Bimanes. 14. Synthesis and Properties of 4,6-Bis(carboalkoxy)-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-diones [4,6-Bis(carboalkoxy)-9,10-dioxa-*syn*-bimanes]. Preparation of the Parent *syn*-Bimane, *syn*-(Hydrogen,hydrogen)bimane

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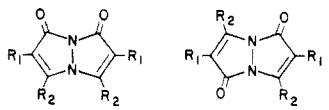
Received June 28, 1981

The 3-(carboalkoxy)pyrazolin-5-ones derived from dialkyl oxaloacetates or diethyl α-methyloxaloacetate through reaction with hydrazine can be converted into the strongly fluorescent 4,6-bis(carboalkoxy)-1,5-diazabicyclo-[3.3.0]octa-3,6-diene-2,8-diones [4,6-bis(carboalkoxy)-9,10-dioxa-*syn*-bimanes, *syn*-(COOR,R_1)B (**6**), R = CH_3 or CH_3CH_2, R_1 = CH_3, Cl, Br] by base treatment of the corresponding chloro or bromo derivative. The structure of one bis ester, 4,6-bis(carbomethoxy)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione [**6f**, *syn*-($COOCH_3$,CH_3)B], has been determined by X-ray crystallography. Lithium bromide and the esters in CH_3CN or DMF yield via dealkylation and decarboxylation the corresponding *syn*-(H,R_1)B (**11**), (R_1 = H, CH_3, Cl, Br, I) or the "mixed" bimanes *syn*-(EtOOC,R_1)(H,R_1)B (**10**, R_1 = Cl or CH_3). A dicarboxylic acid (R_1 = CH_3; LiBr/CH_3CN/60 °C; two $COOCH_3$'s) readily decarboxylates. Hydrogenation of halogenated bimanes over Pd/C(AcOH) replaces one or both halogens, the 2H product from *syn*-(H,Cl)B being the parent *syn*-bimane, *syn*-(H,H)B. *syn*-(COOR,H)B and ICl yield *syn*-(COOR,I)B, which gives *syn*-(H,I)B on dealkylation–decarboxylation. Replacement of Cl in *syn*-($COOCH_2CH_3$,Cl)B by $C_6H_5S^-$ yields *syn*-($COOCH_2CH_3$,C_6H_5S)B. Both ester groups and halogens shift absorption and fluorescence maxima to longer wavelengths than those recorded for *syn*-(CH_3,CH_3)B. In ^1H NMR spectra, the β-hydrogens of the *syn*-bimane appear at considerably lower fields (7.52–8.21 ppm) than the α-hydrogens (5.42–6.13 ppm).

For understanding the chemical and photophysical properties of the 9,10-dioxa-*syn*-bimanes (**1**) and the 9,10-dioxa-*anti*-bimanes (**2**) (1,5-diazabicyclobicyclo-

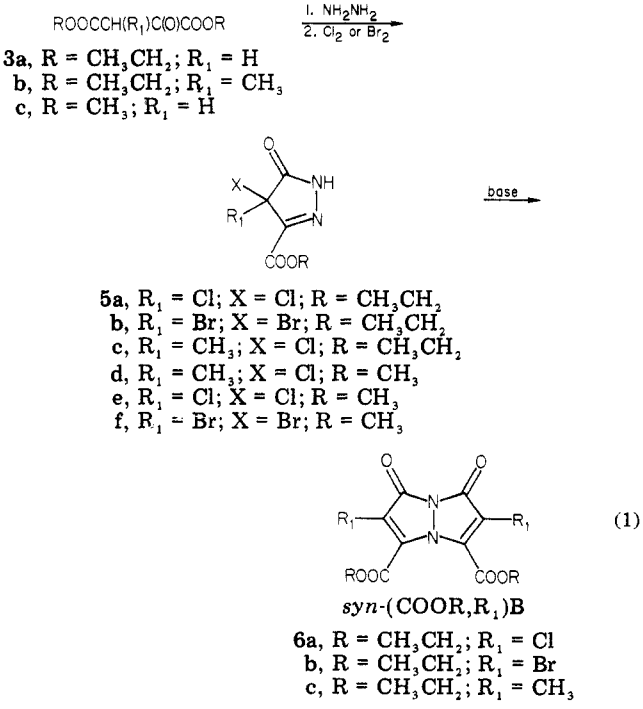


syn-(R_2, R_1)B anti-(R_2, R_1)B

[3.3.0]octanediones),[2-8] compounds in which as many substituents as possible were replaced by hydrogen were desired. Bimanes with hydrogens in the position α to the carbonyl (**1** and **2**, R_1 = H) were accessible via hydrogenation of the readily prepared (R_2,Cl)B, but bimanes with hydrogen at the β-position (i.e., bimanes in which R_2 = H) could not be prepared directly in significant yields. We now report the synthesis of bimanes bearing hydrogen at the β-position, including a preparation of the parent 9,10-dioxa-*syn*-bimane (**1**, R_1 = R_2 = H), via the compounds with carboalkoxy groups at the β-position.

Results

Synthesis of Bimane Esters. Diethyl oxaloacetate (**3a**) was readily converted to 3-(carboethoxy)pyrazolin-5-one by hydrazine in ethanol. Treatment of the pyrazolinone **4a** (R = CH_3CH_2, R_1 = H) with chlorine in dichloromethane led to the 4,4-dichloro-3-(carboethoxy)-pyrazolin-5-one (**5a**). The usual base for the conversion of halopyrazolinones to *syn*-bimanes, potassium carbonate, gave relatively low yields of bimane. However, *N*,*N*-diisopropylethylamine, which favors *anti*-bimane formation in other cases,[4] led to the strongly fluorescent *syn*-(COOEt,Cl)B (**6a**) in 15–30% yield. The reactions are illustrated in eq 1.



ROOCCH(R_1)C(O)COOR —(1. NH_2NH_2, 2. Cl_2 or Br_2)→ **3a**, R = CH_3CH_2; R_1 = H; **b**, R = CH_3CH_2; R_1 = CH_3; **c**, R = CH_3; R_1 = H

—(base)→ **5a**, R_1 = Cl; X = Cl; R = CH_3CH_2; **b**, R_1 = Br; X = Br; R = CH_3CH_2; **c**, R_1 = CH_3; X = Cl; R = CH_3CH_2; **d**, R_1 = CH_3; X = Cl; R = CH_3; **e**, R_1 = Cl; X = Cl; R = CH_3; **f**, R_1 = Br; X = Br; R = CH_3

syn-(COOR,R_1)B

6a, R = CH_3CH_2; R_1 = Cl; **b**, R = CH_3CH_2; R_1 = Br; **c**, R = CH_3CH_2; R_1 = CH_3 (1)

Higher yields of *syn*-bimane were obtained from the derivatives with carbomethoxy in place of the carboethoxy group. Dimethyl oxalate[4a] may be converted into ethyl methoxalylacetate (**3c**) in reasonable yield. Commercial availability of the sodium salt of diethyl oxaloacetate made the direct and indirect syntheses of the (carbomethoxy)-

(1) (a) Tel-Aviv University. (b) State University of New York at Stony Brook.
(2) Kosower, E. M.; Bernstein, J.; Goldberg, I.; Pazhenchevsky, B.; Goldstein, E., *J. Am. Chem. Soc.* **1979**, *101*, 1620.
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(5) Part 6: Kosower, E. M.; Pazhenchevsky, B.; Dodiuk, H.; Kanety, H.; Faust, D., *J. Org. Chem.* **1981**, *46*, 1666–1673.
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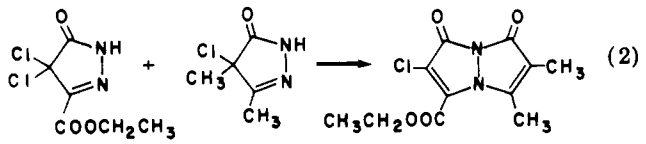
pyrazolinone **4b** (R = CH_3, R_1 = H) via the (carboethoxy)pyrazolinone **4a** (R = CH_3CH_2) (hydrolysis with 15% HCl, esterification with CH_3OH and HCl) roughly equivalent. *syn*-($COOCH_3$,Cl)B (**6d**; R = CH_3, R_1 = Cl) and *syn*-($COOCH_3$,Br)B (**6e**; R = CH_3, R_1 = Br) have been prepared in 30% yield.

The dibromopyrazolinone **5b**, prepared by bromination of the pyrazolinone with *N*-bromosuccinimide, gave *syn*-(COOEt,Br)B (**6b**) after treatment with base.

Diethyl 3-methyl-2-oxobutanedioate (ethyl ethoxalyl propionate, **3b**) is transformed into the bimane *syn*-(COOEt,CH_3)B (**6c**) via the pyrazolinone **4c** (R = CH_3CH_2, R_1 = CH_3) and 4-chloro-4-methyl-3-carboethoxypyrazolin-5-one (**5c**). The (carbomethoxy)pyrazolinone **4d** (R = CH_3, R_1 = CH_3), from the carboethoxy derivative, yields more bimane *syn*-($COOCH_3$,CH_3)B (**6f**; R = CH_3 R_1 = CH_3) than the ethyl ester. An X-ray crystallographic determination of structure confirms the assigned formula for **6f**.

The reaction of equivalent amounts of the two chloropyrazolinones, **5a** and 3,4-dimethyl-4-chloropyrazolin-5-one (**7**), with *N*,*N*-diisopropylethylamine gives a 25% yield of the "mixed" bimane *syn*-($COOCH_2CH_3$,Cl)(CH_3,CH_3)B (**8**) (eq 2).

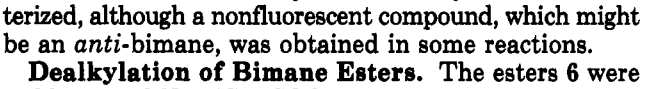


(2)

5a **7** **8**

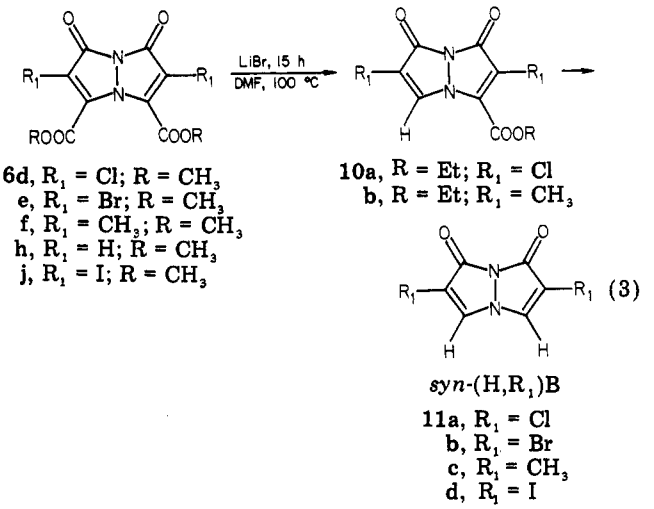
No *anti*-bis(carboalkoxy)bimane has yet been characterized, although a nonfluorescent compound, which might be an *anti*-bimane, was obtained in some reactions.

Dealkylation of Bimane Esters. The esters **6** were stable toward HBr/CH_3COOH at room temperature or at reflux. Although 15% HCl had no effect at room temperature, destruction of the bimane system (loss of fluorescence) occurred after 24 h at reflux. Trimethylsilyl iodide[4] caused a rapid loss of fluorescence. Lithium iodide or bromide in either dimethylformamide (DMF)[9,10] or CH_3CN reacted with the esters to give dealkylated products. The dicarboxylic acids **9** (R_1 = Cl or Br) were apparently unstable, and the products isolated were bimanes in which hydrogen had replaced the ester group at the β-position. Interrupting the reaction after some hours allowed the isolation of the "mixed" bimanes *syn*-(COOR,R_1)(H,R_1)B (**10**) in modest yields. The facile decarboxylation of the β-carboxylic acid provided an excellent route to the β-hydrogen compounds, *syn*-(H,R_1)B (**11**; R_1 = H, CH_3, Cl, Br, I). The conversion of *syn*-($COOCH_2CH_3$,Cl) (**6a**) to *syn*-(hydrogen,chloro)bimane [*syn*-(H,Cl)B (**11a**); R_1 = Cl] occurred via the monodealkylated, monodecarboxylated compound *syn*-(COOEt,Cl)(H,Cl)B (**10a**) (eq 3). Another intermediate product which was isolated in a short-term dealkylation reaction of a diester was *syn*-(COOEt,CH_3)(H,CH_3)B (**10b**). Dealkylation–decarboxylation of the monoester **8** with LiBr/DMF produces the "mixed" bimane *syn*-(H,Cl)-(CH_3,CH_3)B (**8a**).



9

syn-(COOH,R_1)B



6d, R_1 = Cl; R = CH_3
e, R_1 = Br; R = CH_3
f, R_1 = CH_3; R = CH_3
h, R_1 = H; R = CH_3
j, R_1 = I; R = CH_3

10a, R = Et; R_1 = Cl
b, R = Et; R_1 = CH_3

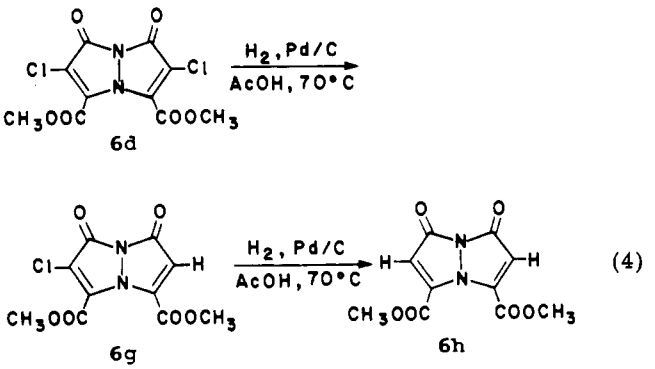
(3)

syn-(H,R_1)B

11a, R_1 = Cl
b, R_1 = Br
c, R_1 = CH_3
d, R_1 = I

In one case, that of *syn*-($COOCH_3$,CH_3)B (**6f**), the ester was sufficiently reactive so that the reaction could be carried out at around 60 °C in CH_3CN; the dicarboxylic acid **9** (R_1 = CH_3) was stable enough for isolation.

Chemical Properties of Bis(carboalkoxy)-*syn*-bimanes. Hydrogenation of *syn*-bimanes with R_1 = halogen over Pd/C in acetic acid at 70 °C leads to successive replacement of one or two halogens. The two possible products are easily separated from one another and the starting material by chromatography. Conversion of the dichloro bis ester **6d** via the "mixed" bimane *syn*-($COOCH_3$,Cl)($COOCH_3$,H)B (**6g**; R = CH_3, R_1 = Cl, R_1' = H) to *syn*-($COOCH_3$,H)B (**6h**; R = CH_3, R_1 = H) is illustrated in eq 4.

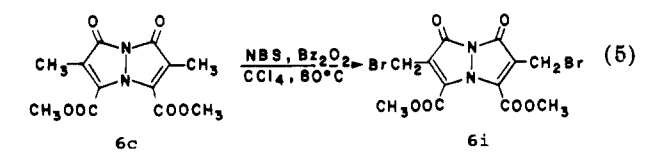


6d

(4)

6g **6h**

The dichloro bis ester **6a** is unreactive toward bromine. The dimethyl bis ester **6c** is recovered unchanged after attempted reaction with 1 or 2 equiv of bromine; a bis(bromomethyl) derivative (**6i**) is obtained by reaction with *N*-bromosuccinimide and benzoyl peroxide in CCl_4 (eq 5).



(5)

6c **6i**

Halogenation of the bis(carboalkoxy)-substituted bimane ring is successful in the cases in which R_1 = H, and reaction with iodine monochloride is the best route to the iodobimane derivatives, as in the conversion of **6h** to **6j** (R = CH_3, R_1 = I).

The *syn*-(COOR,Cl)B (**6d**) reacted rapidly with C_6H_5SLi/THF at room temperature to produce the bis-

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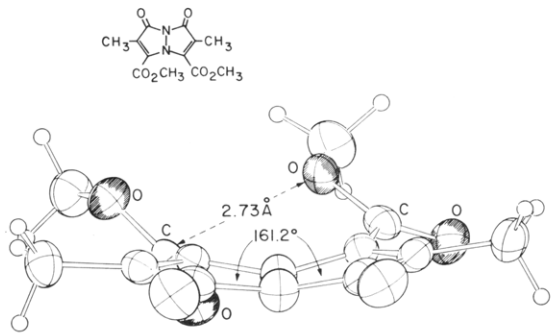
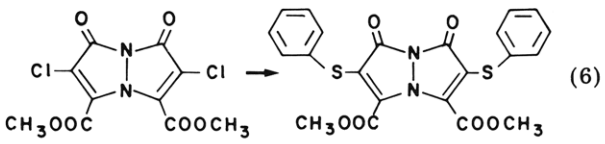


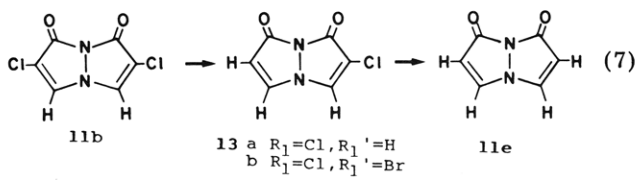
Figure 1. Molecular structure of *syn*-($COOCH_3$,CH_3)B.

(phenylthio) derivative *syn*-($COOCH_3$,SC_6H_5)B (**12**), which exhibited a beautiful carmine red fluorescence on the TLC plate. The reaction is shown in eq 6.



6d 12 (6)

Chemical Properties of β-Hydrogen *syn*-Bimanes. Hydrogenation of either *syn*-(H,Cl)B (**11a**) or *syn*-(H,Br)B (**11b**) over Pd/C in AcOH produced the parent compound of the 9,10-dioxa-*syn*-bimane series, *syn*-(H,H)B (**11e**, R_1 = H). The starting material and the two products differ in chromatographic mobility (TLC), and, in addition, the fluorescence of the three materials is strikingly different. *syn*-(H,Cl)B exhibits a blue fluorescence, the "mixed" bimane *syn*-(H,Cl)(H,H)B (**13a**; R_1 = Cl,R_1' = H) a blue-violet fluorescence, a *syn*-(H,H)B a beautiful deep violet fluorescence. A sequence is shown in eq 7 for *syn*-(H,Cl)B as a reactant.

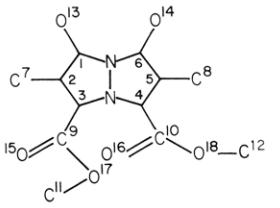


11b 13 a R_1=Cl, R_1'=H; b R_1=Cl, R_1'=Br 11e (7)

Bromination of the "mixed" bimane *syn*-(H,Cl)(H,H)B (**13**) produced the bromo–chloro bimane *syn*-(H,Cl)(H,-Br)B (**13b**; R_1 = Cl, R_1' = Br). Iodination of *syn*-(H,H)B with ICl leads to the bis-iodo derivative, *syn*-(H,I)B (**11d**).

X-ray Crystallographic Structure of *syn*-($COOH_3$,CH_3)B. The structure of *syn*-($COOCH_3$,CH_3)B (**6f**) was determined by X-ray crystallography to confirm assignment of the syn arrangement, made on the basis of the strong fluorescence exhibited by **6f** and all related molecules. The overall molecular structure is shown in Figure 1; detailed geometric data are given in Table I. The bimane system was found to be nonplanar, with a dihedral angle α = 161.2° between the mean planes of the two five-membered rings. This conformation is intermediate between those previously reported, which vary from planar (or nearly planar) to bent (α = 140°).[11,12] The significant deviation from planarity in the dimethyl ester may result from a fairly strong intramolecular O···C=O interaction involving the two ester groups. This is suggested by a rather short nonbonding distance $O^{17}\cdots C^{10}$ of 2.728 (5) Å (the $O^{17}\cdots C^{10}=O^{16}$ approach angle is 84.4°) and a marked

Table I. Bond Length and Bond Angles in *syn*-($COOCH_3$,CH_3)B



atoms	distance, Å	atoms	distance, Å
C2-O13	1.221 (5)	C6-O14	1.215 (5)
C1-N	1.419 (6)	C6-N	1.405 (6)
C1-C2	1.452 (6)	C6-O5	1.455 (5)
C2-C7	1.487 (6)	C5-C8	1.476 (6)
C2-C3	1.353 (5)	C5-C4	1.355 (5)
C3-N	1.382 (5)	C4-N	1.396 (5)
C3-C9	1.491 (5)	C4-C10	1.479 (5)
C9-O15	1.201 (6)	C10-O16	1.201 (6)
C9-O17	1.313 (5)	C10-O18	1.320 (6)
C11-O17	1.457 (5)	C12-O18	1.464 (5)
N-N	1.390 (4)		
atoms	**angle, deg**	**atoms**	**angle, deg**
N-C1-C2	105.3 (3)	N-C6-C5	104.9 (3)
N-C1-O13	123.5 (1)	N-C6-O14	124.5 (4)
O13-C1-C2	131.2 (4)	O14-C6-C5	130.5 (4)
C1-C2-C3	107.4 (4)	C6-C5-C4	108.2 (4)
C1-C2-C7	123.4 (4)	C6-C5-C8	122.2 (4)
C3-C2-C7	129.1 (4)	C4-C5-C8	129.5 (3)
C9-O17-C11	116.6 (3)	C5-C4-N	109.9 (3)
C2-C3-N	110.9 (3)	C5-C4-C10	128.6 (4)
C2-C3-C9	127.5 (4)	N-C4-C10	120.2 (3)
N-C3-C9	121.6 (3)	C4-C10-O18	110.3 (4)
C3-C9-O17	110.7 (4)	C4-C10-O16	123.8 (4)
C3-C9-O15	122.5 (4)	O16-C10-O18	125.7 (3)
O15-C9-O17	126.7 (4)	C10-C18-C12	116.7 (4)
C1-N-C6	136.5 (4)	C3-N-C4	139.8 (4)
C1-N-N	108.9 (3)	C3-N-N	107.3 (3)
C6-N-N	109.7 (3)	C4-N-N	107.2 (3)

out-of-plane distortion of the carbonyl carbon atom toward O^{17} (C^{10} is displaced about 0.03 Å from the plane defined by the three atoms bonded to it).[13] Each carbomethoxy group is twisted by a different amount with respect to the plane of the adjacent ring (Figure 1), with the dihedral angle between their mean planes being 42°. Crystal forces appear to have little influence on the molecular geometry, as all intermolecular distances are greater than or approximately equal to the sums of the van der Waals radii. The distribution of bond distances and angles in *syn*-($COOCH_3$,CH_3)B resembles those observed in other dioxabimane structures and reflects some π electron delocalization.[11,12]

Spectroscopic Properties of *syn*-Bimanes. The UV–visible and fluorescence maxima for the *syn*-bimanes are summarized in Table II. A COOR group at the β-position and/or halogen at the α-position moves the absorption and emission maxima to longer wavelengths than those found for molecules with a β-hydrogen substituent. The compound which shows the longest wavelength absorption maximum of those with both ester and halogen groups is *syn*-($COOCH_2CH_3$,I)B, with λ_{max} at 423 nm (ϵ 12500); the shortest long-wavelength absorption maximum is found for *syn*-(H,H)B with λ_{max} at 368 nm (ϵ 6200). The positions of the emission maxima vary accordingly, with 500 nm (ϕ_F 0.15) for the iodo derivative and 398 nm (ϕ_F 1.0) for *syn*-(H,H)B. The longest wavelength maximum thus far found for any *syn*-bimane is that for *syn*-

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(12) Goldberg, I. *Cryst. Struct. Commun.* **1980**, *9*, 329.
(13) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *Acta Crystallogr., Sect. B* **1974**, *B30*, 1517.

Table II. Ultraviolet-Visible Absorption and Emission Maxima for 9,10-Dioxa-*syn*-bimanes in Acetonitrile

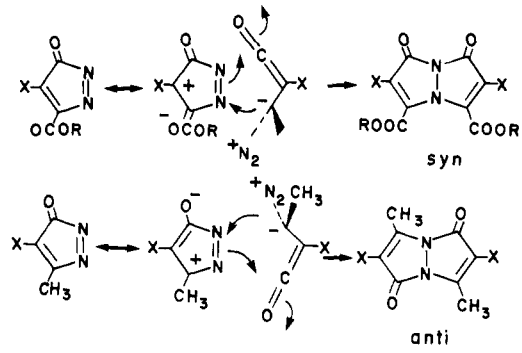
R_2, R_1 for *syn*-(R_2,R_1)B	absorption, λ_{max}, nm (ϵ_{max})[a]	emission, λ_{max}, nm (ϕ_F)
H, H	368 (6200), 218 (7600)	398, 415 sh (1.0)
H, CH_3	373 (7500), 252 (6000), 226 (11700)	436, 460 sh (0.60)
H, Cl	389 (8100), 231 (13800)	443, 465 sh (0.40)
H, Br	392 (8700), 235 (8200)	445, 465 sh (0.45)
H, I	410 (13700), 250 (6400), 226 (7200)	454, 480 sh (0.45)
H, Cl; H, H	380 (5800), 223 (6400)	422 (0.92)
H, Br; H, Cl	387 (6900), 230 (6900)	444 (0.62)
H, Cl; CH_3, CH_3	376 (4200), 230 (5800)	443, 460 sh (0.76)
COOEt, Cl; CH_3, CH_3	375 (7500), 230 (13400)	441, 460 sh (0.60)
COOEt, CH_3	390 (4700), 252 (9800)	465, 500 sh (0.33)
$COOCH_3$, CH_3	390 (4900), 253 (9500)	465, 500 sh (0.50)
COOH, CH_3[b]	393 (4100), 243 (11000)	520 (0.12)
COOEt, H	385 (6100), 246 (8400)	430, 450 sh (0.50)
$COOCH_3$, H	385 (6200), 246 (9000)	430, 455 sh (0.65)
COOEt, Cl; H, Cl	409 (5500), 232 (7600)	462, 490 sh (0.15)
COOEt, Cl	403 (6100), 257 (10300)	480, 505 sh (0.10)
$COOCH_3$, Cl	401 (6300), 257 (10100)	481, 505 sh (0.20)
COOEt, Br	409 (7000), 260 (11000)	470, 500 sh (0.15)
COOEt, I	423 (12500), 273 (7600), 212 (12000)	500 (0.15)
$COOCH_3$, I	415 (13000), 273 (12700), 212 (17300)	490 (0.25)
COOEt, SC_6H_5	445 (3300), 245 (19000)	590 (0.027)

[a] Shoulders occur in many of the absorption spectra. These are recorded in the appropriate section of the Experimental Section. [b] In water.

($COOCH_2CH_3$,SC_6H_5)B (**12**) at 445 nm (ϵ 3300). Although the quantum yield of fluorescence is low in solution (λ_{max} 590 nm (dioxane)) for **12**, a carmine red fluorescence is easily seen on TLC plates. Most measurements were done with acetonitrile solutions.

^{1}H NMR Spectra of *syn*-Bimanes. The chemical shifts for the hydrogens of the alkyl groups are at somewhat lower fields than those for an alkyl benzoate (4.02 vs. 3.88 ppm in the case of CH_3). The chemical shifts of the hydrogens directly attached to the bimane ring at the α-position are similar to those already reported (5.65 ppm for *syn*-(H,H)B) but are shifted to lower field in compounds with an ester group at the β-position (5.98–6.13 ppm). The most interesting chemical shifts are those for the β-hydrogens directly attached to the bimane ring, in which the chemical shift varies from 7.52 to 8.21 ppm, depending upon the nature of the other substituents. The hydrogens of *syn*-(H,H)B split one another, the coupling constant being 4 Hz. The β-hydrogens in the "mixed" bimane *syn*-(H,Cl)(H,Br)B appear at slightly different positions, 7.95 and 7.98 ppm, exactly as might have been expected from the two symmetrical compounds *syn*-(H,Br)B (7.95 ppm) and *syn*-(H,Cl)B (7.98 ppm).

Scheme I



Infrared and Mass Spectra. The infrared spectra show ring carbonyl bands and ester carbonyl groups at somewhat shorter wavelengths. IR maxima are listed in the Experimental Section. Dramatic changes in infrared spectra are observed with changes in the degree of organization in the solid state for *syn*-(H,X)B; these will be communicated separately.[14] Mass spectra were obtained for all bimanes; parent peaks were observed in all cases which corresponded to the expected molecular weight for the compound in question, except for the bis(bromomethyl) derivative **6i**, with a peak corresponding to the loss of two bromine atoms.

Discussion

Bimanes bearing one or two hydrogens at the β-position have now been prepared from pyrazolinones carrying a removable carboalkoxy group in the 3-position. The striking changes in the ultraviolet–visible and near-IR absorption spectra of one of the products, *syn*-(H,Cl)B (**11a**), in thin films[14] and an X-ray crystallographic study of the structure of *syn*-(H,Cl)B (confirmation of the structure)[15] have been communicated separately.

The bimane synthesis (for which a mechanism has been proposed previously[4]) succeeds with halopyrazolinones in which a carboalkoxy group is conjugated with the pyrazolin-5-one ring. Apparently, a 3-substituent into which charge can be delocalized does not decrease the reactivities of the proposed diazacyclopentadienone and diazo intermediates (see Scheme I). Bimanes have been prepared from pyrazolinones bearing phenyl groups at the 3-position; no other pyrazolinone with a conjugating substituent at the 3-position has been investigated.

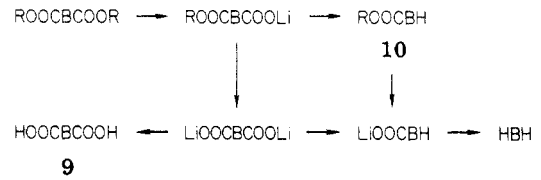
Only syn derivatives have been isolated and characterized from the reaction of base with 4-halo-3-(carboalkoxy)pyrazolinones, in yields as high as 50%. In some reactions, materials isolated in small quantities from late fractions (i.e., an ususual position of elution for *anti*-bimanes) have properties which suggest that these might be *anti*-bimanes. The *syn*-carboalkoxy derivatives are moderately sensitive to base; the kinetics of the ring-opening reaction[16] indicate that *anti*-bimanes are 2–3 times as reactive toward hydroxide ion as the corresponding syn derivatives. Attempted purification of the new compounds results in considerable decomposition. It is thus conceivable that anti compounds were formed and then de-

(14) Part 11: Kosower, E. M.; Hermolin, J.; Ben-Shoshan, M.; Faust, D., *J. Org. Chem.* **1981**, *46*, 4578.
(15) Goldberg, I.; Kosower, E. M. *J. Phys. Chem.* **1982**, in press.
(16) Kanety, H.; Pazhenchevsky, B.; Kosower, E. M., in preparation for publication.

stroyed during the reaction.

The most suitable base for the (carboalkoxy)bimane synthesis is *N,N*-diisopropylethylamine which yields anti derivatives with 3-alkylpyrazolinones. We suggest that the electron-withdrawing carboalkoxy group favors nucleophilic addition at the diazene nitrogen (β) farthest from the carbonyl group; an electron-supplying alkyl group at the 3-position favors anion addition at the diazene nitrogen (α) next to the carbonyl. The relationship of the negative charge introduced (by the nucleophilic addition) into the diazene system and the negative charge already present in the substrate molecule in the transition state is indicated in Scheme I by resonance forms for the intermediate diazacyclopentadienone. For the heterogeneous reaction of the halopyrazolinones with wet potassium carbonate, from which *syn*-bimanes are the major product, binding of the basic oxygen of the carbonyl to a potassium ion on the surface may block the approach of the nucleophile to the "favored" (α) diazene nitrogen, and reaction at the β-nitrogen predominates.

Decarboxylation is the critical step in the formation of β-hydrogen-substituted bimanes. The dealkylation–decarboxylation reactions are summarized in eq 8.



(8)

Utilizing the reactions illustrated in eq 8, a dicarboxylic acid (**9**) and monocarboalkoxy bimanes (**10**) have been isolated. As expected, loss of the second carbon dioxide is slower than that of the first. The decarboxylation of bimane β-carboxylic acids is quite facile (the stabilities of the carboxylate derivatives are reminiscent of those of 1-alkylpyridinium-2-carboxylate betaines[17]) and probably proceeds by a decarboxylation–protonation sequence (eq 9; cf. discussion by Noto[18]).

$$BCOO^- \rightarrow B^- \xrightarrow{H^+} BH \qquad (9)$$

The decarboxylation mechanism (eq 9) implies an acidic β-position; in NMR spectra, the β-hydrogen signals are found at lower fields (7.52–8.21 ppm) than the α-hydrogens (5.42–6.13 ppm). The chemical shift for the β-hydrogen in δ-pyrone, a conjugated system similar to *syn*-(H,H)B (**11e**), is 8.05 ppm.[19] The decarboxylation of the γ-pyrone-β-carboxylic acid is reported as facile (Cu, 160 °C),[20] although not as rapid as that of a bimane-β-carboxylic acid.

The ^{1}H NMR spectrum of *syn*-(H,H)B (**11e**) is beautifully simple, the two hydrogens exhibiting doublet signals at 5.60 and 7.76 ppm, with a splitting of 4 Hz. The pK_a of the bimanedicarboxylic acid **9** ($R_1 = CH_3$) is 2.3, reflecting the electron-withdrawing character of the bimane ring at the β-position.

Thiophenoxide ion attacks the α-position of *syn*-($COOCH_2CH_3$,Cl)B (**6a**) to give under rather mild conditions *syn*-($COOCH_2CH_3$,SC_6H_5)B (eq 6).

The (carboalkoxy)bimanes, especially the bis(carboalkoxy)bimanes, are characterized by a beautiful, bright yellow appearance and an obvious strong fluorescence. The β-hydrogen bimanes are usually strongly yellow in the crystalline form. Comparison of the absorption and fluorescence data given in Table II for solutions indicates that a greater difference in color between the crystals of bimanes with a β-carboalkoxy group and those with a hydrogen in the β-position might have been expected. It turns out that the absorption bands of the β-hydrogen bimanes are shifted to longer wavelengths in the crystal due to intermolecular interactions as the result of alterations in the organization of the solid state.[14,15]

Absorption and fluorescence maxima of bimanes are influenced by substituents,[4] and the parent 9,10-dioxa-*syn*-bimane, *syn*-(H,H)B, provides a useful reference point. In CH_3CN, *syn*-(H,H)B has an absorption maximum at 368 nm; two β-carboalkoxy groups shift the absorption maximum to 385 nm. Halogen at the α-position also has a large effect, *syn*-(H,Cl)B having a maximum at 389 nm. Replacing the chlorine with bromine [*syn*-(H,Br)B] shifts the maximum further to 392 nm, and with iodine [Syn-(H,I)B] the λ_{max} is at 410 nm.

A "β-alkyl group effect", a shift of the absorption maximum to shorter wavelengths with the replacement of a β-hydrogen by an alkyl group, can be recognized. The classical Woodward rules for absorption of α,β-unsaturated carbonyl compounds suggest precisely the opposite result. The λ_{max} and the changes with respect to *syn*-(H,H)B (368 nm) are as follows: α-CH_3, *syn*-(H,CH_3)B, 373 nm (+5 nm, ΔE_T = 1.0 kcal/mol); β-CH_3, *syn*-(CH_3,H)B, 361 nm (−7 nm, ΔE_T = 1.5 kcal/mol); α- and β-CH_3, *syn*-(CH_3,CH_3)B, 368 nm (no shift).

The compounds having both β-carboalkoxy groups and α-substituents which are polarizable (iodo or phenylthio) absorb at the longest wavelengths yet found for 9,10-dioxa-*syn*-bimanes. *syn*-($COOCH_3$,I)B and *syn*-($COOCH_2CH_3$,SC_6H_5)B have absorption maxima in CH_3CN at 415 and 445 nm, respectively.

The shortest wavelength fluorescence emission yet found for 9,10-dioxa-*syn*-bimanes is that for the parent compound of the series. *syn*-(H,H)B, at 398 nm in CH_3CN. The "β-alkyl group effect" is less apparent in emission than in absorption, since all alkyl group substituents shift the emission maximum to longer wavelengths. However, a β-alkyl group is clearly much less effective in this regard than an α-methyl substituent, as seen by the following comparison with *syn*-(H,H)B (398 nm) for a CH_3CN solution: *syn*-(CH_3,H)B, 402 nm (+4 nm); *syn*-(H,CH_3)B, 436 nm (+38 nm); *syn*-(CH_3,CH_3)B, 444 nm (+46 nm).

A β-carboalkoxy group shifts the fluorescence emission maximum to longer wavelengths [398 → 430 nm for *syn*-($COOCH_3$,H)B]; various α-substituents move the maximum to longer wavelengths (in nanometers from 430 nm: CH_3, +35; Cl, +51; Br, +40; I, +60; SC_6H_5, +90).

The quantum yields of fluorescence are generally high, reaching close to 1.0 for *syn*-(H,H)B in CH_3CN and ranging from 0.10 to 0.65 for most of the other compounds. One compound has a rather low quantum yields of fluorescence, *syn*-($COOCH_2CH_3$,SC_6H_5)B (0.027). The solvent effect on the quantum yield of fluorescence was examined only for *syn*-($COOCH_2CH_3$,CH_3)B and found to change from 0.83 in cyclohexane to 0.33 in CH_3CN and 0.03 in H_2O. The carbomethoxy compounds invariably have higher quantum yields of fluorescence than the carboethoxy derivatives. This difference may imply that the alkyl group of the ester has some influence on the conjugation between the two rings. The structure of the *syn*-($COOCH_3$,CH_3)B determined by X-ray crystallography indicates that the two rings are not coplanar in the crystal; other considerations, discussed in great detail in connection with the photo-

(17) Kosower, E. M.; Patton, J. W. *J. Org. Chem.* **1961**, *26*, 1318.
(18) Noto, R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1627.
(19) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; p 191.
(20) Katritsky, A. R.; Lagowski, J. M., "Heterocyclic Chemistry"; Methuen: London, 1960; p 98.

physical behavior of the bimanes, also suggest that the *syn*-bimanes are not completely planar in solution. We may thus infer that the carboethoxy compounds are somewhat more bent than the carbomethoxy compounds in solution.

Experimental Section

The following instruments were used for experimental measurements: Cary Model 17 spectrophotometer (UV–vis spectra), JEOL 60 (60 MHz), Varian EM-360, and Bruker WH-90 (NMR spectra), Hitachi Perkin-Elmer MPF-4 fluorescence spectrometer, Perkin-Elmer Model 257 (IR spectra), Du Pont 21-491B mass spectrometer, Cahn Electrobalance (for <2 mg weights), Enraf-Nonius CAD 4 X-ray diffractometer (X-ray structural data).

3-(Carboethoxy)-4,4-dichloro-2-pyrazolin-5-one (5a). Surfuric acid (4.9 g, 0.05 mol) was added dropwise to a suspension of sodium diethyl oxalacetate (Fluka; 10.5 g, 0.05 mol) in ether (500 mL), the Na_2SO_4 was filtered off after the addition, excess acid was removed by treatment with saturated $KHCO_3$, and the ether was removed to leave diethyl oxalacetate (**3a**; 9.3 g, 0.05 mol). Hydrazine hydrate (2.5 g, 0.05 mol) in ethanol (5 mL) was added dropwise to the ester in ethanol (40 mL), the mixture refluxed for 0.5 h, the solvent evaporated, and the residue crystallized from water to yield 3-(carboethoxy)-2-pyrazolin-5-one (**4a**): 5.4 g (70%); mp 175–178 °C (lit.[21] mp 179 °C); ^1H NMR ($CDCl_3$) 1.51 (t, 3 H), 4.56 (q, 2 H), 9.87 (br s, 1 H) ppm; IR (KBr) 3340, 3000, 1706, 1500 cm^{-1}; mass spectrum, *m/e* 156 (M^+).

Chlorine was passed through a stirred suspension of **4a** (7.8 g, 0.05 mol) in CH_2Cl_2 (25 mL) until a clear greenish solution had been obtained. Excess chlorine and HCl were removed with a stream of air, and the solvent was evaporated to yield the product as a colorless oil which solidified at room temperature: 11.0 g (98%); mp 83–85 °C; IR (KBr) 3260, 1775, 1685, 1560, 1475 cm^{-1}; ^1H NMR ($CDCl_3$) 1.50 (t, 3 H), 4.60 (q, 2 H), 9.85 (br s, 1 H, lost with D_2O) ppm; UV (CH_3CN): λ 295 nm (ϵ_{max} 6500); mass spectrum, *m/e* 224 (M^+).

3-(Carboethoxy)-4,4-dibromo-2-pyrazolin-5-one (5b). *N*-Bromosuccinimide (1.8 g, 0.1 mol) was added over 5 min to a suspension of **4a** (7.8 g, 0.05 mol) in CH_2Cl_2 (250 mL). After a clear orange solution had been obtained, the solvent was removed and the oily residue triturated several times with CCl_4, yielding after removal of the CCl_4 a solid: mp 89–90 °C; IR and ^1H NMR spectra were similar to those of **5a**; mass spectrum, *m/e* 314 (M^+).

3-(Carbomethoxy)-4,4-dichloro-2-pyrazolin-5-one (5e). The carboethoxy compound **4a** was converted in 95% yield to 3-(carbomethoxy)-2-pyrazolin-5-one (**4b**) by refluxing in 15% HCl (6 mL/g) for 15 h, removing the solvent, refluxing the acid thus formed in CH_3OH saturated with HCl for 15 h, and evaporating the solvent to yield **4b** as an off-white solid: mp 190–191 °C (lit.[21] yellowish crystals, mp 226.5–227.5 °C); mass spectrum, *m/e* 142 (M^+); IR (KBr) 3350, 3000, 1710, 1500 cm^{-1}; ^1H NMR (Me_2SO-d_6) 3.70 (s, 3 H), 4.56 (s, 2 H) ppm.

Condensation Procedure. A mixture of dimethyl oxalate (50.0 g, 0.43 mol) and ethyl acetate (37.0 g, 0.42 mol) in dry ether (400 mL) was added dropwise to a heated suspension of clean sodium hydride (ca. 12 g) in dry tetrahydrofuran (100 mL) with mechanical stirring. After a yellowish color appeared, the heating was discontinued (30–60 min), the addition completed (2–3 h), and stirring continued for 12 h. The mixture was cooled with ice, a solution of H_2SO_4 in ether added, the solution filtered, and the solvent evaporated to yield an oil (55 g) containing mostly ethyl methoxalylacetate. The crude ester was refluxed with hydrazine (14 g) in methanol (300 mL), the solution filtered while hot (the pyrazolinone derived from ethyl acetoacetate is not soluble), and the methanol evaporated to yield the 3-(carbomethoxy)-2-pyrazolin-5-one (30 g) in 52% yield overall.

Chlorination of **4b** was carried out as described for **4a** to yield **5e** as a solid product: 100% yield; mp 87–90 °C; IR (KBr) 3250, 1755, 1745, 1545 cm^{-1}; ^1H NMR ($CDCl_3$) 3.98 (s, 3 H), 9.70 (br s, 1 H, lost with D_2O) ppm; mass spectrum, *m/e* 210 (M^+).

3-(Carbomethoxy)-4,4-dibromo-2-pyrazolin-5-one (5f). Bromination of **4b** was carried out as described for **4a** to yield **5f** as a solid: mp 92–94 °C; IR (KBr) 3250, 1755, 1550, 1470 cm^{-1}; ^1H NMR like that for **5e**; mass spectrum, *m/e* 300 (M^+).

3-(Carboethoxy)-4-chloro-4-methyl-2-pyrazolin-5-one (5c). Diethyl 3-methyl-2-oxobutanedioate (ethyl ethoxalyl propionate, **3b**) was synthesized from ethyl propionate and diethyl oxalate by a modification of the published procedure[22] using NaOEt made from molar equivalents of NaH and EtOH in dry Et_2O. The pyrazolinone **4c** was obtained as described for **4a** in 70% yield after crystallization from EtOH–H_2O (3:1) as a white solid: mp 169 °C; IR (KBr) 3310 (br), 1710, 1600, 1500 cm^{-1}; ^1H NMR (Me_2SO-d_6) 1.20 (t, 3 H), 1.90 (s, 3 H), 4.17 (q, 2 H), 8.32 (s, 1 H); mass spectrum, *m/e* 170 (M^+). Chlorination was effected as described for **4a** to yield **5c** as a colorless oil which solidified at room temperature: 9.0 g (90%); mp 90–92 °C; IR ($CHCl_3$) 3360, 2980, 1770, 1750, 1720, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) 1.45 (t, 3 H), 1.99 (s, 3 H), 4.45 (q, 2 H), 3.31 (s, 1 H) ppm; mass spectrum, *m/e* 205 (M^+).

3-(Carbomethoxy)-4-chloro-4-methyl-2-pyrazolin-5-one (5d). Hydrolysis of the ethyl ester was carried out as in the case of **4a** except that CH_3CN was added at the end, the solvent evaporated, and the solid residue triturated with CH_3CN prior to filtration. The acid was a white solid [mp 320 °C; IR (KBr) 3410, 3320 (br), 1670 cm^{-1}], was converted to the methyl ester (cf. procedure for **4b**), and was chlorinated as noted for **4a** to give **5d** in high yield as a crystalline solid: mp 94 °C; IR ($CHCl_3$) 3300, 2990, 1750, 1720, 1560 cm^{-1}; ^1H NMR ($CDCl_3$) 1.98 (s, 3 H), 3.50 (s, 1 H), 3.95 (s, 3 H) ppm; mass spectrum, *m/e* 190 (M^+).

9,10-Dioxa-*syn*-(carboalkoxy,halo or methyl)bimanes 6a–f. *N,N*-Diisopropylethylamine (0.64 g, 0.05 mmol) in CH_2Cl_2 (5 mL) was added over 30 min with stirring to 3-(carboethoxy)-4,4-dichloro-2-pyrazolin-5-one (**5a**; 1.12 g, 5.0 mmol) in CH_2Cl_2 (10 mL) cooled to −10 °C. The reaction mixture became red-black and exhibited a strong green fluorescence. After the addition was complete, the solvent was evaporated and the residue quickly chromatographed on silica gel (Merck 7754) with CH_2Cl_2 as the eluant. A yellow, strongly fluorescent fraction provided the product (**6a**) as a yellow solid, 175 mg (10%). Reactions involving smaller quantities gave yields up to 30%. Application of the same procedure to the dibromo compound **5b** gave 15% yields of **6b**. Use of the methyl ester **5d** in place of the ethyl ester gave **6d** as a product in 30% yield.

9,10-Dioxa-*syn*-(carboethoxy,chloro)bimane [*syn*-($COOCH_3$,Cl)B, 6a]: yellow crystals (from *i*-PrOH–Et_2O); mp 107–110 °C; IR(KBr): 3000, 2950, 1755, 1625, 1550, 1470, 1420, 1400, 1350, 1310, 1230, 1180, 1130, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) 1.44 (t, 3 H), 4.45 (q, 2 H); UV (CH_3CN) λ 403 nm (ϵ_{max} 6080), 258 (10 300); fluorescence (CH_3CN) 465 nm, 490 (sh), ϕ_F 0.1; mass spectrum, mass 348 (M^+). Anal. Calcd for $C_{12}H_{10}N_2O_6Cl_2$: C, 41.29; H, 2.86; N, 8.02. Found: C, 41.21; H, 2.33; N, 7.86.

9,10-Dioxa-*syn*-(carbomethoxy,chloro)bimane [*syn*-$COOCH_3$,Cl)B, 6d]: yellow crystals (from *i*-PrOH); mp 145 °C; IR (KBr) 3000, 1785, 1740, 1710, 1435, 1370, 1175, 1140, 905 cm^{-1}; ^1H NMR ($CDCl_3$) 4.02 (s) ppm; UV (CH_3CN) λ 401 nm (ϵ_{max} 6300), 257 (10 100); fluorescence (CH_3CN) 481 nm, 505 (sh), ϕ_F 0.2; mass spectrum, *m/e* 320 (M^+).

9,10-Dioxa-*syn*-(carboethoxy,bromo)bimane [*syn*-($COOCH_2CH_3$,Br)B, 6b]: yellow crystals (from *i*-PrOH–Et_2O); mp 120–122 °C; IR; (KBr) 3000, 1780, 1745, 1730, 1710, 1590, 1550, 1450, 1390, 1380, 1345, 1295, 1270, 1210, 1160, 1125, 1100, 1040, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) 1.40 (t, 3 H), 4.45 (q, 2 H). UV (CH_3CN) 409 nm (ϵ_{max} 7000), 260 (11 000); fluorescence (CH_3CN) 470 nm, 500 (sh), ϕ_F 0.15. Anal. Calcd for $C_{12}H_{10}N_2O_6Br_2$: C, 32.91; H, 2.28; N, 6.39. Found: C, 32.93; H, 2.02; N, 6.39.

Procedures for the *syn*-(carboethoxy,methyl)bimane (**6c**) (20% yield) and *syn*-(carbomethoxy,methyl)bimane (**6f**; 38% yield) were carried out as described above for the preparation of **6a** except that the reaction mixtures were maintained at 0 °C instead of −10 °C during the addition of the base.

9,10-Dioxa-*syn*-(carboethoxy,methyl)bimane [*syn*-($COOCH_2CH_3$,CH_3)B, 6c]: yellow crystals (from *i*-PrOH); mp 82 °C; IR ($CHCl_3$) 2990, 1760, 1730, 1680, 1600, 1550, 1380, 1230, 1130, 1060, 1010, 860 cm^{-1}; ^1H NMR ($CDCl_3$) 1.45 (t, 3 H), 2.05

(21) von Rothenberg, R. *Ber. Dtsch. Chem. Ges.* **1892**, *28*, 43.

(22) Corson, B. B.; Benson, W. L. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 272.

(s, 3 H), 4.50 (q, 2 H) ppm; UV (CH_3CN) λ 390 nm (ϵ_{max} 4700), 252 (9800); fluorescence (CH_3CN) 465 nm, 500 (sh), ϕ_F 0.33; mass spectrum, m/e 303 (M^+).

9,10-Dioxa-*syn*-(carbomethoxy,methyl)bimane [*syn*-($COOCH_3$,CH_3)B, 6f]: yellow crystals (from *i*-PrOH); mp 85 °C; IR ($CHCl_3$) 3000, 2950, 1770, 1740, 1685, 1600, 1440, 1380, 1240, 1190, 1120, 1060, 960, 860, 810 cm^{-1}; ^1H NMR ($CDCl_3$) 2.06 (s, 3 H), 3.95 (s, 3 H) ppm; UV (CH_3CN) λ 390 nm (ϵ_{max} 4900), 253 (9500); fluorescence (CH_3CN) 465 nm, 500 (sh), ϕ_F 0.50; mass spectrum, m/e 280 (M^+).

Crystal Structure Analysis of 6f. Crystals were obtained by slow cooling of an isopropyl alcohol solution. Accurate cell parameters were determined by least-squares refinement of the setting angles of 20 reflections automatically centered on an Enraf-Nonius CAD 4 diffractometer.

Crystal data: $C_{12}H_{12}N_2O_4$, M_r = 248.2; monoclinic; a = 9.668 (2), b = 18.009 (1), c = 7.985 (1) Å; β = 112.77 (2)°; V = 1282.0 $Å^3$; Z = 4; d_c = 1.286 g cm^{-3}; $F(000)$ = 520; Cu Kα radiation, λ_{mean} = 1.5418 Å; μ(Cu Kα) = 7.4 cm^{-1}; space group $P2_1/c$.

The intensities of all reflections with $1 < 2\theta < 70°$ were measured on a CAD-4 diffractometer by using Ni-filtered radiation and an ω–2θ scan technique (scan width 0.9 + 0.15 tan θ). Three intensity control reflections were frequently monitored and showed no decay of the crystal. Data were corrected for Lorentz and polarization effects, but not for absorption or secondary extinction. Of the 2010 unique observations, 683 reflections had intensities below a threshold of $3\sigma(I)$ and were given zero weight in refinement calculations.

The structure was solved by direct methods using the MULTAN 74 system of computer programs.[23] Refinement was carried out by full-matrix least-squares methods including the positional and anisotropic thermal parameters for the nonhydrogen atoms. All hydrogen atom positions were obtained from difference maps and given a uniform isotropic thermal parameter of U = 0.05 $Å^2$ but were not refined. The least-squares function which was minimized was $\sum W(\Delta F)^2$ with $w = 1/\sigma^2(F)$. The final discrepancy index is R = 0.059 for 1322 observations; the five strongest low-angle reflections (110, 020, $\bar{1}21$, $\bar{2}02$, $\bar{2}12$) which appear to suffer from secondary extinction were omitted in the last cycle of refinement. A final difference map was featureless. Positional and thermal atomic parameters are available as supplementary material.

9,10-Dioxa-*syn*-(carboethoxy,chloro)(methyl,methyl)bimane [*syn*-($COOCH_2CH_3$,Cl)(CH_3,CH_3)B, 8]. *N,N*-Diisopropylethylamine (1.28 g, 10 mmol) in CH_2Cl_2 (5 mL) was added over 15 min to a cooled (0 °C) solution of dichloropyrazolinone **5a** (1.12 g, 5.0 mmol) and dimethylchloropyrazolinone **5c** (0.73 g, 5.0 mmol) in CH_2Cl_2 (10 mL). The solvent was then evaporated and the residue chromatographed on silica gel (eluant CH_2Cl_2) to yield *syn*-($COOCH_2CH_3$,Cl)(CH_3,CH_3)B (**8**) (250 mg, 20%), *syn*-(CH_3,CH_3)B (370 mg, 35%), and *syn*-($COOCH_2CH_3$,Cl)B (**6a**; 70 mg, 4%): yellow crystals (from *i*-PrOH); mp 185 °C; IR (KBr) 3000, 1765, 1735, 1705, 1630, 1555, 1470, 1400, 1355, 1260, 1230, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) 1.41 (t, 3 H), 1.83 (s, 3 H), 2.25 (s, 3 H), 4.48 (q, 2 H) ppm; UV (CH_3CN) λ 375 nm (ϵ_{max} 7500), 250 (sh, 6400), 230 (13 400); fluorescence (CH_3CN) 441 nm, 460 (sh) ϕ_F 0.60; mass spectrum, m/e 270 (M^+).

β-Hydrogen Bimanes 10 and 11 through Decarboxylation–Dealkylation. Procedure A. *syn*-($COOCH_3$,Cl)B (**6d**; 320 mg, 1 mmol) and LiBr (1.0 g, 11.5 mmol) in CH_3CN (10 mL) were refluxed for 15 h. The reaction was followed by TLC, the yellow-green fluoroescence of the starting ester gradually changing to the blue fluorescence of the product in a chromatographically different position. The solvent was evaporated, the residue dissolved in water (20 mL), the solution extracted with CH_2Cl_2 (3 × 100 mL), and the extract dried and evaporated to yield a solid which was chromatographed on silica gel with CH_2Cl_2–EtOAc (4:1) as the eluant. Alternatively, CH_2Cl_2 was added after evaporation of the reaction mixture, and the lithium salts were extracted with water. Pure *syn*-(H,Cl)B (**11a**; 92 mg, 45%) was obtained. Use of crude **6a** (from bimane synthesis before purification) gave an overall yield from the dichloropyrazolinone **5a** of 20% (instead of 0.45 × 30% or 13.5% if the **6a** were purified by column chromatography).

Procedure B. *syn*-($COOCH_2CH_3$,Cl)B (**6a**; 348 mg, 1.0 mmol) and LiBr (1.0 g, 11.5 mmol) in dimethylformamide (DMF; Fluka puriss; 10 mL) were heated to 100 °C for 4–6 h, the reaction being followed as noted in procedure A. After the reaction was complete, the solvent was removed by distillation under high vacuum and the product isolated as in procedure A to yield *syn*-(H,Cl)B (**11a**), 50 mg (25%).

9,10-Dioxa-*syn*-(hydrogen,chloro)bimane [*syn*-(H,Cl)B, 11a]: yellow crystals (from *i*-PrOH); mp 280 °C; IR (KBr) 3160, 3080, 1760, 1675, 1530, 1440, 1290, 1250, 1180, 1120, 900 cm^{-1}; ^1H NMR (CD_3CN) 7.95 (s) ppm; UV (CH_3CN λ 420 nm (ϵ_{max} 4000, sh), 389 (8100), 250 (5500, sh), 231 (10 000); fluorescence (CH_3CN) 445 nm, 465 (sh), ϕ_F 0.40; mass spectrum, m/e 204 (M^+). Anal. Calcd for $C_6H_2N_2O_2Cl_2$: C, 35.15; H, 0.97; N, 13.67. Found: C, 34.98; H, 0.43; N, 13.19.

9,10-Dioxa-*syn*-(hydrogen,bromo)bimane [*syn*-(H,Br)B, 11b]: procedure A, 45% from **6e**, 25% from **5f**; procedure B, 20% from **6b**, 10% from **5b**; yellow crystals (from *i*-PrOH); mp 272 °C; IR (KBr) 3160, 3100, 1770, 1750, 1695, 1665, 1440, 1300, 1255, 1180, 1130, 980, 900 cm^{-1}; ^1H NMR (CD_3CN) 7.98 (s) ppm; (UV (CH3CN) λ 420 nm (ϵ_{max} 5000, sh), 392 (8700), 255 (5200, sh), 235 (8200); fluorescence (CH_3CN) 445 nm, 465 (sh), ϕ_F 0.45; mass spectrum, m/e 294 (M^+).

9,10-Dioxa-*syn*-(hydrogen,iodo)bimane [*syn*-(H,I)B, 11d]: procedure A, 40% from **6j**; procedure B, 20% from **6k** (R = CH_3CH_2, R_1 = I); orange crystals (from *i*-PrOH); mp 265 °C; IR (KBr) 3140, 3070, 1760, 1685, 1500, 1470, 1400, 1250, 1075 cm^{-1}; ^1H NMR (CD_3CN) 7.94 (s) ppm; UV (CH_3CN) λ 410 nm (ϵ_{max} 13 700), 250 (6400, sh), 226 (7200); fluorescence (CH_3CN) 454 nm, 480 (sh), ϕ_F 0.45; mass spectrum, m/e 388 (M^+). Anal. Calcd for $C_6H_2N_2O_2I_2$: C, 18.58; H, 0.51; N, 7.22. Found: C, 18.92; N, 7.09.

9,10-Dioxa-*syn*-(hydrogen,methyl)bimane [*syn*-(H,CH_3)B, 11c]: procedure A, 70% from **6f** (6 h reflux); procedure B, 50% from **6c**; yellow crystals (from CH_3CN); mp 272 °C; IR (KBr) 3100, 3085, 1720, 1650, 1420, 1320, 1250, 1200, 1030, 1000, 980, 910, 880, 740, 730, 630 cm^{-1}; ^1H NMR (CD_3CN) 1.819 (d, 3 H), 7.522 (q, 1 H, J = 1.0 Hz) ppm; UV (CH_3CN) λ 373 nm (ϵ_{max} 7500), 252 (6000), 226 (11 700); fluorescence (CH_3CN) 436 nm, 460 (sh), ϕ_F 0.60; mass spectrum, m/e 164 (M^+).

9,10-Dioxa-*syn*-(carboethoxy,chloro)(hydrogen,chloro)bimane [*syn*-($COOCH_2CH_3$,Cl)(H,Cl)B, 10a]: procedure B, reaction stopped at stage in which TLC indicated substantial amounts of intermediate; yellow crystals (from *i*-PrOH); mp 253 °C; IR (KBr) 3020, 1775, 1720, 1550, 1450, 1370, 1345, 1200, 1150, 1080, 1010, 920 cm^{-1}; ^1H NMR ($CDCl_3$) 1.44 (t, 3 H), 4.50 (q, 2 H), 8.20 (s, 1 H) ppm; UV (CH_3CN) λ 409 nm (ϵ_{max} 5500), 232 (7600); fluorescence (CH_3CN) 462 nm, 490 (sh), ϕ_F 0.13; mass spectrum, m/e 276 (M^+).

9,10-Dioxa-*syn*-(hydrogen,chloro)(methyl,methyl)bimane [*syn*-(H,Cl)(CH_3,CH_3)B 8a]: procedure B, 65% yield of product was obtained from the reaction of LiI (10 mol/mol of ester) and the ethyl ester **8**; yellow crystals (from *i*-PrOH); mp 235 °C; IR (KBr) 3020, 1775, 1720, 1550, 1450, 1370, 1295, 1195, 1165, 1080, 1010, 920 cm^{-1}; ^1H NMR ($CDCl_3$) 1.87 (s, 3 H), 2.26 (s, 3 H), 7.61 (s, 1 H) ppm; UV (CH_3CN) λ 376 nm (ϵ_{max} 4200), 250 (3700, sh), 230 (5800); fluorescence (CH_3CN) 443 nm, 460 (sh), ϕ_F 0.76; mass spectrum, m/e 198 (M^+).

9,10-Dioxa-*syn*-(carboxy,methyl)bimane [*syn*-(COOH,CH_3)B, 9, (R_1 = CH_3)]. The dimethyl ester **6f** (280 mg, 1.0 mmol) and lithium bromide (1.0 g, 11.5 mmol) were heated in CH_3CN (20 mL) at 50 °C for 2 days. The yellow precipitate which formed was filtered off, dispersed in Et_2O, and acidified carefully with concentrated H_2SO_4. The yellow, fluorescent solution was filtered from the precipitated salt and the Et_2O evaporated. CH_3CN was added, and the yellow solid dicarboxylic acid product **9** (80 mg, 32%) was filtered off and dried in a desiccator at room temperature: decomposes above 80–90 °C to *syn*-(H,CH_3)B (**11c**); IR (KBr) 3500, 3000, 1730, 1630, 1580, 1400, 1220, 1050, 850, 710, 650 cm^{-1}; ^1H NMR (D_2O) 2.17 (s) ppm; UV (H_2O) λ 393 nm (ϵ_{max} 4100), 243 (11 900); fluorescence (H_2O) 520 nm, ϕ_F 0.12.

pK_a Determination of 9. The diacid in H_2O (2.0 mL, 0.02 M) was titrated with NaOH (0.10 M) by using a Gilmont microburet and following the pH with a small glass electrode and

(23) Main, P.; Woolfson, M. M.; Lessinger, L.; Germain, G.; Declercq, J. P. "MULTAN 74, A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, York, England, 1974.

an Orion 801 pH meter. Two equivalents of base were consumed over the range from pH 2 to 3; a graphical plot of pH vs. the volume base added indicated an average pK_a of 2.3.

9,10-Dioxa-*syn*-(hydrogen,hydrogen)bimane [*syn*-(H,H)B, 11e]. *syn*-(H,Cl)B (**11a**; 220 mg, 1.1 mmol) was mixed with acetic acid (20 mL) and anhydrous K_2CO_3 (1.0 g, 10 mmol) added. After CO_2 evolution ceased, 10% Pd/C (10 mg) was added and the whole stirred and warmed to 70 °C under 1 atm hydrogen. After 20 min, heating was discontinued, CH_2Cl_2 (100 mL) added, the solution filtered, and the solvent evaporated, acetic acid being removed under high vacuum. The residue was dissolved in CH_2Cl_2 (100 mL), the solution was treated with saturated aqueous $NaHCO_3$ and dried over $Mg,2SO_4$, and the solvent was removed. The residue was dissolved in the minimum quantity of CH_2Cl_2, placed on a silica gel column, and eluted with ethyl acetate. The fraction containing the product exhibits a beautiful deep violet fluorescence and yielded 45 mg (30%) of **11e**: faintly yellow needles (from tetrahydrofuran); mp 302 °C; IR (KBr) 3180, 3100, 1750, 1735, 1670, 1430, 1300, 1280, 1250, 1135, 980 cm^{-1}; ^1H NMR (CD_3CN) 5.60 (d, 1 H), 7.76 (d, 1 H, J = 4 Hz) ppm; UV (CH_3CN) λ 385 nm (ϵ_{max} 5000, sh), 368 (6200), 240 (3300, sh), 218 (7600); fluorescence (CH_3CN) 398 nm, 415 415 (sh), ϕ_F 1.0; mass spectrum, m/e 136 (M^+).

9,10-Dioxa-*syn*-(hydrogen,chloro)(hydrogen,hydrogen)bimane [*syn*-(H,Cl)(H,H)B, 13a]. By following the hydrogenation of *syn*-(H,Cl)B through TLC and stopping the reaction at a stage when the blue fluorescence of the starting material is gone but the blue-violet fluorescence of the intermediate bimane is still present along with the violet fluorescence of *syn*-(H,H)B, the "mixed" bimane **13a** may be isolated by chromatography on silica: yellow crystals (from CH_3CN); mp 253 °C; IR (KBr) 3160, 3120, 3080, 3060, 1740, 1670, 1530, 1440, 1310, 1270, 1210, 1090, 1030, 920, 900, 780 cm^{-1}; ^1H NMR (CD_3CN) 5.650 (d, 1 H), 7.760 (d, 1 H, J = 2.0 Hz), 7.840 (s, 1 H) ppm; UV (CH_3CN) λ 380 (ϵ_{max} 5800), 223 (6400); fluorescence (CH_3CN) 442 nm, ϕ_F 0.92; mass spectrum, m/e 170 (M^+).

9,10-Dioxa-*syn*-(hydrogen,bromo)(hydrogen,chloro)bimane [*syn*-(H,Br)(H,Cl)B, 13b]. Excess bromine was added to a solution of *syn*-(H,Cl)(H,H)B (**13a**, 5 mg) in CH_2Cl_2 (50 mL). After the mixture was stirred for 3 h, the solvent was evaporated to give an essentially quantitative yield of **13b**: yellow crystals (from EtOAc); mp 200 °C dec; IR (KBr) 3140, 1720, 1670, 1530, 1440, 1250, 1180, 1100, 850, 790, 720 cm^{-1}; ^1H NMR (CD_3CN) 7.955 (s, 1 H), 7.985 (s, 1 H) ppm; UV (CH_3CN) λ 387 nm (ϵ_{max} 6900), 230 (6900), 255 (sh); fluorescence (CH_3CN) 444 nm (ϕ_F 0.62); mass spectrum, m/e 249 (M^+).

Hydrogenation of *syn*-(H,Br)B (**11b**) led to results similar to those described for *syn*-(H,Cl)B. Reductions which were allowed to continue for more than 1 h led to considerably decreased yields of *syn*-(H,H)B, presumably due to further hydrogenation.

9,10-Dioxa-*syn*-(carbomethoxy,hydrogen)bimane [*syn*-(COOCH$_3$,H)B, 6h]. *syn*-(COOCH$_3$,Cl)B (**6d**; (320 mg, 1 mmol) was hydrogenated according to the procedure for *syn*-(H,H)B to yield, after chromatography, 98 mg (39%) of **6h**: yellow crystals (from *i*-PrOH); mp 164 °C; IR (KBr) 3160, 3120, 3000, 1725, 1670, 1545, 1470, 1380, 1270, 1250, 1170, 1150, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) 3.95 (s, 3 H), 6.13 (s, 1 H) ppm; UV (CH_3CN) λ 401 nm (ϵ_{max} 5200, sh), 385 (6200), 246 (9000); fluorescence (CH_3CN) 430 nm, 455 (sh), ϕ_F 0.65; mass spectrum, m/e 252 (M^+).

9,10-Dioxa-*syn*-(carboethoxy,hydrogen)bimane [*syn*-(COOCH$_2$CH$_3$,H)B, 6l (R = CH$_3$CH$_2$, R$_1$ = H)]. Hydrogenation of **6a** was carried out according to the procedure for *syn*-(H,H)B to yield, after chromatography, **6l**: 15% yield; yellow crystals (from *i*-PrOH); mp 145 °C; IR (KBr) 3160, 3120, 3010, 1725, 1680, 1580, 1550, 1470, 1380, 1270, 1250, 1215, 1175, 1150, 1110, 1050, 1010 cm^{-1}; ^1H NMR ($CDCl_3$) 1.35 (t, 3 H), 4.30 (q, 2 H), 5.98 (s, 1 H) ppm; UV (CH_3CN) 400 nm (ϵ_{max} 5000, sh), 385 (6100), 245 (8400); fluorescence (CH_3CN) 430 nm, 450 (sh), ϕ_F 0.50; mass spectrum, 286 (M^+).

9,10-Dioxa-*syn*-(carbomethoxy,iodo)bimane [*syn*-(COOCH$_3$,I)B, 6j]. Iodine monochloride (160 mg, 1.0 mmol) was added to *syn*-(COOCH$_3$,H)B (**6h**; 85 mg, 0.3 mmol) in CH_2Cl_2 (10 mL), the mixture stirred for 24 h, the solvent evaporated, and the residue crystallized from *i*-PrOH to yield 120 mg (80%) of **6j**: orange-yellow crystals (from *i*-PrOH); mp 125 °C; IR (KBr) 2950, 1780, 1740, 1700, 1470, 1420, 1400, 1350, 1250, 1170, 1125, 1100, 910 cm^{-1}; ^1H NMR ($CDCl_3$) 4.01 (s) ppm; UV (CH_3CN) 415 nm (ϵ_{max} 13 000), 273 (12 700), 212 (17 300); fluorescence (CH_3CN) 490 nm (ϕ_F 0.24); mass spectrum, m/e 504 (M^+).

9,10-Dioxa-*syn*-(carboethoxy,iodo)bimane [*syn*-COOCH$_2$CH$_3$,I)B, 6m (R = CH$_3$CH$_2$, R$_1$ = I)]. This compound was obtained in 80% yield from **6l** by reaction with ICl according to the procedure for the methyl ester: yellow crystals (from *i*-PrOH); mp 129 °C; IR (KBr) 3000, 1755, 1620, 1550, 1450, 1420, 1380, 1320, 1250, 1180, 1130, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) 1.44 (t, 3 H), 4.45 (q, 2 H) ppm; UV (CH_3CN) λ 423 nm (ϵ_{max} 12 500), 273 (7600), 212 (12 000); fluorescence (CH_3CN) 500 nm (ϕ_F 0.15); mass spectrum, m/e 532 (M^+).

9,10-Dioxa-*syn*-(carboethoxy,phenylthio)bimane [*syn*-(COOCH$_2$CH$_3$,C$_6$H$_5$S)B, 12]. A solution of the diester *syn*-($COOCH_2CH_3Cl$)B (**6a**; 110 mg, 0.3 mmol) in dry THF (5 mL) was added to a solution of lithium thiophenoxide (thiophenol (72 mg, 0.6 mmol) was added with a syringe to butyllithium (4 μL of 15% solution in pentane) in THF (5 mL)). After 5 h, the solvent was evaporated, and the residue was chromatographed on silica gel to yield 55 mg (50%) of **12**: orange-red crystals (from *i*-PrOH); mp 116–118 °C; IR (KBr) 3000, 2950, 1755, 1620, 1570, 1550, 1480, 1470, 1420, 1400, 1385, 1350, 1310, 1180, 1120, 1000, 950 cm^{-1}; ^1H NMR ($CDCl_3$) 1.36 (t, 3 H), 4.43 (q, 2 H), 7.43 (m, 5 H) ppm; UV (CH_3CN) 445 nm (ϵ_{max} 3300), 245 (19 000); fluorescence (dioxane) 590 nm (ϕ_F 0.027); mass spectrum, m/e 496 (M^+).

9,10-Dioxa-*syn*-(carboethoxy,bromomethyl)bimane [*syn*-(COOCH$_2$CH$_3$,BrCH$_2$)B, 6i]. A mixture of *syn*-($COOCH_2CH_3,CH_3$)B (**6c**; 62 mg, 0.2 mmol), *N*-bromosuccinimide (120 mg, 0.8 mmol), and benzoyl peroxide (5 mg) in CCl_4 (15 mL) was refluxed for 3 h, the precipitated succinimide and *N*-bromosuccinimide were filtered off after cooling, the solvent was evaporated, and the residue was quickly chromatographed on a silica gel column (eluant CH_2Cl_2–cyclohexane, 1:1) protected from light to yield **6i**: 56 mg; yellow crystals (from *i*-PrOH); mp 92 °C; IR ($CDCl_3$) 2940, 1770, 1740, 1580, 1450, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) 1.399 (t, 3 H), 2.057 (s, 2 H), 4.400 (q, 2 H); UV (CH_3CN) 412 nm (ϵ_{max} 9400), 243 (9900); fluorescence (CH_3CN) 470 nm (ϕ_F 0.27); mass spectrum, m/e 306 (M^+ – 2Br).

Registry No. 3a, 108-56-5; **3b**, 759-65-9; **4a**, 58607-90-2; **4b**, 79746-67-1; **4c**, 60178-92-9; **5a**, 79746-68-2; **5b**, 79746-69-3; **5c**, 79746-70-6; **5d**, 79746-71-7; **5e**, 79746-72-8; **5f**, 79746-73-9; **6a**, 79746-74-0; **6b**, 79746-75-1; **6c**, 79746-76-2; **6d**, 79746-77-3; **6e**, 79746-78-4; **6f**, 79746-79-5; **6h**, 79746-80-8; **6i**, 79746-81-9; **6j**, 79746-82-0; **6k**, 79746-83-1; **6l**, 79746-84-2; **7**, 68654-32-0; **8**, 79746-85-3; **8a**, 79746-86-4; **9** (R_1 = CH_3), 79769-55-4; **10a**, 79746-87-5; **11a**, 78763-68-5; **11b**, 79746-88-6; **11c**, 79746-89-7; **11d**, 79746-90-0; **11e**, 79769-56-5; **12**, 79746-91-1; **13a**, 79746-92-2; **13b**, 79746-93-3.

Supplementary Material Available: Table of atomic coordinates and thermal parameters for *syn*-($COOCH_3,CH_3$)B (1 page). Ordering information is given on any current masthead page.