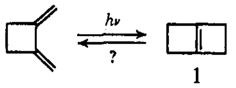
Mechanism and Stereochemistry of the Degenerate Photochemical Rearrangement of 1,2-Dimethylenecyclobutanes. The Possibility of Vibrationally Excited Intermediates and the Nonintervention of $\Delta^{1,4}$-Bicyclo[2.2.0]hexene

Sir:

In view of the possible relationship between the allene thermal dimerization and the degenerate thermal rearrangement of 1,2-dimethylenecyclobutanes,[1] the possibility of a photochemically induced degenerate rearrangement of 1,2-dimethylenecyclobutanes is of concern.[1g] An additional point of interest is the fact that the strained olefin, $\Delta^{1,4}$-bicyclo[2.2.0]hexene, **1**, is a potential product or intermediate in this photolysis.[1g]



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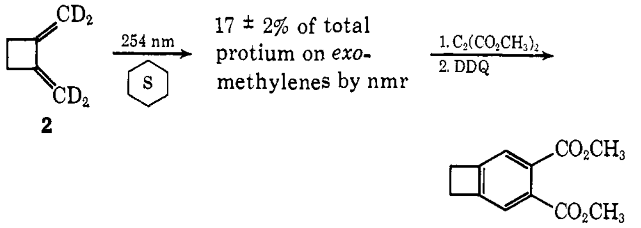
Direct photolyses of 1,2-(bisdideuteriomethylene)cyclobutane, **2**,[1d] at 254 nm in the vapor phase (10–550 Torr) or in cyclohexane-d_{12} solutions (1–2%) in quartz vessels resulted in rapid, intramolecular hydrogen–deuterium exchange in recovered starting material with no other products being detected.[2] In the vapor phase the relative quantum yield for exchange was inversely proportional to added inert gas pressure while the relative quantum yield for the solution reaction was very low compared to the gas-phase experiments. The relative quantum yield for the solution reaction was independent of whether the solution was saturated with nitrogen or oxygen prior to photolysis; even addition of di-*t*-butyl nitroxide (10% relative to **2**) had no effect. Finally, attempted sensitization of the reaction with acetophenone by irradiation at 300 nm in cyclohexane-d_{12} or chloroform-*d* at the same concentrations as in the liquid-phase direct photolysis gave no detectable exchange. Higher molecular weight materials (mol wt 160) were formed which were not characterized further.

The conceivable gross pathways for the photochemical exchange in **2** are: (a) reversible formation of **1**; (b) a process similar to the thermal[1c,d] one in which C_3–C_4 bond fission occurs with consequent or subsequent rotation around the C_1–C_2 bond to give a D_2 2,2′-bisallyl species, **4**, which could re-form 1,2-dimethylenecyclobutane by four equivalent pathways; and (c) reversible 1,3-hydrogen shifts *via* a 2-methyl-3-methylenecyclobutene intermediate. These were distinguished experimentally by converting exchanged material to 3,4-dicarbomethoxybicyclo[4.2.0]octa-1,3,5-triene, **3**, *via* a Diels–Alder reaction with excess dimethyl acetylenedicarboxylate and dehydrogenation with excess dichlorodicyano-*p*-benzoquinone (DDQ).[1d] Photolysis in cyclohexane carried to 17% conversion gave **3** with a d_3/d_4 ratio of 2[3] after the reaction sequence with each reaction being carried to completion to avoid complications due to isotope effects. Even at only 5% conversion the d_3/d_4 ratio was 2.[3] Since the mass spectral analyses for total rearrangement allow a calculation of the percentage of total protium on the *exo*-methylenes of exchanged **2** that corresponds closely to that actually determined by the nmr of exchanged **2**, the dehydrogenation must have occurred without hydrogen or deuterium shifts.



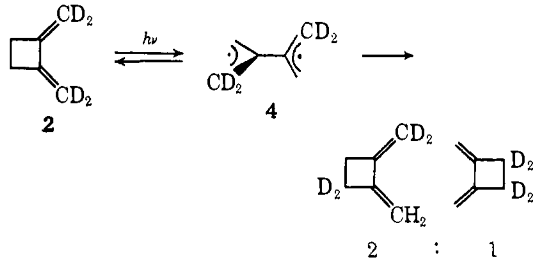
2

3

d_2, 69.7
d_3, 20.5
d_4, 9.8

These results rule out sole intermediacy of **1** (path a) and exclude path c. If hydrogen exchange by path c occurred, the precursor to **3**-d_4 could rise only by two sequential reversible shifts with the first of these giving the **3**-d_3 species. At the low conversions studied a d_3/d_4 ratio of 2:1 is impossible to achieve kinetically if both steps have the same rates.[4] Thus, an orthogonal or effectively so 2,2′-bisallyl diradical, **4**, either ground or excited state, is the most probable intermediate (path b).

path b:



2 4

The sensitization data make it clear that the diene triplet excited state is not responsible for the degenerate rearrangement,[5] and the lack of effect of oxygen and di-*t*-butyl nitroxide suggests that triplet states are not involved.[6] The inverse pressure dependence suggests that vibrationally excited ground states of **2** are involved and rearrange *via* **4**.[7] In this connection it is worthwhile noting that the activation energy for the de-

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[1] (a) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967); (b) T. L. Jacobs, J. R. McClenen, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969); (c) J. J. Gajewski and C. N. Shih, *ibid.*, **91**, 5900 (1969); (d) *ibid.*, **89**, 4532 (1967); (e) W. von E. Doering and W. R. Dolbier, Jr., *ibid.*, **89**, 4534 (1967); (f) J. J. Gajewski and W. A. Black, *Tetrahedron Lett.*, 899 (1970); (g) E. F. Kiefer and C. H. Tanna, *J. Amer. Chem. Soc.*, **91**, 4478 (1969).

[2] Vapor-phase photolyses were performed in 450-ml flasks in a Rayonet reactor with a single bulb for 2–30 min. Liquid-phase photolyses were performed with the same amount of **2** as in the vapor-phase photolyses but for longer periods.

[3] The total percentage of **3**-d_3 and **3**-d_4 is higher by 50% than the percentage of total protium on the *exo*-methylenes of the precursor to **3** because the precursor to **3**-d_3 has only half the *exo*-methylene protium as the precursor to **3**-d_4.

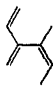
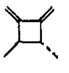
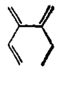
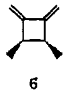
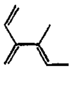
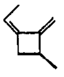
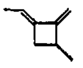
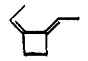
[4] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1953, pp 153–155.

[5] (a) Triplet sensitization of cisoid 1,3-dienes normally results in dimeric product[5b,c] as is apparently the case with the triplet state of **2**. (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 213. (c) W. T. Borden, L. Sharpe, and I. L. Reich, *Chem. Commun.*, 461 (1970).

[6] (a) D. W. Setzer, D. W. Placzek, R. J. Cvetanovic, and B. S. Rabinovitch (*Can. J. Chem.*, **40**, 2179 (1962)) point out with good reason that lack of oxygen quenching does not necessarily rule out triplet states in olefin and diene photochemistry, so our suggestion should be subject to that same reservation. (b) To our knowledge the efficacy of quenching of diene triplet states with di-*t*-butyl nitroxide has not been established. (c) The fact that Dowd[6d] has observed what appears to be triplet bisallyl diradical upon photolysis of perprotio **2** at 77°K does not require that triplet states be formed immediately upon photolysis of **2**; indeed, intersystem crossing in dienes is a process of low efficiency.[5b] (d) P. Dowd, *J. Amer. Chem. Soc.*, **92**, 1066 (1970) (footnote 12).

[7] (a) R. Srinivasan, *Advan. Photochem.*, **4**, 113 (1966); (b) ref 5b, pp 188–190.

Table I. Vapor Phase Photolysis of *trans*- and *cis*-3,4-Dimethyl-1,2-dimethylenecyclobutanes,[a] **5** and **6**, at 254 nm in Quartz Vessels

Compd	Total pressure, Torr[b]/ time, min[f]	 [c]	 5·		 6						
5	2/2	0.475	88.5	1.18	4.0	1.28	1.28	2.13	0.12	0.66	0.475
5	45[d]/2	0.37	94.6	0.34	2.29	0.1	0.78	1.23	0.024	0.092	0.114
5	304[e]/30	0	93	0	1.2	0	1.2	4.6	0	~0.1	~0.05
6	2/2	0.35	1.17	1.17	91.2	1.87	1.17	2.1	0.12	0.7	0.23
6	45[d]/2	0.04	7.2	0.04	89.9	0.042	1.27	1.27	0.017	0.085	0.04
6	315[e]/15	0	4.16	0	87.5	0	4.16	4.16	0	Trace	0

[a] For the structural and stereochemical assignments of these materials and the photolysis products, see ref 1c. [b] The partial pressure of **5** or **6** in each experiment was 2 Torr. [c] This material which was not previously reported in the thermal rearrangement (ref 1c) had appropriate spectroscopic properties. [d] Pentane was the added gas. [e] Nitrogen was the added gas. [f] All photolyses were conducted in the same flask with the same uv source.

generate thermal rearrangement is 46.8 kcal/mol[1e] while 254-nm radiation corresponds to an energy of 114 kcal/mol.

In order to determine the stereochemistry of the rearrangement, the *trans*- and *cis*-3,4-dimethyl-1,2-dimethylenecyclobutanes, **5** and **6**,[1c] were also photolyzed at 254 nm in the vapor phase, and again the relative quantum yields for rearrangement were inversely proportional to pressure. Moreover, the product distribution depended on inert gas pressure with hydrogen-shifted materials being major products at low pressure (Table I). At higher pressures hydrogen shifts were suppressed, and the products consisted of all of the other isomeric nongeminal dimethylenecyclobutanes derivable from 1,1′-dimethyl-**4**.[2] These were formed with some but not complete stereospecificity under conditions where the products were stable indicating a slight preference for conrotatory ring opening;[1c] however, this should be contrasted with the thermal process where conrotatory ring opening is highly favored.[1c] It should also be noted that recovery of material was very high in these photolyses indicating that cleavage to methylallene is not a favorable competing process.

Remarkably, the photolytic rearrangement of **5** and **6** in cyclohexane solution could not be detected, and after extended photolyses the starting material disappeared and no isomeric species could be detected even in solutions whose concentrations of **5** and **6** were equivalent to that in the vapor-phase experiments. This can be rationalized on the basis of a lower rate of spontaneous rearrangement of vibrationally excited **5** or **6** relative to **2** due to extra vibrational modes in the former cases. Thus, collisional deactivation competes more favorably with rearrangement in the former cases,[8] resulting in an inexorably slow rate of rearrangement of **5** and **6** in solution.

We do not regard it as critical that vibrationally excited intermediates produced upon photolysis give exactly the same product distribution as in the thermal process, particularly regarding stereochemistry as is the case here. Indeed, hydrogen shifts which are relatively high energy paths in the degenerate thermal rearrangements of **5** and **6** are the major pathways upon photolysis of **5** and **6** at low pressure. This observation is not unlike that of Srinivasan with photolysis of 1,3-butadiene where vibrationally excited species were also invoked.[7a] However, the nature of the relationship between photolysis and thermolysis either here or in other systems[7a] has yet to be delineated.

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(8) For a discussion of this point, see S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, Chapter 9.

Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XVIII. The Conformation of Cycloheptanesemidione[1]

Sir:

Relatively few conformational studies have been performed for cycloheptene derivatives. It has been reported that 1,2-benzocyclohepten-5-one exists mainly in the chair form[2] but it has been calculated that the boat form of cycloheptene is more stable than the chair form.[3]

Nmr studies of substituted cycloheptenes and benzocycloheptenes have shown that in some cases only one conformation is populated,[4] while in other instances more than one conformation is populated at room temperature.[5]

We have previously demonstrated that cyclohexane semidione and cyclohexene have similar conformations with similar energy barriers for ring inversion.[6] We have thus examined by esr spectroscopy cycloheptanesemidione, a paramagnetic analog of cycloheptene. It

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(1) Semidiones. XIII. This work was supported by grants from the National Science Foundation and National Institutes of Health.

(2) N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 722 (1962).

(3) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Amer. Chem. Soc.*, **90**, 5773 (1968).

(4) S. Kabuss, H. Friebolin, and H. Schmid, *Tetrahedron Lett.*, 469 (1965); R. Knorr, C. Ganter, and J. D. Roberts, *Angew. Chem., Int. Ed. Engl.*, **6**, 556 (1967).

(5) S. Kabuss, A. Luttringhaus, H. Friebolin, H. G. Schmid, and R. Mecke, *Tetrahedron Lett.*, 719 (1966); H. Hart and J. L. Corbin, *J. Amer. Chem. Soc.*, **87**, 3135 (1965); E. Grunwald and E. Price, *ibid.*, **87**, 3139 (1965).

(6) G. A. Russell, G. Underwood, and D. C. Lini, *ibid.*, **89**, 6636 (1967).