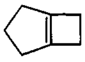
Photochemical Synthesis and Reactivity of Strained Polycyclic Cyclobutenes. $\Delta^{2(5)}$-Tricyclo[4.2.1.0^{2,5}]nonene[1]

Sir:

Synthesis of highly strained polycyclic cyclobutenes,[2] **1** and **2**, and strained propellanes,[3] **3** and **4**, has been of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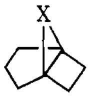
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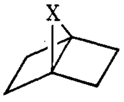
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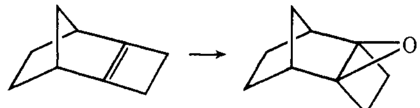
much interest because of the unusual hybridization, bonding,[3e,f] and reactivity of such molecules. We present here an attractive photochemical route to strained polycyclic cyclobutenes which has led to the synthesis of $\Delta^{2(5)}$-tricyclo[4.2.1.0^{2,5}]nonene (**5**). Addition reactions and the rate of thermal ring opening of **5** suggest that it is intermediate in strain energy between **1** and **2**. Epoxidation of **5** has led to the new strained propellane **6**.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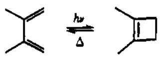
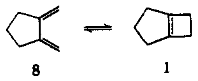
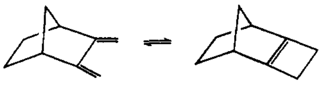
The photolysis (see Table I) of 2,3-dimethylenebicyclo[2.2.1]heptane (**7**) (2×10^{-2} *M* in pentane, 0°, medium-pressure mercury arc, Vycor filter) gives **5** in 80% yield: bp 57–58° (20 Torr); ir (gas cell) 2957, 2920, and 2860 cm^{-1}; mass spectrum *m/e* 120.0942 (120.0939, calcd for C_9H_{12}). The 100-MHz proton magnetic resonance spectrum (CH_2Cl_2) is consistent with the proposed structure with a multiplet at δ 2.46 (4 H), the AA'BB' multiplets of an AA'BB'XX' pattern centered at δ 1.53 (2 H) and δ 0.85 (2 H), the AB multiplet of an ABX_2 pattern centered at δ 1.16 (2 H) (J_{AB} = 8.2 Hz), and the X_2 multiplet at δ 2.84 (2 H). The structure of **5** is supported further by the thermal reversion to **7** and conversion to epoxide **6** and the known ketone **12**[4] (*vide infra*). Furthermore, we find that the photoconversions of 1,2-dimethylenecyclohexane (**8**) to $\Delta^{1(6)}$-bicyclo[4.2.0]octene (**10**)[5] and 1,2-dimethylenecyclopentane (**9**) to **1**[2a] are rapid and nearly quantitative. Thus **1** can be prepared in 30% overall yield from diethyl 1,2-cyclohexanedicarboxylate[6] and **10** prepared in 26% overall yield from pimelic acid.[7] These synthetic procedures for **1** and **10** give yields about twice those obtained from the Kirmse and Pook procedures *via* tosylhydrazone pyrolysis.[2a] Interestingly, the most strained cyclobutene of the series, **5**, is the most easily prepared in 54% overall yield in four steps from 1,4-dichloro-2-butene and cyclopentadiene.[8]

Table I. Quantum Yield for Ring Closure and Activation Energy for Ring Cleavage of Cyclobutenes

	Quantum yield[a]	% photocyclization yield (glpc)	Activation energy	% diene yield
	0.12[b]	71[c]	36.0[d]	100[d]
 9 10	0.11	>95	32.7[e]	57[f]
 8 1	0.11	>95	30.4[e]	58[f]
 7 5	0.025	80	26.6[g]	58[f]
 13 2	<0.01[i]		~18[h]	

[a] Photolyses in pentane at 10° were carried to 55% conversion. Quantum yields were determined from rate of disappearance of diene (by glpc) on irradiation in vycor with a low-pressure mercury lamp (2537 Å). [b] In agreement with R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962). [c] K. J. Crowley, *Tetrahedron*, **21**, 1001 (1965). [d] H. M. Frey, *Trans. Faraday Soc.*, **59**, 1619 (1963). Gas-phase pyrolysis gives no detectable product other than diene. [e] Pyrolysis in decalin 120–150°, monitored by glpc. [f] Yield represents 30% minimum conversion of olefin. [g] Pyrolysis in benzene, monitored by nmr. [h] Activation energy was estimated from ref 3d and the Arrhenius parameters from thermolysis of **1**, **5**, and **10**. [i] Based on slow rate of disappearance of 875-cm^{-1} band in ir spectrum of **13** on irradiation at −180° with a medium-pressure mercury arc.

The quantum yield for **1** is high (Table I), but that for **5** is fourfold lower. This appears to be a strain effect on the relative rates of ring closure for the excited states of **7** and **9**, since the diene chromophores are identical and probably have similar rates of radiative and nonradiative decay.[9] Prolonged irradiation of 1,2-dimethylenecyclobutane (**13**) at −79° (where the $\Delta^{1(4)}$-bicyclo[2.2.0]hexene, **2**, is known to be stable[3d]) leads to disappearance of **13**, but gives no observable Diels–Alder product from **2** after warming with cyclopentadiene. Irradiation of **13** in a mineral oil matrix at −180° leads to very little disappearance of the 875-cm^{-1} band in **11** under conditions where **9** rearranges rapidly to **10**. These experiments set an upper limit of 0.01 on the quantum yield for rearrangement of **13** to **2**. The strain effect observed in the quantum yield

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research, and to M. J. Meshishnek for preparation of **8** under a summer NSF Undergraduate Scholarship.

(2) (a) W. Kirmse and H. H. Pook, *Angew. Chem., Int. Ed. Engl.*, **5**, 594 (1966); (b) K. B. Wiberg, J. E. Hiatt, and G. Burgmaier, *Tetrahedron Lett.*, 5855 (1968).

(3) (a) K. B. Wiberg and G. J. Burgmaier, *ibid.*, 317 (1969); (b) P. G. Gassman, A. Topp, and J. W. Keller, *ibid.*, 1093 (1969); (c) K. B. Wiberg, E. C. Lupton, Jr., and G. J. Burgmaier, *J. Amer. Chem. Soc.*, **91**, 3372 (1969); (d) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *ibid.*, **93**, 246 (1971); (e) W. D. Stohrer and R. Hoffmann, *ibid.*, **94**, 779 (1972); (f) M. D. Newton and J. M. Schulman, *ibid.*, **94**, 773 (1972); (g) C. F. Wilcox and C. Leung, *J. Org. Chem.*, **33**, 877 (1968).

(4) C. F. Wilcox and R. G. Jesaitis, *ibid.*, **33**, 2154 (1968).

(5) Photochemical ring closure is reported for 3,4-dimethylenecyclohexene [J. M. Garrett and G. J. Fonkin, *Tetrahedron Lett.*, 191 (1969)] and dienes **8** and **9** [J. M. Garrett, Ph.D. Thesis, University of Texas, Austin, Tex., 1966].

(6) A. T. Blomquist and D. T. Longone, *J. Amer. Chem. Soc.*, **79**, 3916 (1957).

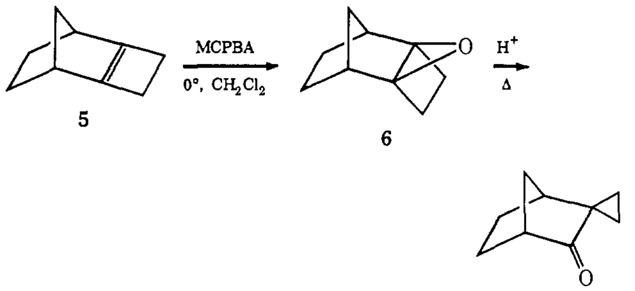
(7) A. T. Blomquist, J. W. Wolinsky, Y. C. Meinwald, and D. T. Longone, *ibid.*, **78**, 6057 (1956).

(8) M. A. P. Bowe, R. G. J. Miller, J. B. Rose, and D. G. M. Wood, *J. Chem. Soc.*, 1541 (1960).

(9) Absorption maxima for **7**, **8**, and **13** are all at 247 ± 1 nm with log ϵ of 4.02 ± 0.01: A. T. Blomquist and J. A. Vendol, *J. Amer. Chem. Soc.*, **77**, 1806 (1955); A. T. Blomquist, *ibid.*, **78**, 6057 (1956); W. J. Bailey and W. B. Lawson, *ibid.*, **77**, 1606 (1955). We know of no other cases of strain energy effects on rate constants of photoreactions.

for ring closure of **7** is apparently responsible for the low efficiency of ring closure of **13**. Gajewski's conclusion that efficient photochemical isotopic scrambling in **13** results from opening to an intermediate bis allyl radical rather than closure to **2** is confirmed by these experiments.[10]

Epoxidation of **5** with *m*-chloroperbenzoic acid in methylene chloride at 0° under nitrogen and careful water work-up gave a mixture of two products (separated by preparative glc) identified as 2-spirocyclopropylbicyclo[2.2.1]heptanone (**12**)[4] and 10-oxatetracyclo[4.2.1.1^{2,5}.0^{2,5}]decane (**6**) [mass spectrum *m/e* 136.0894 (136.0888, calcd for $C_9H_{12}O$)]. A 100-MHz nmr spectrum in dichloromethane is consistent with the proposed structure **6** with multiplets centered at δ 1.95 (4 H) and 1.58 (4 H), the AB multiplet of an ABX_2 pattern centered at δ 0.97 (2 H) (J = 9.2 Hz), and the X_2 multiplet at δ 2.62 (2 H). The acid-catalyzed conversion of **6** to the known ketone **12**[4] is very rapid and quantitative and confirms the structure of **6**. In contrast to its instability to acid, **6** is relatively stable thermally. At 192° the half-life for conversion of **6** to **12** in diphenyl ether is 5 hr.



5 **6** **12**

Further studies on the synthesis of related strained cyclobutenes and electrophilic and cycloaddition reactions of these molecules are under active investigation.

[10] J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **92**, 4457 (1970).

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Internal Conversion in the Photolysis of 1,3-Cyclohexadiene in the Gas Phase. Relationships between the Thermal and Photochemical Reactions of 1,3-Cyclohexadiene

Sir:

The photolysis of 1,3-cyclohexadiene (Chd) in the gas phase has been studied previously by Srinivasan[1–4] who divided the products into two classes:[3,4] (class I) those observed only in the photolysis, *i.e.*, the isomers 1,2,4- and 1,3,5-hexatriene; and (class II) those presumably observed in both the photolysis and the thermal reactions of Chd, *i.e.*, H_2, benzene, C_2H_2, C_2H_4, dimer, and/or polymer. It was argued by Srinivasan[3,4] that in the photolysis the class II compounds might be formed from "thermal" reactions of vibrationally excited ground-state molecules which originate from the initially formed excited singlet state by internal conversion.

The relationship between the photolytic and thermal products of Chd does not seem to be as simple as postulated by Srinivasan.[3,4] Indeed more recent studies on the thermal reactions of Chd[5–7] indicate (1) that C_2H_2 and C_2H_4 are unimportant pyrolysis products over the temperature ranges used[5,7] (these products accounted for about 5% of the Chd reacted at 1233°K),[8] (2) that hydrogen and benzene are not formed in equal yields and are formed in short chain reactions involving the cyclohexadienyl ($C_6H_7\cdot$) radical[5,7]

$$2\text{Chd} \longrightarrow C_6H_7\cdot + C_6H_9\cdot \tag{1}$$

$$C_6H_7\cdot \longrightarrow \text{benzene} + \text{H} \tag{2}$$

$$\text{H} + \text{Chd} \longrightarrow H_2 + C_6H_7\cdot \tag{3}$$

rather than in the unimolecular process 4 proposed for

$$\text{Chd}\dagger \longrightarrow \text{benzene} + H_2 \tag{4}$$

the formation of these products in the photolysis (Chd†, in the internal conversion hypothesis, is a vibrationally excited molecule in its ground electronic state), and (3) that polymer is not formed in the thermal reactions, the pressure drop being entirely due to dimer (*exo*- and *endo*-dicyclohexadiene) formation.[6]

The present study was undertaken to determine the relative importance of dicyclohexadiene formation in the photolysis of Chd in the gas phase. *No evidence for the formation of the dimers has been found.* The Chd (K & K Labs) was purified as described previously.[9] The reaction cell consisted of a cylindrical quartz sleeve which was placed concentrically around a Philips Philora HPK 125 medium-pressure mercury lamp. Chd at 50.0 ± 0.05° and at pressures up to 120 Torr was irradiated by the unfiltered light from the lamp. The resulting pressure drop was followed by means of a Pyrex Bourdon gauge. The photolysis was stopped after the total pressure had decreased by 20–70%, and the reaction products were analyzed using the gas chromatographic technique and column used previously.[9] A small peak (corresponding to less than 1% of the Chd reacted) with a retention time similar to that of *trans,cis,trans*-tricyclo[6.4.0.0^{2,7}]-dodeca-3,11-diene (the major product of photosensitization of Chd by triplet energy donors)[9–12] was observed. This product may have been formed by heterogeneous photosensitization of Chd[13] in spite of the precautions taken; the presence of this peak should therefore not be taken as evidence of the occurrence of the intersystem crossing $S_1 \rightarrow T_1$ in the photolysis. The only other gas chromatographic peaks observed have shorter retention times than those of the cyclohexadiene dimers formed in the thermal[6,10,11]

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