaction with hydroxide ion,[17] a difference useful in analysis of lactone mixtures formed from "mixed" bimanes. NMR spectra yielded isomer ratios, but not a definite structural assignment. Either the major product or the minor lactone exhibited the highest rate of hydrolysis, and on the basis of physical organic chemical principles, a decision was made as to which of the two lactones should be most reactive. This analysis was applied to the photoproducts (**12A, B** and **13A,B**) of *anti*-(CH_3,CH_3)(CH_3,Cl)B (**14**) produced in CH_3CN and *i*-PrOH and to those of *anti*-(CH_3,CH_3)(CH_3,Br)B (**15**) formed in *i*-PrOH.

Ring Closure of the Lactone Hydrolysis Products. Treatment of the lactone hydrolysis products with acid or acetic anhydride leads to either the original *anti*-bimane or to a mixture of the *anti*-bimane and the lactone. The lactone (**4**) produced by irradiation of *anti*-(CH_3,CH_3)B (**3**) is converted back into **3** after treatment with NaOH followed by acid (1 N HCl).

Quantum Yields of Photoisomerization. Photoisomerization quantum yields (ϕ_{ph}) are summarized in Table III.

(a) Oxygen Effect. High quantum yields (0.3–0.4) are often obtained by using thoroughly degassed, oxygen-free solutions of *anti*-bimanes. Much lower yields (ϕ_{ph} = ca. 0.03) are obtained without degassing, and photoisomerization is completely inhibited in oxygen-saturated solutions.

(b) Triplet Sensitization. The triplet sensitizer, thioxanthen-9-one (E_T = 65 kcal/mol), induces photoisomerization efficiently without light absorption by the *anti*-bimane. For *anti*-(CH_3,CH_3)B (**3**) in CH_3CN, ϕ_{ph} = 0.34 by direct irradiation, and ϕ_{ph} = 0.40 by sensitized photoisomerization.

(c) Substituent Effect. *anti*-(CH_3,H)B (**5**) in CH_3CN gives a sensitized ϕ_{ph} of 0.35, while ϕ_{ph} = 0.014 for direct irradiation. *anti*-Bimanes with H at R_1 rather than CH_3

(17) The rate constrants for the reaction of *syn*- and *anti*-bimanes with hydroxide ion will be discussed in a separate paper along with rate constants for lactone hydrolysis. Several examples of the chemical consequences of hydrolysis have been described in ref 3.

or halogen have a lower ϕ_{ph} for lactone in CH_3CN (factor of 20 or more). The quantum yields of lactone from "mixed" bimanes bearing only one H at the R_1 position are even lower, with ϕ_{ph} = 0.004 for *anti*-(CH_3,CH_3)-(CH_3,H)B (**16**) in CH_3CN but with a high quantum yield (0.22) for sensitized photoisomerization. The replacement of hydrogen by deuterium has only a minor effect on the photochemical quantum yields.

Photochemical quantum yields for *anti*-(CH_3,H)B (**5**) rise as viscosity increases, with ϕ_{ph} = 0.23 (1,2-ethanediol) or 0.28 (glycerol). In contrast, the high quantum yield for *anti*-(CH_3,CH_3)B (**3**) in a low-viscosity solvent is lowered by an increase in viscosity, falling to 0.20 (1,2-ethanediol) or 0.18 (glycerol). Increased viscosity raises the photochemical quantum yield for a "mixed" bimane with one R_1 = H, but less than might have been expected, with ϕ_{ph} = 0.056 (1,2-ethanediol) or 0.028 (glycerol) for *anti*-(CH_3,CH_3)(CH_3,H)B (**16**). Increasing temperature (i.e., decreasing viscosity) decreases ϕ_{ph} for *anti*-(CH_3,D)B (**17**) in 1,2-ethanediol from 0.27 (15 °C, n = 26 cP) to 0.22 (30 °C, n = 13 cP) to 0.18 (50 °C, n = ca. 5 cP). In rigid media, photoisomerization is inhibited. Irradiation of *anti*-(CH_3,CH_3)B (**3**) in an EPA (ether–pentane–ethanol) matrix at 77 K for 1 h or in a pure thin film on a sapphire window at 77 K[18] for 30 min led neither to photoisomerization nor to any other photochemical change.

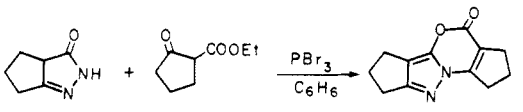
The lactones are very stable toward irradiation and exhibit no detectable fluorescence or phosphorescence.

Discussion

The photoisomerization of 9,10-dioxa-*anti*-bimanes to lactones is (a) an important and clean reaction of *anti*-bimanes, (b) a convenient route to a relatively new class of heterocyclic lactones, and (c) an interesting subject for mechanistic investigation. The photoisomerization is a useful addition to the thermal reactions which interconvert the *syn*-bimanes, *anti*-bimanes, and isomeric lactones.

The photoisomerizations proceed quantitatively even in nucleophilic solvents like methanol and water and are easy to carry out since the lactones are photochemically and thermally stable. Exclusion of oxygen (which quenches the triplet) makes the conversions efficient and fast.

The lactones were first reported by Michaelis;[15] heating (2-carboxyphenyl)hydrazine with ethyl acetoacetate gave *syn*-(benzo)(CH_3,H)B, *anti*-(benzo)(CH_3,H)B (**8**), and a benzohydroxypyrazolylacrylolactone (**7**). Only lactone is produced in modest yield in the related reaction of 3,4-trimethylenepyrazolin-5-one with 2-(carboethoxy)cyclopentanone (eq 4).[3]



(4)

The dibenzo lactone (indazolo[2,3-*a*][3,1]benzoxazin-5-one) was first prepared by Heller[20] by the action of acetic anhydride on 1,2-bis(2-carboxyphenyl)hydrazine. A new preparation of substituted dibenzo lactones involves the thermal decomposition of (2-azidophenyl)benzoxazin-5-ones or the reaction of the corresponding (2-nitrophenyl)benzoxazin-5-ones with triethyl phosphite[21] (eq 5).

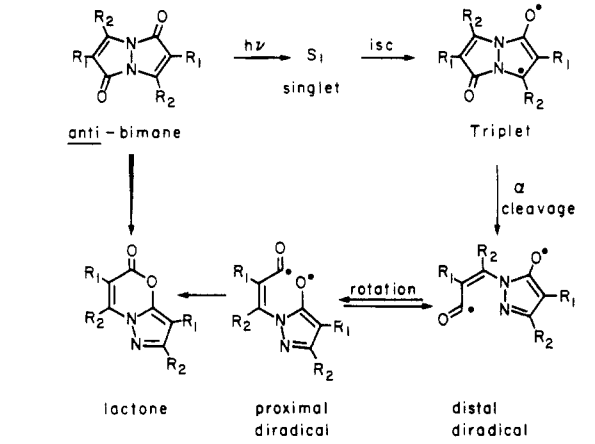
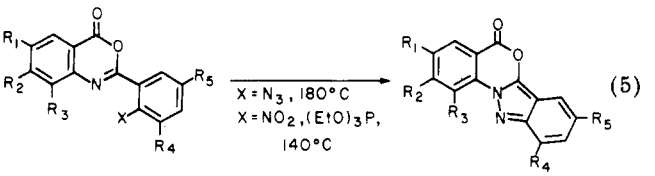


Figure 2. Mechanistic scheme for the photoisomerization of *anti*-bimanes to lactones.

Heating *anti*-(CH_3,H)B for 6 h at 250 °C led to 10% lactone formation and 65% recovery of *anti*-bimane.[3]



(5)

The foregoing syntheses are not particularly convenient. Photoisomerization of the readily available *anti*-bimanes[3] represents a general, selective, and simple method for the preparation of many (hydroxypyrazolyl)acrylolactones.

Mechanism of the Photoisomerization Reaction. To construct a mechanism for photoisomerization, we must consider (1) the role of the triplet state, (2) the quantitative conversion of the *anti*-bimane into the lactone, and (3) the bonding changes involved in the chemical reaction. A reasonable scheme is shown in Figure 2 and includes (a) excitation of S_0 to S_1, (b) intersystem crossing of S_1 to T_2 followed by relaxation to T_1,[5] (c) α cleavage of the T_1 (at the N—CO bond) to distal diradical, (d) rotation around the N—C=C bond, forming a proximal diradical, and (e) ring closure to the lactone.

The *anti*-bimane triplet state is clearly involved in the photoisomerization reaction. First, oxygen is an effective quencher of the reaction. Second, a triplet sensitizer, thioxanthen-9-one (E_T 65 kcal/mol), effectively promotes photoisomerization. Third, a high rate of triplet formation ($k > 10^{11}$ s^{-1}) is characteristic of *anti*-bimanes, as shown by picosecond pulse measurements.[4] Further evidence of the efficiency of triplet formation for *anti*-bimanes is shown by the substantial phosphorescence quantum yield at 77 K (0.3–0.45).[5]

The photoisomerization of *anti*-bimanes has some resemblance to the photo-Fries rearrangement of aromatic amides,[22,23] but the latter is thought to occur via a singlet state.

The estimated T_1 energies for *anti*-(CH_3,H)B and *anti*-(CH_3,CH_3)B are 66 and 64 kcal/mol, respectively.[5] Thioxanthen-9-one has a triplet energy (65 kcal/mol) which corresponds quite well to what should be needed for triplet sensitization; its effectiveness as a sensitizer supports the validity of the estimates for the triplet state energies.

(18) The techniques of thin-film spectroscopy[19] were used to prepare a film of defined thickness in a glassy state.
(19) Hermolin, J.; Levin, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 4801.
(20) Heller, G. *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 523.
(21) Alkhader, M. A.; Smally, R. K.; Mohajerani, B. *Synthesis* **1980**, 381.
(22) Bellus, D. *Adv. Photochem.* **1973**, *8*, 109.
(23) Fischer, M. *Tetrahedron Lett.* **1969**, 2281; *Chem. Ber.* **1969**, *102*, 342.

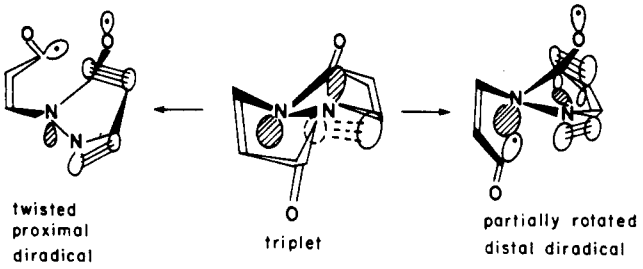


Figure 3. Schematic representation of the triplet state and two of the diradicals which might be formed after cleavage of the N–CO bond. With twisting, the acyl radical can form a proximal radical by rotation around the N—C=C bond. Without twisting, the acyl radical chain can rotate in only one direction and only as far as the nonbonding electrons on the second nitrogen.

The quantitative yield of lactone indicates that the photoisomerization is intramolecular; the lack of solvent effect on the nature of the products (accompanying a small effect on the ratios of lactones from "mixed" *anti*-bimanes) points in the same direction. The transformation requires an α-N—CO cleavage, a likely choice being ring opening of a twisted triplet to a distal diradical, which is converted into a proximal diradical by rotation around the N—C=C bond (see Figure 3). The small solvent effect on the lactone isomer ratios (α-methyl vs. α-halogen) and the direction of ring opening in favor of opening on the side of electron-attracting substituents imply a small charge separation on the side which does not open.

A triplet distal diradical is the initial product of ring opening. Rotation of the three-carbon chain bearing the acyl radical should be fast, forming a proximal diradical. The spin state of the proximal diradical is not so clear; during rotation, the spin of the acyl radical would become uncorrelated with the spin of the ring radical. After each rotation, the proximal diradical would have a 25% chance of being a singlet and should rapidly form the covalent lactone. In "mixed" bimanes having one α-hydrogen, ring opening on the side of the hydrogen predominates, as expected for "light fragment" motion (see below).

The lifetime of the triplet is quite dependent on the viscosity of the solvent and on whether or not a hydrogen is present at the R_1 position.[24] The triplet state in fluid media decays either to S_0 or to the lactone. From the triplet decay rates and the photochemical quantum yields, the rate constant of lactone formation (k_L) and the rate for radiationless decay ($T_1 \rightarrow S_0$, k_{TS}) can be estimated. The k_L are higher in fluid media and for hydrogen-substituted bimanes. Increased viscosity decreases k_L, the range being 5×10^2 s^{-1} for *anti*-(CH_3,CH_3)B in glycerol to 1×10^7 s^{-1} for *anti*-(CH_3,H)B in CH_3OH. The k_{TS} values are increased by hydrogen at the R_1 position, with values of 10^7–10^8 s^{-1} for *anti*-(CH_3,H)B in fluid media. The k_{TS} values decrease greatly in viscous media. Thus, a low quantum yield of lactone is correlated with a fast conversion of T_1 to S_0.

The maximum rate of lactone formation is very close to the rate for interconversion of the nitrogen conformers in a 1,5-diazabicyclo[3.3.0]octane system (i.e., ring inversion, $k > 10^6$ s^{-1})[25] or in the corresponding radical cation ($k \approx 10^8$ s^{-1},[26] suggesting that twisting and lactone formation are related. If α-bond cleavage were to occur without conformational change in the ring which remains, the acyl radical could only rotate partially due to the nonbonding electrons on the other nitrogen. A light fragment, i.e., one containing hydrogen or deuterium, might rotate at a rate faster than the twisting motion, leading to formation of a partially rotated diradical, in which return to the distal diradical could produce 25% singlet species or, in other words, the ground state.

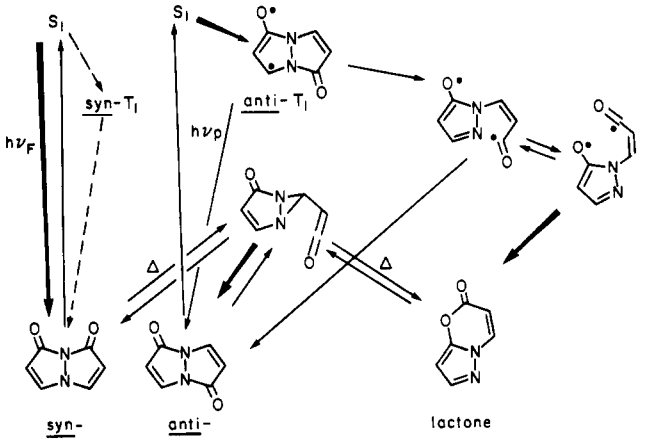


Figure 4. Thermal and photochemical conversions of *syn*- and *anti*-bimanes. The major pathways (heavy arrows) include fluorescence from the syn S_1 state,[5] intersystem crossing from the anti S_1 state,[4] lactone formation from the anti T_1 state (present paper), and thermal rearrangement of the *syn*-bimanes to the *anti*-bimanes[3] (of lactone: Gibson, G. K. J.; Lindsey, A. S. *J. Chem. Soc. C* **1967**, 1792).

We are thus able to understand (a) the rapid triplet decay (high k_{TS}) for *anti*-(CH_3,H)B in highly fluid solvents, (b) the marked effect of viscosity on the quantum yield of lactone, (c) the low quantum yields of lactones from "mixed" bimanes in which only one R_1 group is hydrogen, and (d) the predominance of one lactone from certain "mixed" bimanes that formed through ring opening on the side which carries the α-hydrogen. The partially rotated diradical is shown in Figure 3.

The twisting motions of the *anti*-bimanes in the triplet state are slowed down in viscous media, with k_{TS} being decreased much more than k_L, thus increasing the photochemical quantum yield. The fact that a triplet sensitizer promotes the formation of lactone from *anti*-(CH_3,H)B in CH_3CN in relatively high yield strongly suggests that the sensitizer remains associated with the triplet bimane after energy transfer and provides the equivalent of a high "local viscosity".

The interconversions of *syn*-bimanes, *anti*-bimanes, and lactones are illustrated in Figure 4 in order to show the relationship of the photoisomerization to the thermal reactions.

Experimental Section

Materials. Some *anti*-bimanes were available from previous work.[3] The synthesis and properties of new *anti*-bimanes and lactones are described below.

9,10-Dioxa-*anti*-(methyl,hydrogen)(methyl,bromo)bimane (18). Bromine (250 mg, 1.6 mmol) in dichloromethane (10 mL) was added dropwise to *anti*-(CH_3,H)B (**5**; 300 mg, 1.9 mmol) in the same solvent (10 mL). Evaporation of the solvent and chromatography on alumina (petroleum ether–$CHCl_3$, 1:1) yielded **18** (170 mg, 37%) and **5** (140 mg, 46%). *anti*-(CH_3,H)(CH_3,Br)B (**18**): white crystals (from CH_3CN); mp 158 °C; IR (KBr) 3120, 1675, 1580, 1400, 1340, 1300, 1190, 1150, 1130, 1020, 1000, 890, 800, 730, 720, 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.53 (s, 3 H), 2.51 (d, 3 H), 5.46 (q, 1 H) ppm; UV (dioxane) λ 325 nm (ϵ_{max} 14800); mass spectrum, *m/e* 242, 244 (M^+).

9,10-Dioxa-*anti*-(methyl,hydrogen)(methyl,deuterium)-bimane (19). *anti*-(CH_3,H)(CH_3,Br)B (**18**; 100 mg, 0.4 mmol) in acetic acid (10 mL) containing KOAc (2.1 mmol) and 10% Pd/C

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(25) Kinztinger, J. .; Lehn, J. M.; Wagner, J. *J. Chem. Soc., Chem. Commun.* **1967**, 206–207.
(26) Nelsen, S. F.; Weisman, G. R.; Hintz, P. J.; Olp, D.; Fahey, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 2916.

(50 mg) was treated with deuterium at 70 °C. After somewhat more than 1 equiv of D_2 had been taken up, dichloromethane (10 mL) was added, and the solution was filtered and evaporated to dryness. The residue was extracted with dichloromethane, the solution washed (aqueous $NaHCO_3$, H_2O) and dried (Na_2SO_4), the solvent removed, and the residue crystallized from CH_3CN to yield *anti*-(CH_3,H)(CH_3,D)B (**19**): 26 mg (39%); white crystals (from CH_3CN); mp 177–178 °C; IR (KBr) 3120, 1670, 1560, 1400, 1350, 1190, 1160, 1090, 1040, 1000, 920, 840, 820, 750, 715, 680, 640 cm^{-1}; ^1H NMR ($CDCl_3$) 2.438 (s, 6 H), 5.389 (d, 1 H) ppm; UV (dioxane) λ 325 nm (ϵ_{max} 14 600); mass spectrum, *m/e* 165 (M^+).

9,10-Dioxa-*anti*-(methyl,deuterium)bimane (17). *anti*-(CH_3,Br)B (550 mg, 1.7 mmol) in acetic acid (40 mL) containing KOAc (9 mmol) and 10% Pd/C (100 mg) at 70 °C was treated with deuterium until somewhat more than 2 equiv of D_2 had been taken up. The reaction mixture was worked up as described above to yield *anti*-(CH_3,D)B (**17**): 150 mg (55%); white crystals (from CH_3CN); mp 177–178 °C; IR (KBr) 3120, 1730 (sh), 1680, 1590, 1445, 1355, 1215, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) 2.487 (s) ppm; UV (dioxane) λ 325 nm (ϵ_{max} 14 600); mass spectrum, *m/e* 166 (M^+).

9,10-Dioxa-*anti*-(methyl,hydrogen)(methyl,chloro)bimane (20). *anti*-(CH_3,Cl)B (**9**; 600 mg, 2.5 mmol) in acetic acid (25 mL) containing KOAc (7 mmol) and 10% Pd/C (100 mg) was treated with hydrogen at 70 °C until TLC indicated that substantial conversion into the half-reduced compound had occurred. The reaction mixture was worked up as in the case of the mixed H,D derivative and chromatographed on silica (eluant petroleum ether–$CHCl_3$, 1:1) to yield *anti*-(CH_3,Cl)B (20 mg, 3%), **20** (100 mg, 20%), and **5**, (120 mg, 30%). *anti*-(CH_3,H)(CH_3,Cl)B (**20**): white crystals (from CH_3CN); mp 136 °C; IR (KBr) 3100, 2920, 1680, 1590, 1400, 1300, 1190, 1020, 1000, 890, 820, 720, 710 cm^{-1}; ^1H NMR ($CDCl_3$) 2.47 (s, 3 H), 2.52 (d, 3 H), 5.35 (q, 1 H) ppm; UV (dioxane) λ 323 nm (ϵ_{max} 15 000); mass spectrum, *m/e* 198,200 (M^+).

9,10-Dioxa-*anti*-(methyl,methyl)(methyl,hydrogen)bimane (16). *anti*-(CH_3,CH_3)(CH_3,Cl)B (**14**; 240 mg, 1.1 mmol) was reduced with hydrogen as described above to yield *anti*-(CH_3,CH_3)(CH_3,H)B (**16**): 70 mg (35%); white crystals (from CH_3CN); mp 129 °C; IR (KBr) 3120, 2920, 1670, 1400, 1380, 1350, 1300, 1220, 1160, 1100, 1030, 1000, 960, 860, 800, 730, 700 cm^{-1}; ^1H NMR ($CDCl_3$) 1.80 (s, 3 H), 2.40 (s, 3 H), 2.42 (d, 3 H), 5.25 (q, 1 H) ppm; UV (dioxane) λ 323 nm (ϵ_{max} 15 000); mass spectrum, *m/e* 178 (M^+).

9,10-Dioxa-*anti*-(methyl,methyl)(methyl,bromo)bimane (15). 3-Methyl-4,4-dibromo-2-pyrazolin-5-one (**21**; 1.0 g, 4 mmol) in CH_2Cl (10 mL) was added dropwise to a vigorous stirred ice-cold mixture of 3,4-dimethyl-4-chloro-2-pyrazolin-5-one (**22**; 0.6 g, 4 mmol) and *N,N*-diisopropylethylamine (1.04 g, 8 mmol) in CH_2Cl_2 (5 mL). After 1 h, the ice bath was removed, but stirring was continued for 24 h. The solution was filtered, the solvent removed, and the residue chromatographed on alumina (eluant petroleum ether–CH_2Cl_2). After three chromatographies, the six components isolated were as follows, in order of elution: *anti*-(CH_3,Br)B, 50 mg (9%); **15**, 250 mg (24%); *anti*-(CH_3,CH_3)B (**3**), 40 mg (10%); *syn*-(CH_3,Br)B, 10 mg (2%); *syn*-(CH_3,CH_3)(CH_3,Br)B, 20 mg (2%); *syn*-(CH_3,CH_3)B, 20 mg (3%). For *anti*-(CH_3,CH_3)(CH_3,Br)B (**15**); white crystals (from CH_3CN); mp 165 °C; IR ($CHCl_3$) 2930, 1690, 1630, 1590, 1350, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) 1.825 (q, 3 H), 2.460 (q, 3 H), 2.524 (s, 3 H) ppm; UV (dioxane) λ 324 nm (ϵ_{max} 14 900); mass spectrum, *m/e* 256, 258 (M^+).

9,10-Dioxa-*anti*-(methyl,(carbomethoxy)methyl)bimane (23). Chlorine was passed into a solution of 3-methyl-4-[(carboethoxy)methyl]-2-pyrazolin-5-one[27] (12.5 g; from hydrazine and diethyl acetylsuccinate)[28] in CH_2Cl_2 (250 mL) until the solid had dissolved and the solution had become faintly yellow. After removal of Cl_2 and HCl with a stream of air, the solvent was evaporated and the yellowish oily residue crystallized from benzene to yield 3-methyl-4-[(carboethoxy)methyl]-4-chloro-2-pyrazolin-5-one (**24**) as a white solid: 11.3 g (75%); mp 90 °C; ^1H NMR ($CDCl_3$) 1.20 (t, 3 H), 2.10 (s, 3 H), 3.20 (d, 2 H), 4.20 (q, 2 H), 8.80 (br s, 1 H) ppm;IR (KBr) 3200–3250, 2950, 1700 cm^{-1}. *N,N*-Diisopropylethylamine (1.3 g, 10 mmol) was added to **24** (2.1 g, 10 mmol) in CH_2Cl_2 (25 mL), and the mixture was stirred 10 h. After solvent removal, the residue was chromatographed on silica gel (eluant $CHCl_3$–EtOAc, 1:1), yielding **23** (550 mg, 33%) and then *syn*-(CH_3,$CH_2COOC_2H_5$)B (170 mg, 10%).[29] *anti*-(CH_3,$CH_2COOC_2H_5$)B (**23**): white needles (from CH_3CN); mp 180 °C; IR (KBr) 2960, 2920, 1725, 1690, 1410, 1370, 1340, 1290, 1270, 1230, 1190, 1150, 1110, 1060, 1020, 960, 940, 900, 880, 820, 750, 710 cm^{-1}; ^1H NMR ($CDCl_3$) 1.281 (t, 3 H), 2.475 (s, 3 H), 3.283 (s, 2 H), 4.183 (q, 2 H) ppm; UV (dioxane) λ 325 nm (ϵ_{max} 16 000); mass spectrum, *m/e* 336 (M^+).

The synthesis and properties of *anti*-(C_2H_5,CH_3)B are reported elsewhere.[30]

Lactone Preparations. β-Methyl-β-[3-methyl-5-hydroxypyrazol-1-yl]acrylic Acid Lactone (6). *anti*-(CH_3,H)B (**5**; 50 mg, 0.30 mmol) in N_2-purged CH_3CN (20 mL) was irradiated at 360 nm for 3 days in a Rayonet reactor. Removal of the solvent and crystallization of the residue gave 45 mg (90%) of **6**: white crystals (from *i*-PrOH); mp 123 °C; IR (KBr) 3120, 3050, 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 (q, 1 H), 5.68 (s, 1 H) ppm; UV (dioxane) λ 286 nm (ϵ_{max} 11 800); 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, 57.59; H, 5.22; N, 17.02.

Five other symmetrical *anti*-bimanes were irradiated for 2–6 h to give good yields of the isomer lactones, for which the following properties were recorded. In addition, the products from three "mixed" bimanes which photoisomerize to only one lactone are included.

α,β-Tetramethylene-β-[3,4-tetramethylene-5-hydroxypyrazol-1-yl]acrylic acid lactone (25): white crystals (from *i*-PrOH); mp 135 °C; IR (KBr) 2920, 1735, 1630, 1490, 1420, 1340, 1310, 1270, 1230, 1200, 1170, 980, 950, 860, 740, 720 cm^{-1}; ^1H NMR ($CDCl_3$) 1.82 (m, 8 H), 2.40–3.00 (m, 8 H) ppm; UV (dioxane) λ 296 nm (ϵ_{max} 12 400); mass spectrum, *m/e* 244 (M^+).

α,β-Dimethyl-β-[3,4-dimethyl-5-hydroxypyrazol-1-yl]acrylic acid lactone (4): white crystals (from *i*-PrOH); mp 112 °C; IR (KBr) 2920, 1735, 1630, 1490, 1450, 1410, 1370, 1270, 1190, 1110, 1040, 930, 800, 740, 720 cm^{-1}; ^1H NMR ($CDCl_3$) 1.90 (s, 3 H), 2.00 (s, 3 H), 2.20 (s, 3 H), 2.45 (s, 3 H) ppm; UV (dioxane) λ 294 nm (ϵ_{max} 11 200); 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, 61.85; H, 6.36; N, 14.51.

α-Chloro-β-methyl-β-[3-methyl-4-methyl-4-chloro-5-hydroxypyrazol-1-yl]acrylic acid lactone (10): crystals (from *i*-PrOH); mp 144 °C; IR (KBr) 1740, 1620, 1580, 1490, 1450, 1400, 1370, 1320, 1210, 1130, 960, 890, 780, 740, 700, 670, 650 cm^{-1}; ^1H NMR ($CDCl_3$) 2.35 (s, 3 H), 2.72 (s, 3 H) ppm; UV (CH_3CN) λ 300 nm (ϵ_{max} 12 500); mass spectrum, *m/e* 232, 234, 236 (M^+). Anal. Calcd for $C_8H_6N_2O_2Cl_2$: C, 41.23; H, 2.60; N, 12.02. Found: C, 40.83; H, 2.85; N, 11.97.

α-[(Carboethoxy)methyl]-β-methyl-β-[3-methyl-4-[(carboethoxy)methyl]-5-hydroxypyrazol-1-yl]acrylic acid lactone (26): white crystals (from, *i*-PrOH); mp 88 °C; IR (KBr) 2980, 2920, 1745, 1725, 1640, 1490, 1410, 1370, 1330, 1280, 1220, 1200, 1180, 1160, 1110, 1030, 1000, 930, 910, 860, 810, 780, 750, 720, 670 cm^{-1}; ^1H NMR ($CDCl_3$) 1.275 (t, 6 H), 2.289 (s, 3 H), 2.559 (s, 3 H), 3.459 (s, 2 H), 3.525 (s, 2 H), 4.173 (q, 2 H), 4.188 (q, 2 H) ppm; UV (dioxane) λ 294 nm (ϵ_{max} 12 700); mass spectrum, *m/e* 336 (M^+).

α-Ethyl-β-methyl-β-[3-ethyl-4-methyl-5-hydroxypyrazol-1-yl]acrylic acid lactone (27): white solid; mp 47 °C; IR ($CHCl_3$) 2920, 1725, 1635, 1480, 1420, 1380, 1220, 1170, 1020, 980, 920, 880, 780, 650 cm^{-1}; ^1H NMR ($CDCl_3$) 1.24 (t, 3 H), 1.30 (t, 3 H), 1.99 (s, 3 H), 2.06 (s, 3 H), 2.64 (q, 2 H), 2.98 (q, 2 H) ppm; UV (dioxane) λ 295 nm (ϵ_{max} 10 900); mass spectrum, *m/e* 220 (M^+).

β-Methyl-β-[3-methyl-4-chloro-5-hydroxypyrazol-1-yl]-acrylic acid lactone (28): white crystals (from *i*-PrOH); mp 135 °C; IR (KBr) 2860, 1730, 1630, 1450, 1120, 920, 850, 810, 790, 770 cm^{-1}; ^1H NMR ($CDCl_3$) 2.32 (s, 3 H), 2.53 (d, 3 H), 5.64 (q, 1 H) ppm; UV (CH_3CN) λ 288 nm (ϵ_{max} 12 300); mass spectrum, *m/e* 198,200 (M^+).

(27) McMillan, F. H.; King, J. A. *J. Am. Chem. Soc.* **1955**, *77*, 3376.
(28) Adkins, H.; Isbell, N.; Wojcik, B. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, pp 262–263.
(29) The properties of the syn derivative will be reported in another paper.
(30) Kosower, E. M., Radowsky, A., in preparation.

β-Methyl-β-[3-methyl-4-bromo-5-hydroxypyrazol-1-yl]acrylic acid lactone (29): white crystals (from *i*-PrOH); mp 154 °C; IR (KBr) 2920, 1735, 1635, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) 2.33 (s, 3 H), 2.53 (d, 3 H), 5.64 (q, 1 H) ppm; UV (CH_3CN) λ 290 nm (ϵ_{max} 12 500); mass spectrum, *m/e* 242, 244 (M^+).

β-Methyl-β-[3,4-benzo-5-hydroxypyrazol-1-yl]acrylic acid lactone (7): yellow-white crystals (from *i*-PrOH); mp 132 °C; IR (KBr) 3105, 2920, 1760, 1600, 1560, 1500, 1430, 1380, 1330, 1230, 1160, 1150, 1100, 1030, 1010, 970, 880, 800, 750, 680, 640 cm^{-1}; ^1H NMR ($CDCl_3$) 2.318 (s, 3 H), 5.836 (s, 1 H), 7.38–8.24 (m, 4 H) ppm; mass spectrum, *m/e* 200 (M^+).

Four mixed *anti*-bimanes which give rise to mixtures of lactone were irradiated under the same conditions used for the preparative experiments described above. ^1H NMR spectra provided sufficient information to assign structures and to give approximate product ratios. The NMR data are listed in Table II. In three cases, the kinetics of reaction with hydroxide ion were followed in order to obtain evidence confirming the NMR analysis.

The product mixture from irradiation of *anti*-(CH_3,H)(CH_3,D)B had a melting point of 115–120 °C and was shown by NMR analysis to be a 1:1 mixture of the two possible lactone products, α-deuterio-β-methyl-β-[3-methyl-4-protio-5-hydroxypyrazol-1-yl]acrylic acid lactone (**30A**) and α-protio-β-methyl-β-[3-methyl-4-deuterio-5-hydroxy-pyrazol-1-yl]acrylic acid lactone (**30B**).

Irradiation of *anti*-(CH_3,CH_3)(CH_3,H)B in CH_3CN gave 2 lactones β-methyl-β-[3,4-dimethyl-5-hydroxypyrazol-1-yl]acrylic acid lactone (**31A**) and α,β-dimethyl-β-[3-methyl-5-hydroxypyrazol-1-yl]acrylic acid lactone (**31B**). The ratio was 11.5:1 by ^1H NMR analysis, the predominant lactone being that in which a hydrogen-carrying chain had moved. In CH_3OH, only the latter lactone was observed.

Irradiation of *anti*-(CH_3,CH_3)(CH_3,Cl)B in CH_3CN led to a mixture of two isomeric lactones, α-chloro-β-methyl-β-[3,4-dimethyl-5-hydroxypyrazol-1-yl]acrylic acid lactone (**12A**) and α,β-dimethyl-β-[3-methyl-4-chloro-5-hydroxypyrazol-1-yl]acrylic acid lactone (**12B**). The ratio was approximately 2:1 by ^1H NMR analysis. The identity of the major component as the lactone in which the chlorine-bearing chain had moved was confirmed by a kinetic study of hydrolysis at pH 9.00 and 25 °C. A plot of ln OD vs. *t* showed two slopes; extrapolation of the slopes to zero time gave the ratio of the initial absorbances for the two lactones. On the assumption of similar absorption coefficients, the ratio of the two products was found to be 1.7:1, a figure in agreement with that determined by NMR. The lactone mixture obtained by irradiation of *anti*-(CH_3,CH_3)(CH_3,Cl)B in either *i*-PrOH or CH_3OH were analyzed in the same way.

Irradiation of *anti*-(CH_3CH_3)(CH_3,Br)B in different solvents led to a mixture of two isomeric lactones (**13A** and **13B**) which were analyzed as described for *anti*-(CH_3,CH_3)(CH_3,Cl)B.

Physical Measurements. Absorption spectra were measured with a Cary Model 17 spectrophotometer, NMR spectra with various instruments, including a Bruker WH-90 FT NMR spectrometer, and IR spectra with Perkin-Elmer Models 177 and 297 spectrophotometers. Photochemical quantum yields were determined at low conversions (1–10%) by using absorption spectra after actinometrically defined narrow-band irradiation with a Hitachi Perkin-Elmer MPF-4 spectrofluorimeter.[31] The photochemical quantum yields changed little over the range of conversion used; the value for 1% conversion was used in the few instances in which a decrease with extent of conversion was noted. The yields were calculated according to eq 1, in which the symbols

$$\phi_{ph} = \text{moles product/einsteins absorbed} = (D_0 - D_t)/(D_0 - D_{inf})CV/(I_0At[1 - e^{\epsilon C}]) \quad (1)$$

have the following definitions: D_0, initial optical density; D_t, optical density at time *t*; D_{inf}, optical density at infinite *t*; *C*, initial concentration of *anti*-bimanes; *V*, volume irradiated; I_0, light flux (6.35×10^{-9} einstein $(cm^2)^{-1}$ s^{-1} at 320 nm); *A*, sample area toward light source; *t*, irradiation time; ε, absorption coefficient of *anti*-bimane. A correction was made for light absorbed by the product at time *t*.

All solutions were either prepared on a vacuum line by using highly purified and degassed solvents (CH_3CN, CH_3OH) or within a nitrogen-flushed glovebag, followed by degassing on a high-vacuum line (1,2-ethanediol, glycerol). Aqueous solutions were degassed carefully by using the freeze–thaw technique on a high-vacuum line.

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