Molecular Structures and Photochemical Behavior of Doubly Bridged Prismanes

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The molecular structures of four prismanes were determined by X-ray analysis. The diester derivatives **1a**, **1b**, and **3** show a lengthening of the vicinal bonds and a shortening of the distal bonds in the cyclopropane moieties, whereas in bis(hydroxymethyl) compound **2** no significant bond length differences were found. These structural properties affect their chemical behavior: if prismanes **1a** and **1b** are irradiated with UV light a selective cleavage of the elongated cyclopropane bonds affords exclusively Dewar benzenes **4a** and **4b** as primary products whereas from **2** both possible isomeric Dewar benzenes **8** and **9** are obtained.
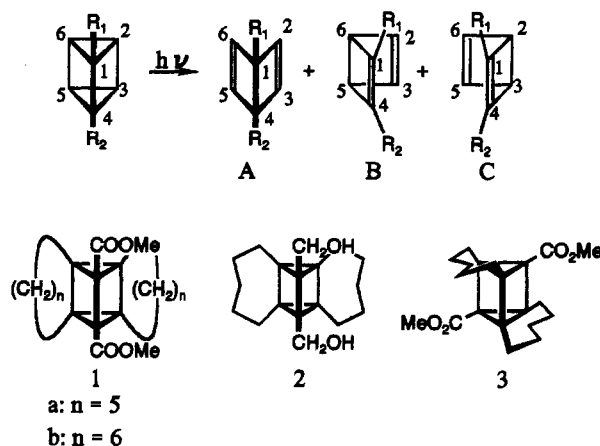
Introduction

Recently, we described the synthesis of doubly bridged prismanes from Dewar benzene precursors.[1] In this paper we want to present the molecular structures of these prismanes which were elucidated by X-ray analysis. We also examined their photochemical [2 + 2]cycloreversion into Dewar benzenes and found that the nature of the photoproducts can be rationalized on the basis of the bonding situation in the prismanes. As depicted in Scheme 1 cleavage of a prismane may occur along all three cyclobutane faces affording three possible Dewar benzenes **A**, **B**, and **C**. In prismanes with full D_{3h} symmetry (e.g., $R^1 = R^2 = H$) these Dewar benzenes are indistinguishable. In the case of our prismanes **1a**, **1b**, and **2** (see Scheme 1) the symmetry is decreased to C_{2v}. With the bridges spanning the 2,3- and 5,6-positions and $R^1 = R^2 = COOCH_3$ or CH_2OH we expect two distinguishable isomeric Dewar benzenes **A** and **B** = **C**. So far only proton and Lewis acid catalyzed fragmentations of prismanes have been reported.[2,3] There are two publications in which Dewar benzenes were irradiated affording positional isomerized Dewar benzenes and/or benzenes.[4,5] In both cases prismane intermediates were observed and bond cleavage according to Scheme 1 was invoked to account for these isomerizations.

Results and Discussion

(a) Molecular Structures. The structure determinations of prismane derivatives suffer from deterioration on treating these compounds with X-rays.[6a-e] Therefore, we determined the structures of the propella[3]prismanes **1a**,

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1b, **2**, and **3** in order to obtain precise unbiased structural data. Because of the protecting oligomethylene clamps all four derivatives were stable enough against X-rays to collect a complete set of data. The most relevant bond distances and bond angles of the prismane moiety of **1-3** are collected in Table 1. Compound **1a** (Figure 1) lies on a crystallographic mirror plane and compound **3** (Figure 4) on a crystallographic 2-fold rotation axis. The derivative **1b** (Figure 2) crystallizes with two independent molecules in the asymmetric unit. The conformations of both molecules of **1b** are diastereomeric. Whereas the prismane frame and the hexamethylene groups are almost identical, the ester groups have opposite orientation. The torsional angles C19-C2-C1-C21 are -9.2(7)° and +13.0(7)°, respectively. The cycloheptane rings assembled from five methylene groups and two prismane carbon atoms have chair conformations in **1a** (Figure 1), **2** (Figure 3), and **3** (Figure 4), respectively. The orientations of the methylene bridges in **1a** and **2** are symmetric with respect to a molecular mirror plane perpendicular to the three-membered ring of the prismane frame passing through the atom substituted by the ester groups and the center of the opposite ring bond (Figure 1 and Figure 3). The corresponding eight-membered ring of **1b** has a twisted

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Table 1. Selected Geometrical Parameters of 1–3[a]

compd 1a		compd 3	
	Bond Distances (Å)		
C1–C2	1.562(3)	C1–C2'	1.549(6)
C1–C3	1.548(3)	C1–C3	1.554(5)
C2–C3	1.504(3)	C2'–C3	1.504(5)
C1–C1'	1.554(3)	C1–C2	1.545(4)
C2–C2'	1.560(3)	C3–C3'	1.553(4)
C3–C3'	1.562(3)		
	Bond Angles (deg)		
C1–C2–C7	131.1(2)	C1–C2'–C8'	130.4(3)
C3–C2–C7	132.5(2)	C3–C2'–C8'	126.8(3)
C2'–C2–C7	129.5(2)	C1–C2–C8	133.0(3)
C1–C3–C4	131.8(2)	C2'–C1–C9	127.5(3)
C2–C3–C4	131.5(2)	C3–C1–C9	129.7(3)
C3'–C3–C4	129.4(2)	C2–C1–C9	135.0(3)
C2–C1–C10	124.2(2)	C1–C3–C4	132.8(3)
C3–C1–C10	126.0(2)	C2'–C3–C4	126.8(3)
C1'–C1–C10	138.7(2)	C3'–C3–C4	132.1(3)

compd 1b		compd 2	
	Bond Distances (Å)		
C2–C3	1.567(4)/1.544(4)	C1–C2	1.534(3)
C2–C4	1.554(4)/1.562(3)	C1–C3	1.546(3)
C3–C4	1.507(4)/1.503(4)	C2–C3	1.531(3)
C1–C5	1.557(4)/1.551(3)	C9–C10	1.531(3)
C1–C6	1.552(4)/1.558(4)	C9–C11	1.536(3)
C5–C6	1.507(4)/1.500(4)	C10–C11	1.537(3)
C1–C2	1.544(4)/1.545(4)	C1–C11	1.549(3)
C3–C6	1.570(4)/1.557(4)	C2–C10	1.561(3)
C4–C5	1.558(4)/1.566(4)	C3–C9	1.550(3)
	Bond Angles (deg)		
C2–C3–C12	125.6(2)/127.9(3)	C1–C2–C17	131.8(2)
C4–C3–C12	133.7(3)/132.2(2)	C3–C2–C17	131.7(2)
C6–C3–C12	131.9(2)/131.6(3)	C10–C2–C17	129.9(2)
C2–C4–C13	130.4(2)/129.3(3)	C2–C1–C16	132.5(2)
C3–C4–C13	130.6(3)/128.3(2)	C3–C1–C16	131.3(2)
C5–C4–C13	131.0(2)/133.8(2)	C11–C1–C16	129.5(2)
C3–C2–C19	122.2(2)/125.9(2)	C1–C3–C4	130.5(2)
C4–C2–C19	125.5(2)/121.2(2)	C2–C3–C4	133.1(2)
C1–C2–C19	140.3(3)/139.9(2)	C4–C3–C9	129.6(2)
C1–C5–C18	128.0(3)/128.2(2)	C9–C10–C19	132.8(2)
C6–C5–C18	133.0(2)/133.3(3)	C11–C10–C19	131.7(2)
C4–C5–C18	130.8(3)/130.7(2)	C2–C10–C19	129.2(2)
C1–C6–C7	132.2(3)/129.6(2)	C9–C11–C12	130.8(2)
C5–C6–C7	130.0(2)/132.1(3)	C10–C11–C12	134.7(2)
C3–C6–C7	130.9(3)/130.3(3)	C1–C11–C12	128.3(2)
C5–C1–C21	122.9(2)/125.5(3)	C8–C9–C10	132.9(2)
C6–C1–C21	125.4(2)/121.6(3)	C8–C9–C11	131.7(2)
C2–C1–C21	139.1(2)/140.6(2)	C3–C9–C8	128.8(2)

[a] Two values for compound 1b represent the corresponding bond distances and angles of both independent molecules in the asymmetric unit. For the numbering of the atoms, see Figures 1–4.

boat–chair form. The orientation of the methylene bridges are paddle-wheel-like (Figure 2).

Bond Lengths. As shown in Figures 1, 2, and 4 all the ester groups are oriented in a nearly perfect bisected conformation with respect to the attached three-membered ring. The deviation τ of the ester groups is listed in the second column of Table 2. In this table we also list the average bond lengths in the three- (M34) and four-membered (M44) rings. The ester substituents oriented in the bisected conformation give rise to a shortening of the distal bond and half as much to a lengthening of the vicinal bonds. The difference of the distal bond length to M34 (δ_{dist}) is listed in Table 2. It is also shown in Table 2 that the electronic influence of the ester groups in the prismanes are 1.3 times larger than in cyclopropane derivatives ($\delta_{dist} = -0.026$ Å[10]). The bent bonds in the

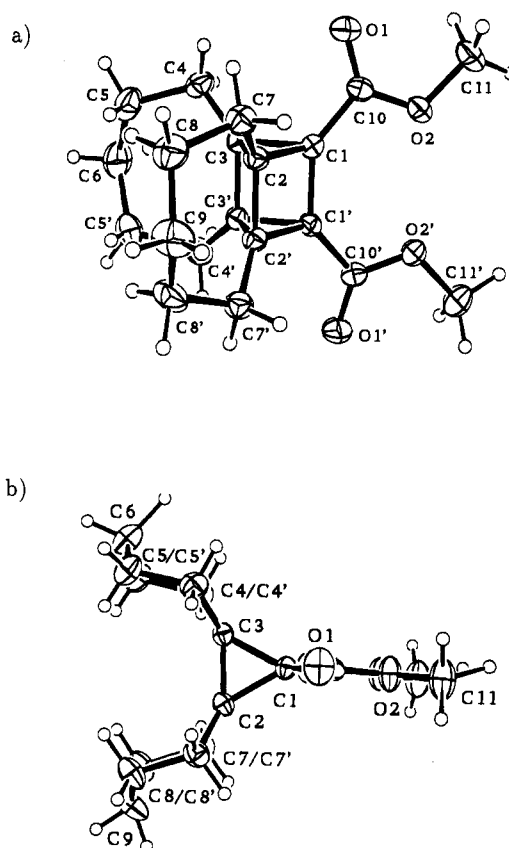(10) Allen, F. H. *Acta Crystallogr. Sect. B* 1980, *36*, 81.

a)

b)

Figure 1. Perspective view of 1a: (a) side view, (b) top view of the prismane frame. The thermal ellipsoids are plotted at 50% probability (ORTEP[7]).

strained prismane frame of 1a have been demonstrated by difference electron density determinations at low temperature.[11]

The observed bond alternation in the three-membered rings of the prismane derivatives is due to the π-accepting properties of the ester groups. They exert the same electronic effect on the three membered rings in prismane derivatives as in cyclopropane derivatives,[9] established theoretically[6c,8] and experimentally.[6,8,10] To rationalize the bond alternation we have shown in Figure 5 a qualitative MO interaction diagram between the HOMO of prismane (left) and the LUMO (π^* linear combination) of two CHO groups (right). As a result of this interaction, electron density from the cyclopropane rings is transferred to the LUMO. As a consequence the antibonding interaction at the distal bonds and the bonding interaction along the vicinal bonds is reduced. Compound 2 (Figure 3) has no π-accepting substituent, and consequently it does not show significant variation of bond lengths (Table 2).

The bonds of the three-membered rings in prismanes are bridging bonds of bicyclic subunits. Their bond lengths M34 of the three-membered rings (Table 2) have a magnitude between the average of cyclopropane (1.510 Å)[12] and planar cyclobutane derivatives (1.559 Å).[13] The four-membered ring bonds M44 (Table 2; averaged bond length 1.557 Å) connecting the three-membered ring subunits have the same order of length as the bonds in planar cyclobutane derivatives.[13]

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(12) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* 1987, S1.
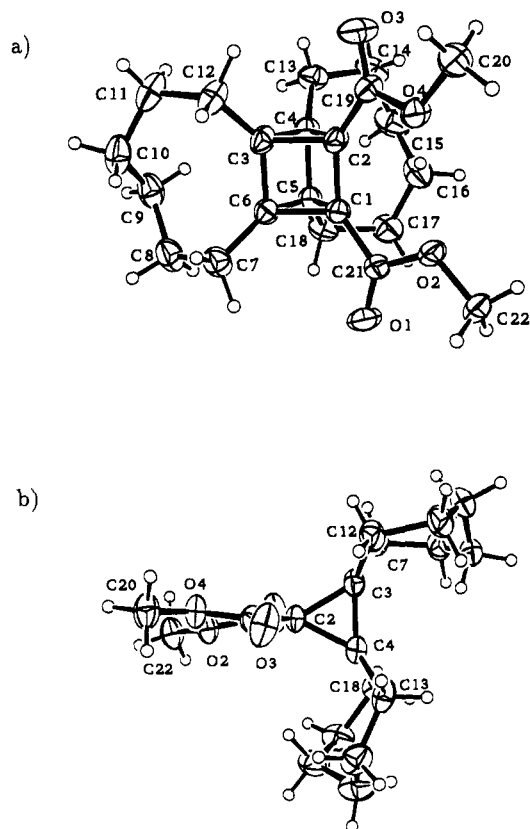(13) Allen, F. H. *Acta Crystallogr. Sect. B* 1984, *40*, 64.

Figure 2. Perspective view of one of both independent molecules of **1b**. Further remarks as in Figure 1.
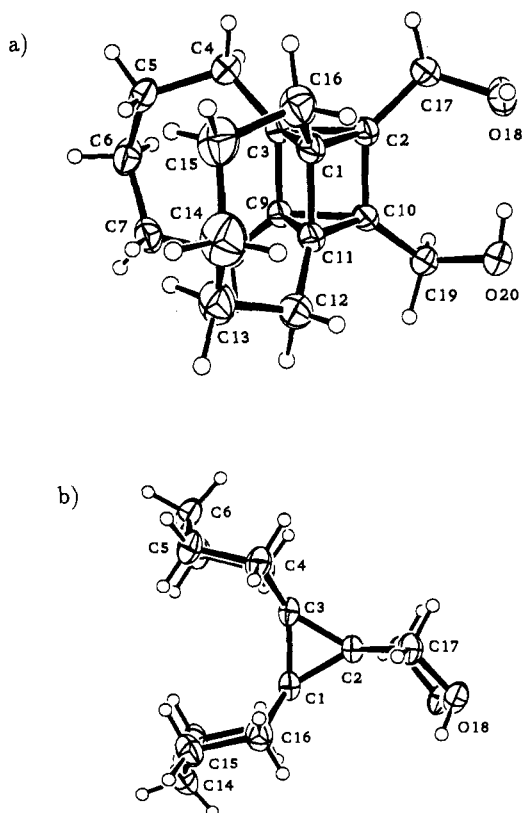
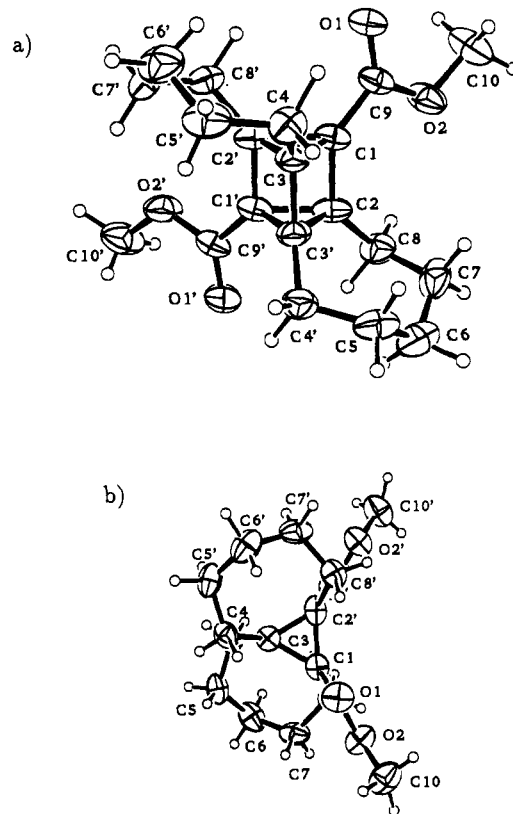**Figure 3.** Perspective view of **2**. Further remarks as in Figure 1.

Figure 4. Perspective view of **3**. Further remarks as in Figure 1.

Table 2. Electronic Influences[a] on the Bond Length of the Three-Membered Rings in 1–3 Compared with Cyclopropane Derivatives[10]

compd	τ (deg)	M34 (Å)	M44 (Å)	δ_{dist} (Å)
1a	−5.9	1.538	1.559	−0.034
1b	−11.4	1.543		−0.036
			1.557	
	−8.9	1.539		−0.032
	8.1	1.536		−0.033
			1.556	
	10.5	1.536		−0.036
3	0.4	1.536	1.548	−0.032
cyclopropane–CO[10]	≤±30	1.504		−0.026
2		1.537		0.009
			1.553	
		1.535		0.001

[a] τ is the deviation of the ester groups from bisected orientation (torsional angle O–C(ester)–C(prismane)–X; X is the center of the distal bond); M34 is the averaged three-membered-ring bond; M44 is the average of those four-membered-ring bonds connecting both three-membered-ring subunits; δ_{dist} is the difference of the distal bond length to M34. The standard deviations of the bond lengths and torsional angles are in the order of 0.003–0.005 Å and 0.3–0.6° respectively.

(b) Photochemical Behavior. The possible photoproducts of the C_{2v}-symmetrical prismanes **1a** and **1b** are depicted in Scheme 2. Cleavage of the vicinal (with respect to the ester functionalities) cyclopropane bonds affords Dewar benzenes **4** while an opening of the distal bond affords Dewar benzenes **6** as primary products. As secondary products paracyclophanes **5** and terephthalic esters **7** are also expected. Statistically the products **4/5** versus **6/7** should be obtained in a 2:1 ratio. Photolyses of prismane **1b**, with hexamethylene bridges, were carried out at three different wavelengths λ ≥ 320 nm, ≥280 nm, and 254 nm in diethyl ether as solvent. The product ratio was determined by ¹H NMR spectroscopy via the integrals of the methoxy singlets. The results are compiled in Table 3.

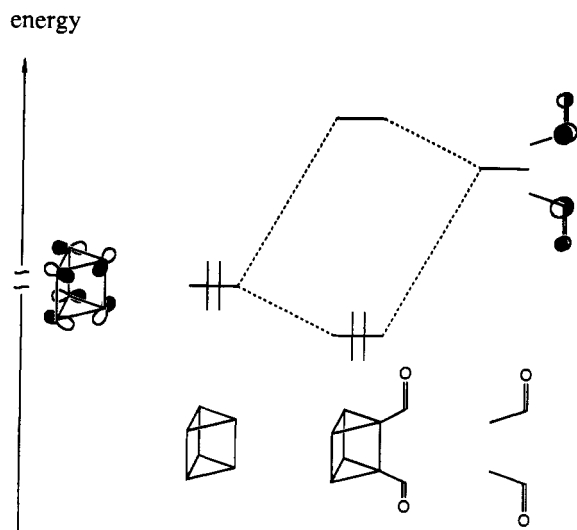Dewar benzene **6b** and terephthalic ester **7b** are not

energy

Figure 5. Interaction diagram between the HOMO of prismane (left) and the π^* MOs of two formyl groups (right).
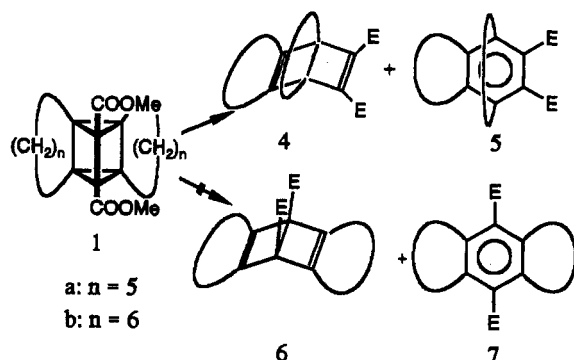
Scheme 2. Photochemistry of Prismanes 1a and 1b

Table 3. Irradiation Excperiments with Prismane 1b

wavelength (nm)/time (h)	amt of 1b (%)	amt of 4b (%)	amt of 5b
≥320/8	80	≈1	7
≥280/8	57	5	22
254/2	39	9	45
254/4	≈15	≈17	≈68

found in the product mixture. Bond cleavage in 1b occurs selectively along the vicinal cyclobutane faces of the prismane moiety affording exclusively Dewar benzene 4b as primary product and [6]paracyclophane 5b as secondary product. The rate of the reaction depends on the applied wavelength; at shorter wavelengths 1b decomposes faster. At $\lambda \geq 320$ nm prismane 1b is quite photostable, after 8 h of irradiation still 80% can be recovered beneath small amounts of 4b (≈1%) and 5b (7%). At 280 nm, under identical conditions, we observe a decrease of 1b to 57% and already 5% of 4b as well as 22% of 5b. At 254 nm the conversion is considerably accelerated; after only 2 h of photolysis we observe a 61% decrease in prismane 1b. If the irradiation is continued beyond this time an increased amount of decomposition products complicates the evaluation of the NMR spectra, and the results obtained after 4 h are not very reliable. Within the margin of error the observed ratio of Dewar benzene 4b to [6]paracyclophane 5b represents their photostationary state ratio of 20:80. As found earlier this equilibrium is not dependent on the wavelength in the applied range.[1]

The lower homologue prismane 1a, with pentamethylene bridges, was irradiated at $\lambda \geq 295$ nm for 4 h. In this

Scheme 3. Photochemistry of Prismane 2
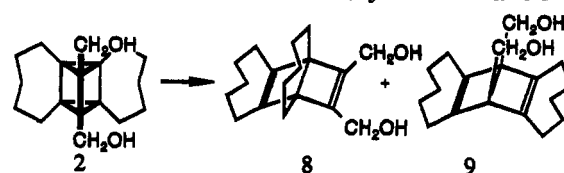
experiment we recovered about 50% of starting material and found ≈10% of 4a as the only Dewar benzene. The remaining 40% were decomposition products. The generation of Dewar benzene 6a and/or terephthalic ester 7a in concentrations exceeding 1% can be ruled out, as we did not find the sharp and characteristic absorption of their methoxy singlets in the ^1H NMR spectrum of the reaction mixture. Prismane 2, with two hydroxymethyl substituents instead of the ester groups, shows a deviating photochemical behavior. In this series the CH_2OH resonances are used as NMR satellites. After 1 h of irradiation at 280 nm the signal of the starting material has disappeared. In this case, as shown in Scheme 3, we observe both possible Dewar benzenes 8 (cleavage of the vicinal cyclopropane bonds) and 9 (cleavage of the distal cyclopropane bonds) in an almost statistical ratio of 0.64 to 0.36. Some decomposition is observed as well.

The outcome of these three experiments can be correlated with the molecular structures of the three investigated prismanes. For example, in prismanes 1a and 1b a conjugation between the ester substituents and the Walsh orbitals of the cyclopropane rings stabilizes the two distal bonds and destabilizes the four vicinal bonds in the prismane;[6,8,10] this is represented by a significant shortening of the former and a lengthening of the latter as discussed above. Our experiments show that photochemical [2 + 2]cycloreversion in these compounds occurs exclusively along the destabilized vicinal bonds affording only 4a/4b as primary products. Dewar benzene 4b can react further to the stable [6]paracyclophane 5b. The lower homologue Dewar benzene 4a seems to react analogously to form paracyclophane 5a. However, unlike 5b the [5]paracyclophane 5a is too strained to be stable at room temperature and decomposes.[14] This explains nicely the fact that the irradiation of 1a affords a large amount of decomposition products. A similar tendency toward decomposition was observed in the reverse experiment, when Dewar benzene 4a was irradiated to generate prismane 1a. A detailed discussion on this was presented in our previous paper.[1] In prismane 2, with no conjugative interaction between hydroxymethyl substituents and the cyclopropane ring, no significant bond length differences can be found in the cyclopropane moieties. Vicinal and distal bond energies are very similar, [2 + 2]cycloreversion occurs statistically across all three cyclobutane faces, and both isomeric Dewar benzenes 8 and 9 are obtained in a ratio of almost 2:1. So the cleavage of prismanes is controlled by the nature of the substituents. Electron-withdrawing substituents promote a cleavage of the vicinal bonds, and nonconjugated substituents lead to a statistical cleavage of the prismane bonds. The connection between the geometry of ground and excited states is given by the Franck Condon principle which states that the initially formed electronic excited state of a molecule has ground-state geometry. It seems that the excitation of prismanes

(14) Kostermans, G. B. M.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron Lett.* 1987, *43*, 2955.

Scheme 4. Predicted Photochemistry of Prismane 3

E = CO₂Me
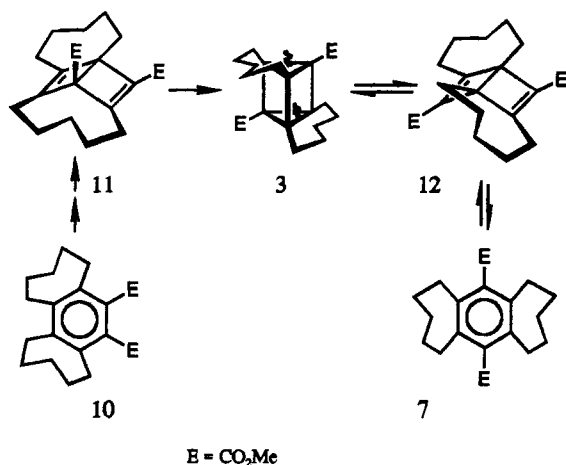
leads to electronically excited as well as vibrationally hot molecules which undergo "hot excited state reactions", in this case [2 + 2]cycloreversions with a selective cleavage of the weakest bonds.

The above-described irradiation experiments with 1a and 1b in connection with the results of the X-ray determination of the molecular structure allow a prediction of the photochemical behavior of prismane 3. Again, as for 1a and 1b, the molecular structure of 3 shows a shortening of the distal bonds and a lengthening of the vicinal bonds. For the photochemistry we predict a cleavage along a cyclobutane face which possesses two destabilized cyclopropane bonds. Due to the lower C_2 symmetry there is only one such face in the molecule, and cleavage along this face, as indicated in Scheme 4, affords Dewar benzene 12.

The remaining two cyclobutane faces possess one stabilized (distal) and one destabilized (vicinal) cyclopropane bond each. Their cleavage, affording Dewar benzene 11, should be disfavored. We could not bear out this prediction because 3 is only accessible in very small amounts and difficult to purify. However, this compound represents an intermediate in a complex photochemical isomerization reaction in which phthalic ester 10 is transformed into terephthalic ester 7.[1,15] In this rearrangement 11 is the direct precursor of 3 and therefore the step 11 → 3 is largely irreversible. We consider the irreversibility of this step as the driving force behind this complex phthalic/terephthalic ester rearrangement.

Conclusion and Outlook

The molecular structures of prismanes can be correlated with their photochemical behavior. Prismanes with ester substituents as in 1a, 1b, or 3 show a significant shortening and lengthening of their cyclopropane edges and undergo a selective photochemical ring opening along the face with the elongated cyclopropane bonds. With nonconjugative substituents as in 2 no significant bond length differences are found in the cyclopropane rings, the ring opening occurs statistically across all three cyclobutane faces. So far we

have only three examples. In order to prove the generality of this concept it is necessary to synthesize further prismane derivatives, e.g., with other electronic-withdrawing groups than esters, with aromatic or olefinic substituents, or with electron-rich substituents, elucidate their molecular structures, and investigate their photochemistry.

Experimental Section

(1) X-ray Analysis. The X-ray data (Table 1) were collected on an automated diffractometer (Enraf-Nonius CAD4, graphite monochromator, Mo Kα radiation, $\omega - 2\theta$ scan). Intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods (Multan[16]). Refinements on F^2 were carried out by full-matrix least-squares techniques (non-hydrogen atoms anisotropic, hydrogen atoms isotropic). The MOLEN program system[17] was used for the crystallographic calculations.[18]

(2) Photochemical Experiments. NMR spectra were recorded on Bruker WH300 and Bruker AS200. All irradiations were carried out in dry diethyl ether and under argon atmosphere. The photolyses were carried out in a 20-mL vessel (quartz glass), and a high-pressure mercury lamp OSRAM HBO 500 W/2 was used in a lamp housing type Oriel Corp. 66187. Wavelength selection was achieved with cutoff filters from Schott, Mainz. All compounds have been characterized previously.[1]

(a) Photolysis of 1b (320 nm). Thirteen mg (0.036 mmol) of 1b was dissolved in 20 mL of diethyl ether and irradiated through a 320-nm cutoff filter at 10 °C for 8 h. Then the solvent was removed and the product ratio determined by integration of the methoxy singlets in the ¹H NMR; the results are documented in Table 3, margin of error ≈10%. ¹H NMR (CDCl₃, 300 MHz, COOCH₃) δ: 3.67 (for 1b), 3.78 (for 4b), 3.83 (for 5b).

(b) Photolysis of 1b (280 nm). Experiment analogous to (a) except that a 280-nm cutoff filter was used; the results are documented in Table 3, margin of error ≈10%.

(c) Photolysis of 1b (254 nm). Experiment analogous to (a) except that no cutoff filter was used and ¹H NMR spectra were recorded after 2 and 4 h, respectively. The results are documented in Table 3, margin of error (2 h) ≈10%, (4 h) ≈20%.

(d) Photolysis of 1a (295 nm). Ten mg (0.03 mmol) of 1a was dissolved in 20 mL of diethyl ether and irradiated through a 295-nm cutoff filter at 10 °C for 4 h. Then the solvent was removed and the product ratio determined by ¹H NMR. Results: <50% of 1a, ≈10% of 4a, >40% decomposition, margin of error ≈20%. ¹H NMR (CDCl₃, 300 MHz, COOCH₃) δ: 3.67 (for 1a), 3.78 (for 4a).

(e) Photolysis of 2. Ten mg (0.036 mmol) of 2 was dissolved in 20 mL of diethyl ether and irradiated through a 280-nm cutoff filter at 10 °C for 1 h. Then the solvent was evaporated and the product ratio determined by integration of the CH₂OH signals in the ¹H NMR. Results: <1% of 2, 58% of 8, 32% of 9. ¹H NMR (300 MHz, CDCl₃, CH₂OH) δ: 3.72 (for 2), 4.21 (for 8), 3.89 (for 9).

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(17) MOLEN: *Structure Determination System*, Enraf-Nonius, Delft Instruments X-ray Diffraction B. V., Delft, Netherlands, 1990.

(18) The authors have deposited tables of crystallographic refinement parameters, atomic coordinates, and thermal parameters of 1a, 1b, 2, and 3 with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.