Double-Bond Geometric and Degenerate Structural Photoisomerization of 1,2-Dimethylenecyclobutanes[1]

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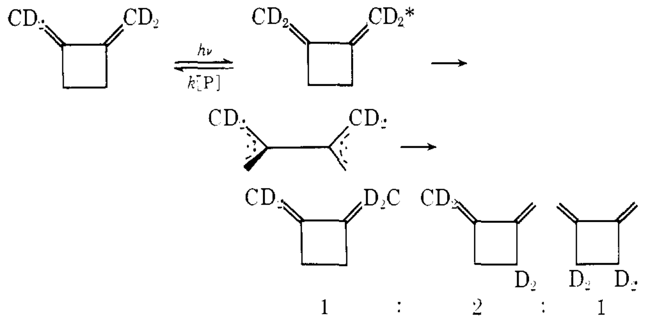
Abstract: Photolysis of 1,2-bis(dideuteriomethylene)cyclobutane (DMCB-d_4) at 254 nm in hexane resulted in a degenerate structural rearrangement. Degradation of the recovered starting material revealed a deuterium distribution consistent with the intermediacy of a rapidly central-bond-rotating 2,2′-bisallyl biradical. Triplet sensitizers and quenchers had no effect on this reaction. Photolysis of DMCB-d_4 in the vapor phase resulted in the degenerate structural arrangement as well as cleavage to allene, butatriene, and ethylene. The deuterium distribution in the latter two products required that they arise from structurally isomerized material, and the relative yield of these products decreased with increasing pressure. Vapor-phase photolyses of *cis*- and of *trans*-3,4-dimethyl-1,2-dimethylenecyclobutane indicated an 80% preference for conrotatory opening of the cyclobutane ring, and the relative quantum yield for structural rearrangement decreased with increasing pressure to the point that no reaction was observed in solution. Vapor-phase photolyses of the 1,2-diethylidenecyclobutanes revealed geometric isomerization about only one double bond as well as structural rearrangement. The relative quantum yield for geometric isomerization increased with increasing pressure, while that for structural isomerization decreased. Thus the pressure effects and stereochemical results are consistent with electronic excitation to cause diene geometric isomerization producing vibrationally hot dienes which then undergo structural isomerization. Since the degenerate structural isomerization of the parent DMCB occurs even in solution, the vibrationally hot DMCB species is not collisionally deactivated before undergoing ring fission.

We have reported, in a preliminary way,[3a] that 1,2-dimethylenecyclobutane (DMCB) underwent a degenerate structural rearrangement upon photolysis in either the vapor phase or solution, and that degradation of deuterium-labeled materials, as well as the reaction of 3,4-dimethyl-DMCB's indicated formation of a freely rotating bisallyl biradical. Since the relative quantum yields for isomerization appeared to be inversely proportional to pressure, vibrationally hot DMCB's were indicated as precursors to the bisallyl biradicals whose intermediacy in the thermal degenerate structural rearrangements of DMCB's has been well established.[3b-e]



In view of widespread interest in diene photolyses due to the variety of reaction pathways, observed, namely formation of cyclobutenes,[4-13] bicyclobutanes,[5,13-15] alkyl cyclopropenes,[4,5,13] 1,3- and 1,5-hydrogen shift materials,[7,9,10,15-18] as well as fragmentation products,[19,20] we wish to record the details of this new type of structural isomerization in diene photochemistry. Moreover, the pressure dependence of this reaction and the accompanying double-bond geometric isomerization were studied in relation to recent reports of efficient one-bond geometric isomerization of conjugated dienes.[17]

The photochemistry of conjugated dienes depends greatly on electronic multiplicity. The reactions described above for dienes upon direct photolysis are not quenched by oxygen or other radical species nor do they occur upon deliberate triplet sensitization indicating that singlet states are involved.[21,22] On the other hand, dimerization[23] and two-bond geometric isomerization[24,25] are characteristic of diene triplet states. In connection with the possible production of 2,2′-bisallyl in the photochemistry of DMCB, it is of importance to discover the effect of direct and triplet sensitized excitation since the bisallyl biradical appears to have a triplet ground state,[25] and its role in the photolytic rearrangement is of concern.

Finally, the role of vibrationally excited species in diene photochemistry has been of interest. Srinivasan has suggested that diene photoproducts, resulting from hydrogen shift and cleavage, which are also thermal products of dienes, are formed from vibrationally hot dienes. As expected, the quantum yield for formation of these is inversely proportional to pressure.[19,20] However, most diene photoisomers are thermodynamically less stable than the dienes and revert to them upon thermolysis. Thus, vibrationally hot ground states of dienes cannot be responsible for these products. Another pathway, namely formation of excited isomer from excited diene, is easily excluded on grounds of energetics.[10] By elimination, therefore, a vibrationally hot ground state of the product must be formed directly from an excited state of the diene with collisional deactivation being faster than rearrangement.[27] Srinivasan has evidence for this,[18] and there is good quantum mechanical justification as well.[28] The production of and reactions of vibrationally hot species in solution photochemistry of dienes or even of chemically activated dienes have yet to be delineated, although circumstantial evidence[29] as well as theory[30] points to their possible role particularly in small molecules when the rates of spontaneous reaction may effectively compete with collisional deactivation. Since DMCB undergoes a photoinduced structural isomerization with an inverse pressure dependence but still reacts even in solution, further exploration of this system was deemed necessary.

Results

Photolysis of 1,2-Dimethylenecyclobutane-d_4. Photolyses of 1,2-bis(dideuteriomethylene)cyclobutane (DMCB-d_4) were conducted in quartz vessels with a Rayonet source emitting 254-nm radiation. In the vapor phase or liquid phase (cyclohexane-d_{12}), a hydrogen-deuterium exchange was observed in the recovered starting material. The relative quantum yield for the solution reaction did not change

Table I. Direct Photolysis of 1,2-Bis(dideuteriomethylene)-cyclobutane in Cyclohexane[a] at 254 nm

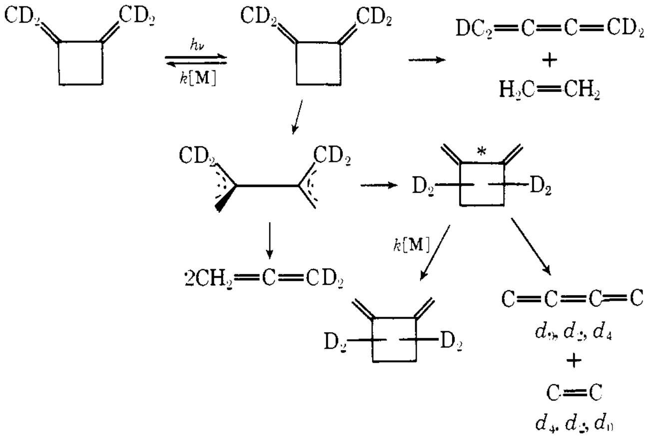
Reaction time, min	8.25	20[b]	20
% total protium on exo methylenes	5.0	13.6	17.3
M/e 222:223:224	114:23:6	103:35:14.5	84:37:17
% DBC-[c]d_2	92.5	77.7	69.7
% DBC-d_3	5.0	15.0	20.5
% DBC-d_4	2.4	7.3	9.8
(DCB-d_3/2) + DCB-d_4[d]	4.96	14.8	20.05

[a] Degassed by bubbling nitrogen through the solution for 20 min. [b] In degassed C_6D_{12}; this experiment was conducted at a different time than the other two. [c] The recovered material was treated with excess dimethyl acetylenedicarboxylate and dehydrogenated with DDQ to give the dicarbomethoxybenzocyclobutenes, DBC-d_2, -d_3, and -d_4.[3b,d] [d] This gives the per cent total protium that should have been observed in the nmr given the observed d_2, d_3, d_4 ratios.

regardless of whether the solvent was saturated with nitrogen or oxygen prior to photolysis or if di-*tert*-butyl nitroxide was present (10% relative to DMCB-d_4). Attempted sensitization of the solution reaction by irradiation at 300 nm with acetophenone present resulted in no H-D exchange; only dimeric products were found as subsequently reported by Borden,[31] and these dimers had no protium on double bonds. Thus we conclude that the H-D exchange in solution proceeded *via* singlet excited states without intervention of triplet states and, by reasonable extrapolation, in the vapor phase as well.

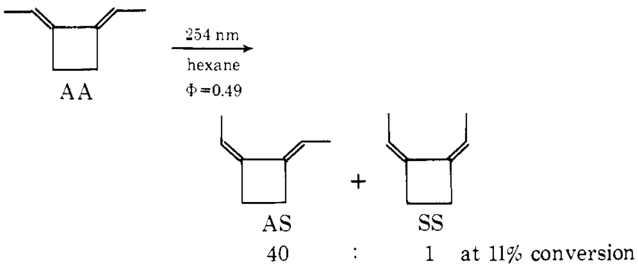
Gross Mechanistic Pathway. In order to determine the deuterium distribution in the rearranged product, the recovered photolysate from the liquid-phase reactions was treated with excess dimethyl acetylenecarboxylate to give the Diels-Alder adducts, and these were dehydrogenated with excess dichlorodicyano-*p*-benzoquinone.[3b,d] Analysis of the mass spectrum of the resulting dicarbomethoxybenzocyclobutenes (DCB) revealed a DCB-d_3 to DCB-d_4 ratio of 2.07 ± 0.02 regardless of whether the reaction was carried to 5 or 17% rearrangement. The per cent rearrangement determined from nmr integrations agreed reasonably well with the per cent rearrangement calculated from the mass spectrometric determinations (Table I). It is difficult to rationalize a constant DCB-d_3 to DCB-d_4 ratio at different relatively low conversion reactions, unless there are carbon shifts occurring to interchange the four methylenes in a single step. The simplest scheme for doing this involves formation of a 2,2-bisallyl biradical (BA) which is free to rotate about the central bond, and reclosing to the three possible isomers giving twice as much of the unsymmetrical isomer as either of the other two for reasons of statistics.

Cleavage Products and Effect of Pressure. When great care was taken to isolate all possible products from the vapor-phase irradiation of DMCB-d_4, the cleavage products allene, ethylene, and butatriene were also observable by nmr. Irradiation in the presence of 50 Torr of argon resulted in 49% rearrangement of DMCB-d_4; 3% was converted to allene and 17% to ethylene and butatriene. Irradiation in the presence of 760 Torr of argon under otherwise identical conditions, resulted in 52% rearrangement of DMCB-d_4, and 3% was converted to allene but only 1% to ethylene plus butatriene. Mass spectroscopy revealed that the butatriene, from an irradiation in the presence of 250 Torr of helium, contained d_0. d_2. and d_4 materials in the ratio of 4:8:7 respectively, and butatriene from irradiation at very low pressures had a d_0 to d_2 to d_4 ratio of 1:2:1, respectively. These observations suggest that the butatriene product resulted from vibrationally hot DMCB-d_4 which had already rearranged to a great extent. Collisional deactivation of the vibrationally hot, rearranged, DMCB-d_4 by added argon or helium resulted in less cleavage and overall less reaction. Thus the relative quantum yield for conversion of starting material is inversely proportional to pressure, but at low pressures, cleavage is an important mode of decomposition of the rearranged material.



Double-Bond Geometric *vs.* Structural Isomerization. Because the photoinduced rearrangements of DMCB-d_4 must have resulted from $\pi\pi^*$ excitation of the diene chromophore, it is was important to examine the partitioning of energy between the diene system (which could result in double-bond geometric isomerization) and the ring system (which would be responsible for the structural rearrangement). Thus, a study of the solution and vapor-phase photolysis of *anti,anti*-1,2-diethylidenecyclobutane (AA) was initiated.

Irradiation of AA in hexane solution at 254 nm resulted only in geometric isomerization to *syn,anti*-1,2-diethylidenecyclobutane (SA) and *syn,syn*-1,2-diethylidenecyclobutane (SS). At 11% conversion, the SA:SS ratio was greater than 40:1 indicating photoisomerization about only one bond of AA just as with the 2,4-hexadiene.[17] It should be noted that both AS and SS have a smaller extinction coefficient at 254 nm than AA. The quantum yield for geometric isomerization was determined to be 0.49 using the trans-cis isomerization of *trans,trans*-2,4-hexadiene as the actinometer.



Irradiation of AA in the vapor phase at 254 nm gave significantly different results from the solution experiments. These are given in Table II. The relative quantum yield for reaction of AA decreased with increasing pressure, and the product distribution varied with pressure. The geometric isomerization products, SA and SS, were formed as well as the other methyl-labeled dimethylenecyclobutanes that could result from ring opening to a bismethallyl biradical. Furthermore, all the isomeric trienes which could arise from the products by 1,5-hydrogen shifts were formed. These hydrogen-shifted materials are also formed upon thermolysis of the dimethyl-DMCB's.[3d]

At 80 Torr of added gas, the hydrogen-shifted trienes were quenched to 10-25% of their "zero" pressure (initial) values, and the rearrangement products were quenched to about 50% of their zero pressure values, while the geomet-

Table II. Direct Vapor-Phase Photolysis of Dimethyl-DMCB's at Various Pressures of Nitrogen

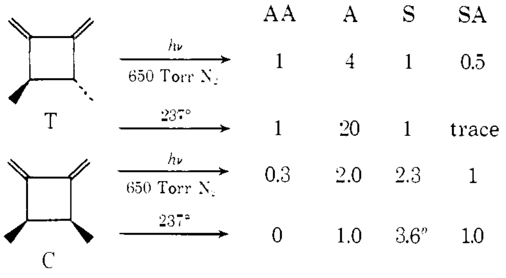
	Pressure, Torr	*c*-HD[a]	T[b]	PD[c]	C[b]	*t*-HD[d]	S[b]	A[b]	Unknown	SS[b]	SA[b]	AA[b]
AA[b,e]	0	0.080	0.676	0.894	0.376	0.443	0.866	1.589	0.010	0.164	1.23	93.7
	79.6	0.008	0.385	0.261	0.232	0.044	0.465	0.724	0.022	0.107	2.48	95.3
	148.8	0.003	0.257	0.144	0.159	0.023	0.306	0.458	0.022	0.084	2.82	95.7
	300.4	0.002	0.200	0.102	0.127	0.018	0.241	0.349	0.022	0.068	2.92	96.0
	646.8	Trace	0.072	0.023	0.048	0.007	0.094	0.119	0.012	0.055	3.30	96.3
SS[b,e]	0	0.485	0.543	3.46	0.395	1.89	0.910	1.47	0.08	89.58	0.768	0.41
	75.4	0.077	0.445	1.146	0.467	0.243	1.539	0.754	0.10	91.80	2.932	0.277
	151.2	0.042	0.292	0.692	0.337	0.107	1.126	0.602	0.12	92.81	3.620	0.24
	301.2	0.029	0.175	0.362	0.209	0.054	0.696	0.367	0.134	93.84	3.962	0.18
	648.6	0.013	0.089	0.158	0.114	0.030	0.355	0.235	0.1348	94.29	4.363	0.11
T[b,e]	0	0.148	94.08	0.634	0.390	0.704	0.908	2.07		0.109	0.414	0.536
	76.0	0.016	96.642	0.03	0.292	0.057	0.535	1.747		0.075	0.221	0.385
	151.0	0.011	97.72	Trace	0.220	0.017	0.348	1.237		0.038	0.136	0.272
	300.0	0.004	98.72	Trace	0.115	0.006	0.192	0.719		0.015	0.074	0.159
	650.0	Trace	99.30	Not obsd	0.065	Trace	0.101	0.404		Trace	0.024	0.104
C[b,e]	0	0.321	0.707	1.233	92.2	1.395	1.082	1.718	0.017	0.162	0.692	0.466
	75.4	0.0353	0.659	0.140	94.8	0.181	1.542	1.521	Trace	0.140	0.694	0.247
	150.6	0.016	0.481	0.059	96.3	0.070	1.186	1.072	Trace	0.098	0.516	0.160
	219.4	0.008	0.293	0.025	97.8	0.021	0.738	0.612	0	0.050	0.330	0.095
	649.0	Trace	0.171	0.014	98.7	0.006	0.437	0.356	0	0.033	0.194	0.055

[a] *cis*-3-Methylene-4-methyl-1,4-hexadiene. [b] For structure see text. [c] 3-Methylene-4-ethyl-1,4-pentadiene. [d] *trans*-3-Methylene-4-methyl-1,4-hexadiene. [e] Compound pressure varied between 10 and 2.0 Torr.

ric-isomerization product, SA, increased by a factor of 2. At 650 Torr of added gas, only very small amounts of product other than SA were formed, and the amount of this latter substance had increased to nearly a constant value. Thus the high-pressure run resembled the solution photolysis of AA. *syn,syn*-1,2-Diethylidenecyclobutane (SS) was also irradiated in the gas phase with results comparable to those from irradiation of AA, *i.e.*, trienes were major products at low pressures, but with increasing pressures, the SA isomer became the major product. Here again the relative quantum yield for loss of starting material decreased with increasing pressure.

Stereochemistry of the Structural Isomerization. In order to examine the stereochemistry of the structural rearrangement and thereby gain information about the structures of the intermediate(s), *trans-* and *cis*-3,4-dimethyl-1,2-dimethylenecyclobutane (T and C, respectively) were photolyzed at 254 nm. In solution, no reaction was observed save very slow conversion to high-molecular-weight materials. In the vapor phase at low pressure, all of the products observed from AA were found from photolysis of both T and C (Table II). At higher pressures, the hydrogen-shifted materials were quenched to a greater extent than the carbon-shifted products, and at higher pressures, the reaction mixtures approached a constant ratio of products.

Significantly, the photolysis of T and C at high pressures gave product distributions that somewhat resembled those obtained upon thermolysis of T and C. Thus from T, the major products were AA, *anti*-1-ethylidene-2-methylene-3-methylcyclobutane (A), and *syn*-1-ethylidene-2-methylene-3-methylcyclobutane (S) in a 1:4:1 ratio, while those from C were AS, A, and S in a 1:2:2.3 ratio.



[a] This could be as high as 6.4 if the hydrogen-shifted product derived from S were included.

Discussion

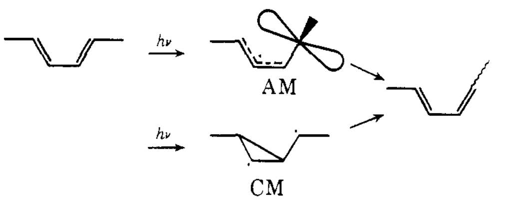
The photolyses of dimethylenecyclobutanes at 254 nm lead to geometric isomerization of one of the double bonds and to a degenerate structural isomerization of the type similar to that induced by thermolyses of these compounds. The purpose of this study was to delineate the electronic pathways for these interconversions by examining (a) the effect of pressure on the reactions and (b) the stereochemistry of the processes.

Electronic Multiplicity of the Photolyses. Since irradiation of conjugated dienes at 254 nm in solution usually results in geometric isomerization of one double bond as well as cyclobutene and bicyclobutane formation, and since triplet sensitization of dienes results in loss of stereochemical integrity of both double bonds as well as dimer formation (particularly with fixed cisoid dienes), it is safe to assume that the photoreactions of 1,2-dimethylenecyclobutane are singlet reactions. Proof of this assumption comes from the observations that di-*tert*-butyl nitroxide, a good triplet quencher, had no effect on the reaction in solution, and deliberate sensitization gave only dimeric products and no structural rearrangement in solution where direct irradiation of DMCB-d_4 resulted in rearrangement. *It is significant that the dimeric products from sensitization of DMCB-d_4 had no protium on the exocyclic methylenes, indicating that rearrangement via a symmetrical triplet state of the bisallyl biradical did not occur prior to dimerization.* Thus the dimerization occurred *via* the triplet state of the diene moiety.

Double-Bond Geometric Isomerization of DMCB. Upon irradiation in solution, AA isomerizes to AS with little crossover to SS. It is difficult to obtain the AS/SS partitioning ratio from AA without a study comparable to that of Saltiel of the 2,4-hexadienes; nonetheless, it is clear that the ratio is higher than 40.

Two general mechanisms have been proposed to rationalize one-bond isomerization, one being formation of allyl-orthogonal methylene biradical or zwitterion, AM, the other being a cyclopropyl methylene biradical or zwitterion, CM. These are shown below for a cisoid diene.

The AM intermediate has been suggested by Dauben[13] who, moreover, felt that it ought to be an allyl cation-methylene anion species. It was assumed that this species was no longer electronically excited and that the allyl cation moiety could retain its stereochemistry. Srinivasan favored the CM

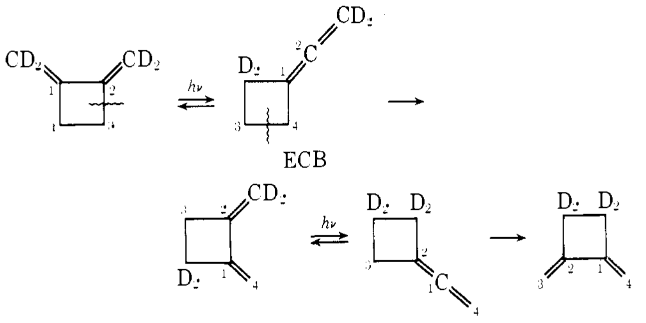


biradical pathway because it would also account for alkylcyclopropene and bicyclobutane formation in the solution photolysis of dienes.[18] Saltiel suggested that the CM biradical could be formed stereospecifically from the excited state of the diene *via* conrotation if just the highest occupied molecular orbital controlled the reaction; rotation could then occur about just the exocyclic bond, and conrotatory reopening of the cyclopropyl radical in only the reverse sense of its formation could give one bond-isomerized diene.[17a]

In the photogeometric isomerization of AA and SS, either pathway can be traversed. The AM species should be considerably less strained than a CM species here, but there may be enough energy available on excitation with 254-nm light to overcome any difference due to strain.

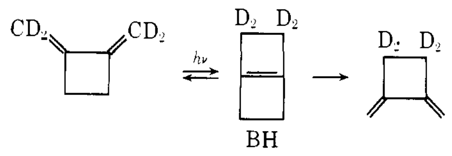
Structural Isomerization. The types of products derived upon photolysis of the dimethylenecyclobutanes suggest that rupture of the 3,4 bond occurs giving a bisallyl biradical which can either reclose to its precursor or to the other dimethylenecyclobutanes with carbons scrambled. The fact that a near-statistical distribution of the bis(dideuteriomethylene)-DMCB's was formed from 1,2-bis(dideuteriomethylene)cyclobutane, and that the same carbon-scrambling rearrangement was observed with the dimethyl-DMCB's, makes unlikely the possibility that reversible hydrogen shifts were responsible for the reaction.

The possibility of structural isomerization occurring by 2,3-bond fission and rearrangement to make ethenylidenecyclobutane (ECB), which reopens under the reaction conditions and rearranges back *via* two equivalent pathways, appears unlikely since a second quantum of energy is necessary to give the rearrangement product with both CD_2 groups on the the ring; at very low conversions, the ring mono-CD_2 to ring di-CD_2 ratio was 2:1.

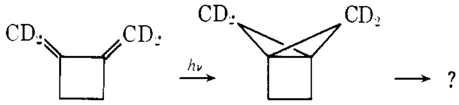


The assumption of 2 quantum of absorption being necessary for conversion to ring di-CD_2 material could be invalid if the DMCB formed from the allene were still hot and reacted further. We suspect, however, that C_1-C_4 fission is a very much higher energy process than C_3-C_4 fission judging by the ease of quenching of the ethylene-butatriene product relative to that of allene at increasing pressures.

A second pathway for isomerization is formation of a cyclobutene, namely $\Delta^{1,4}$-bicyclo[2.2.0]hexene (BH), in this case followed by ring opening. However, this pathway only interconverts starting DMCB-d_4 and the ring di-CD_2 material; therefore, it cannot be solely involved. Both above mechanisms operating simultaneously in fortuitously a 2:1 proportion will account for the results. However, the stereochemistry of the product from the dimethyl-DMCB's is not correct. For instance, at low conversions, AA should give just C by the cyclobutene path, just as with *trans,trans*-2,4-hexadiene,[6] but, in fact, both T and C are produced in about a 3:2 ratio at all pressures. The simultaneous intervention of both pathways is unlikely.[32]

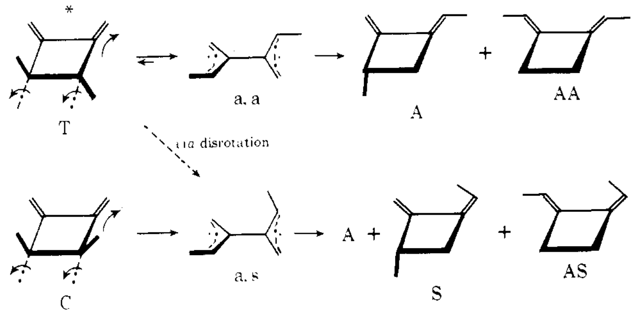


A bicyclobutane could conceivably be formed upon photolysis of DMCB but it is, in reality, a [2.1.1]propellane. Without commenting on the stability of this species,[33] it seems unlikely that it could be involved in the structural isomerization of DMCB unless a rather complicated, unprecedented series of bond shifts occurs.



Thus by exclusion and by analogy with the thermal rearrangements of DMCB's, an orthogonal or rapidly rotating central-bond bisallyl biradical is assumed to be the intermediate responsible for the structural photoisomerization of the DMCB's.

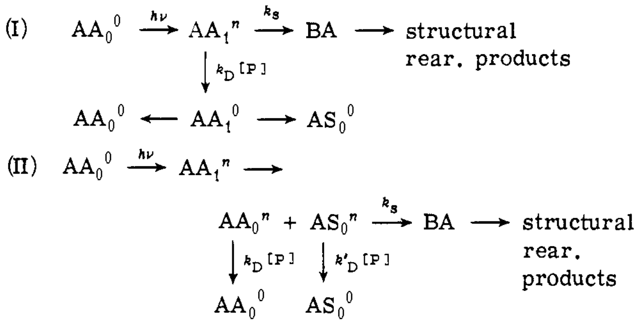
Structure of the Bisallyl Biradical. Examination of the products of the photolysis of the 3,4-dimethyl-DMCB's should give some insight into the structure of the bisallyl biradical produced in the reaction as in the thermolyses. At high pressures, the major diethylidenecyclobutane formed from T is AA, while that from C is AS. This is similar to the thermolysis of these compounds and, like the thermolysis, implies that the cyclobutane ring opens conrotatory to give the *anti,anti*-1,1′-dimethylbisallyl biradical which can close to either AA or A. By a similar set of motions, C, can give a *anti,syn*-1,1′-dimethylbisallyl biradical which can close to AS, as well as to both A and S.



The best indicator of stereospecificity in the ring opening of T and C is the relative amounts of the diethylidenecyclobutanes. Inspection of Table II reveals an AA/AS ratio of 4 from T at high pressures but a nearly inverse ratio from C. Furthermore, the ratio of the monoethylidenes A/S from T is also 4, suggesting a fourfold preference for conrotatory over disrotatory opening of T and probably the same for C. The specificity in the photochemical ring opening of T, however, is not as high as the thermal opening in which a 20-fold preference is exhibited.[3d] This difference may well be due to the high internal energies of the biradical produced upon photolysis or formation of vibrationally excited products which rearrange further as suggested by the lower specificity at low pressures.

Structural and Geometric Isomerization as a Function of Pressure. There must be at least two states of photoexcited DMCB that are responsible for the chemistry: one to account for the geometric isomerization quantum yield being proportional to pressure-leveling out at 0.49 and a second to account for an inverse pressure dependence of structural isomerization. Two different gross pathways can be written that will account for the pressure dependencies observed in both the geometric and structural isomerizations. These two pathways differ in the origin of the structural rearrangement product. In the first, it is assumed to result from a bisallyl biradical derived from a ring fission in a vibrationally hot, electronically excited state, and increasing pressure deactivates this state so that only double-bond geometric isomerization can occur. The second pathway assumes that geometric isomerization occurs to give vibrationally hot ground-state dienes which can either open to a bisallyl biradical or be quenched to ground-state diene. Of course, the geometric isomerization cannot be observed with T and C, but whatever the process, the ring opening must occur predominantly in a conrotatory way in order to account for the observed stereoselectivity. The mechanisms drawn in Scheme I do not take into account hydrogen-shifted products, but we assume that the structurally rearranged products are formed vibrationally hot and must be collisionally deactivated before hydrogen shifts will occur to give the thermodynamically more stable triene products.

Scheme I



If the steady-state assumption is applied to these, then there should be a linear relationship between Φ (structural) and P_{N_2} which was, in fact, observed. If either mechanism were involved, there should be a linear relationship between Φ (geometric) and $1/P$ which appears to be roughly true, although here the low-pressure point is less than expected by extrapolation from the others, but linearity is difficult to assess because of the distance between the low point and all others on a reciprocal scale. Moreover, the low-pressure point is with only AA present, and its collisional quenching efficiency is no doubt higher than that of N_2, and this could account for the nonlinearity observed.

A distinction between the two mechanisms in favor of the vibrationally hot ground state (mechanism II) derives from the stereochemistry of the products from AA (Table II). Even at high pressures, AA gives both T and C in a ratio of 1.5:1 and both A and S in nearly equal quantities. Since photolyses of T and C give rearrangement products with substantial stereospecificity implying that the intermediate BA biradical possesses some geometric stability, the BA biradical derived directly from AA should be the same as that from T and give the same distribution of products. The products most easily compared are the A and S monoethylidenes, and clearly AA does not give the 4:1 ratio of A:S as does T. Thus, it appears that AA gives rise to the BA biradicals derived from both T and C, a conclusion reinforced by the formation of both T and C in the photolysis of AA. Since the structural isomerization of AA occurred with little stereospecificity, the geometric integrity of the diene system must have been lost prior to localization of the energy in the C_3-C_4 bond resulting in cleavage. If geometric isomerization of dienes involves photochemical generation of singlet biradicals followed by recombination to ground-state dienes as suggested by Dauben[13] and by Saltiel,[17a,b] then the structural rearrangement of DMCB must proceed *via* vibrationally hot ground-state dienes, *i.e.*, mechanism II.

Further support for the origin of structural rearrangement being vibrationally hot species comes from the fact that the parent compound DMCB-d_4 does rearrange in solution to a measurable extent; however, the dimethyl-DMCB's undergo only double-bond geometric isomerization in solution. This is consistent with the RRKM formulation for the relative rates of spontaneous reaction of hot species: the more vibrations over which vibrational energy can be partitioned, the lower the rate of spontaneous reaction due to the lower probability at localizing the energy in the bonds that are to be broken; thus, collisional deactivation becomes an important process with larger molecules.[34]

We can make a rough guess about reaction rates of vibrationally hot ground-state DMCB. Using the RRKM expression with DMCB possessing 114 kcal/mol excess energy and having an activation energy for rearrangement of 46 kcal/mol,[3c] and having 36 vibrational modes, a rate constant of 1.4×10^5/sec is calculated. For the dimethyl-DMCB, a rate constant of 3.5×10^2/sec is calculated. Since collision frequencies in solution are about 10^{11}/sec,[34] the effective number of vibrations in each case would have to be substantially less for reaction to compete with collisional deactivation. For instance, if only half the modes stored energy in DMCB, its rate constant for rearrangement would be about 10^9/sec and dimethyl-DMCB would be about 6×10^7/sec. Depending on how effective collisional deactivation is, the rearrangement, particularly with the parent DMCB, could become competitive and observable.

Finally, the fact that the product distributions from photolysis reveal less stereospecificity than from the thermolyses does not rule out vibrationally hot DMCB ground states as being responsible for the photoproducts. Indeed, highly vibrationally excited species approaching an energy surface from a higher potential would be expected to be less discriminating than those produced upon collisional activation of ground-state molecules.

Experimental Section

General. Nuclear magnetic resonance spectra were recorded on Varian A-60, HR-100, and HR-220 spectrometers. Carbon tetrachloride was used as a solvent with TMS as an internal reference; chemical shifts are reported as δ values in parts per million downfield from TMS. Analytical vapor-phase chromatography was performed on a Varian Aerograph 1220-2 (capillary) instrument using a 200 ft × 0.01 in. i.d. di-*n*-butyl tetrachlorophthalate (DBTCP) column or on an F & M 776 gas chromatograph equipped with a low-volume injector and a 18 ft × ⅛ in. oxydipropionitrile column with a 6 ft × ⅛ in. scrubber column of Carbowax 20M.

Preparative vapor-phase chromotography was performed on a Varian Aerograph A-90 P3 instrument with the following columns: 15 ft × 0.25 in. DBTCP and a 15 ft × 0.25 in. oxydipropionitrile, all on nonacid-washed Chromosorb P, 60–80 mesh. Mass spectra were taken on a Varian MAT CH-7 or on an AEI-MS-9. Photolysis were performed in a Rayonet reactor using the bulbs provided. The synthesis of 1,2-bis(dideuteriomethylene)cyclobutane and the structural and stereochemical assignment of all C_8H_{12} hydrocarbons discussed in this work, except 3-methylene-4-methyl-*cis*-1,4-hexadiene, have been reported.[3a]

Photolysis of 1,2-Bis(dideuteriomethylene)cyclobutane (DMCB-d_4). (a) Liquid Phase. Two solutions of 10 μl. of DMCB-d_4 in 600 μl. of cyclohexane-d_{12} (1.67%, v/v) were freshly degassed by freeze–pump–thaw for three cycles and were irradiated with one 254-nm bulb for 20 hr. The nmr spectra (220 MHz) of the irradiated solutions revealed 13.6% of total protium on exo methylenes for each solution and no loss of olefin relative to internal cyclohexane. The solutions were then heated with 15 μl. each of dimethyl acetylenedicarboxylate in sealed tubes under nitrogen at 82° for 25.5 hr. These two solutions were combined, and after evaporation of the solvent, 48 mg of a crude oil was obtained. This oil was subjected to a molecular distillation at 50° (0.5 mm) to remove excess dimethyl acetylenedicarboxylate and finally at 100–110° (0.5 mm) giving 40 mg (93% yield) of a low-melting solid, presumed to be tetradeuterio-3,4-dicarbomethoxybicyclo[4.2.0]octa-1(6),3-diene. In 2 ml of refluxing benzene, 30 mg (0.132 mmol) of this purified adduct was treated with 50 mg (0.22 mmol) of recrystallized dichlorodicyano-*p*-benzoquinone (DDQ) for 22 hr. Following the same work-up procedures described previously for the corresponding pyrolysis[3d] and a molecular distillation at 100–120° (0.5 mm), 27 mg of a waxy solid was obtained. As in the case of pyrolysis,[3d] this purified material was subjected to mass spectral analyses and *m/e* 222:223:224 = 103:35:14.5 was observed. After correction of natural abundance ^{13}C by using 2,5-dideuterio-3,4-dicarbomethoxybicyclo[4.2.0]octa-1,3,5-triene (DBC-d_2) which was prepared from unrearranged starting material with *m/e* 222:223:224 = 100:14.7:1.82, as standard,[3d] the mixture contained: 77.7% DBC-d_2, 15% DBC-d_3, and 7.3% DBC-d_4 materials. Consequently, the results of three runs carried out under the same conditions with the same bulb but at various lengths of time are summarized in Table I.

Attempted Quenching Studies. A solution of 10 µl. of DMCB-d_4 in 600 µl. of oxygen-saturated cyclohexane-d_{12} was irradiated at 254 nm with the same bulb as above for 20 hr. The nmr spectrum (220 MHz) of the photolysate revealed 12.5% of total protium on exo methylenes.

Likewise, a solution of 10 µl. of DMCB-d_4 and 1 µl. of di-*tert*-butyl nitroxide in 600 µl. of cyclohexane, which had been freshly degassed by bubbling nitrogen gas for 20 min, was irradiated at 254 nm for 20 hr. After treatment with 15 µl. of dimethyl acetylenedicarboxylate at 82° for 44.25 hr, the solvent was evaporated. The nmr spectrum (100 MHz, CCl_4) of the adduct revealed 12.5% of total protium on the doubly allylic methylene positions.

(b) Vapor Phase. DMCB-d_4 (5 Torr) was photolyzed in two separate experiments in the vapor phase with 50 and 760 Torr of argon in a 450-ml quartz vessel using one 254-nm Rayonet bulb for 15 min. On a vacuum line, the photolysate was transferred directly to an nmr tube along with carbon tetrachloride for analysis at 220 MHz. In addition to rearranged DMCB-d_4 (singlets at δ 3.58, 4.61, and 5.05), allene (δ 4.61) was also present as evidenced by a δ 4.61:5.05 ratio greater than 1, as well as butatriene (δ 5.20) and ethylene (δ 5.28). Additional evidence that low-molecular-weight materials were present comes from the fact that the nmr spectrum of the photolysate was devoid of ethylene and allene and had only a small peak from butatriene in addition to DMCB-d_4 after nitrogen had been bubbled through the solution for 2 min. In 50 Torr of argon there was 49% rearrangement, 3% allene, and 17% butatriene and ethylene. At 760 Torr of argon, there was 52% rearrangement, 3% allene, and 1% butatriene and ethylene. These are in mole per cent of starting material, and rearrangement includes that portion of unrearranged starting material that must have returned from a freely rotating bisallyl biradical.

The distribution of deuterium in the cleavage products allene, butatriene, and ethylene was determined from a photolysis in 250 Torr of helium under otherwise identical conditions. Mass spectrometry at 14 eV, where DMCB does not fragment, dideuterioallene (*m/e* 42); d_0-, d_2-, and d_4-butatriene (*m/e* 52, 54, and 56) in the ratio 4:8:7, respectively; and d_0-, d_2-, and d_4-ethylene (*m/e* 28, 30, and 32) in the ratio 2:2:1, respectively, were formed. In two experiments where ethane at 16 and at 210 Torr was used as the inert gas, the ratio of butatriene-d_0, -d_2, and -d_4 was 1:2:1, respectively.

(c) Sensitization. A solution of 40 µl. of pure 1,2-dimethylenecyclobutane[33] and 20 µl. of acetophenone in 2 ml of deuteriochloroform (2%, v/v) in a Pyrex nmr tube was irradiated at 300 nm with eight bulbs for 17.5 hr in a Rayonet reactor in a 5° cold room. The nmr spectrum (100 MHz) of the irradiated solution showed only a trace of starting diene remained. After evaporation of the solvent, the residue was separated on 12 ft × 0.25 in. 1,2,3-tris(2-cyanoethoxy)propane column (20% on Chromosorb W, 60–80) operated at 150° and 60 ml/min of helium flow giving two products in the ratio 3:4:1 in addition to acetophenone. Mass spectral analyses revealed that both products had molecular ion peaks at 160. Simultaneously, a blank solution of 10 µl. of 1,2-dimethylenecyclobutane in 0.5 ml of deuteriochloroform was irradiated for the same length of time and was found unchanged by nmr (100 MHz).

Similarly, irradiation of 10 µl. of DMCB-d_4 in cyclohexane-d_{12} containing 5 µl. of acetophenone at 300 nm for 13 hr with four bulbs resulted in an nmr spectrum characteristic of the unrearranged starting material and dimer but with no hydrogens in the range of 4–7 ppm.

Quantum Yield for Geometric Isomerization of *anti,anti*-1,2-Diethylidenecyclobutane in Solution. Parallel irradiation of a 0.0792 *M* spectrograde hexane solution of *anti,anti*-1,2-diethylidenecyclobutane and of a 0.123 *M* hexane solution of vpc purified *trans,trans*-2,4-hexadiene with three Rayonet 254 nm bulbs for 16 min resulted in the formation of 11% of a 40:1 mixture of *anti,syn*- and *syn,syn*-diethylenecyclobutane, respectively, in the former solution and 4.9% *cis,trans*-2,4-hexadiene in the latter solution.

Both reactions were conducted in quartz test tubes in a merry-go-round apparatus constructed for a Rayonet reactor. Since each solution was optically thick over most paths through its volume and taking $\Phi_{tt \rightarrow ct} = 0.37$, the quantum yield for AA → SA = 0.49 after correction for the relative transparencies of the phototubes checked by parallel runs with just *trans,trans*-2,4-hexadiene.

The analyses were performed using cyclooctane as an internal standard with the diethylidenecyclobutane and *n*-nonane as a standard with the 2,4-hexadiene.

Vapor-Phase Photolyses of Dimethyl-1,2-dimethylenecyclobutanes. The vapor-phase hydrocarbon mixtures were prepared in a greaseless Pyrex vacuum line. Fischer-Porter or Kontes Pyrex–Teflon valves and Fischer-Porter solvent seals were employed throughout. The system was protected from contamination by pump oil vapors and mercury vapors by liquid-nitrogen-cooled traps.

The starting material was placed in a sealed-off Fischer-Porter solvent seal (COSS), attached to the vacuum system and degassed by three freeze-pump-thaw cycles.

The necessary portion of the vacuum line, the photolysis vessels, a dark vessel and, if necessary, a separate mixing vessel were pressurized appropriately as indicated by a manometer employing a low density working fluid. The manometer was closed off from the line, and the starting material was frozen into the mixing vessel. A small amount of a degassed internal standard, a saturated hydrocarbon, was also transferred to the mixing vessel. The components were warmed to room temperature and allowed to mix statically for greater than 30 min.

The mixture was allowed to expand into the necessary portion of the vacuum line plus the photovessels and the dark vessel. The photovessels and the dark vessel were closed off, and the residual materials were removed from the line.

Pressurization of the C_8 hydrocarbon photomixtures with inert gas was accomplished in the following manner. Pressurization of the vacuum line was initiated at a moderate rate. When a pressure of roughly half the desired value was obtained, the photovessel valve was cracked open, while pressurization continued. As the pressure approached the desired value, the rate of pressure increase was slowed, and the hot vessel valve was closed when the desired pressure was indicated.

The photovessels and the dark vessel were stored overnight in the dark at room temperature to allow the new mixture to equilibrate.

Irradiations were performed in a Rayonet photochemical reactor employing a single Rayonet 2537-Å light source enclosed in a 1.5-mm thick Vycor (Corning 7193) cylinder and a perforated 1.2-mm thick Pyrex cylinder. Five 200-ml quartz photovessels were placed reproducibly in the same absolute position in a merry-go-round and rotated during irradiation.

The temperature of the cooling air exhausted from the reactor never increased more than 1° during an irradiation, and the irradiation times were sufficiently long to ensure greater than 100 rotations during an irradiation. The five photovessels were calibrated by the analogous irradiation of a single mixture having optical density similar to those employed in the pressure studies.

The nitrogen was removed, and the contents of each photovessel was divided into five parts by static transfer into a cow with five cold fingers. The content of each finger was quantitatively transferred into a loop formed between two Valco v-4-4p, two position, four-part valves. After being vaporized, the material in the loop was flushed from the loop by the carrier gas into the injector–splitter of a Varian-Areograph Series 1220-2 gas chromatograph fitted with a 200-ft, di-*n*-butyl tetrachlorophthalate-coated capillary column and a flame-ionization detector. Peak areas were determined by a Vidar 6210 digital integrator when possible and by Disc or Triangulation.

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Photochemical α Cleavage of Benzoin Derivatives. Polar Transition States for Free-Radical Formation[1]

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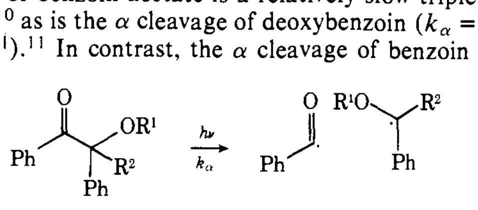
Abstract: The photochemical α cleavage reactions of benzoin, benzoin ethers, benzoin acetate, and several related phenyl ketones have been investigated. α cleavage is the only primary process observed for benzoin and the benzoin alkyl ethers in benzene solution. β cleavage is a minor competing reaction for benzoin phenyl ether. Substituents at the α carbon have little effect on the efficiency (quantum yield) of cleavage; however, they have a pronounced effect on the rate constant for cleavage. Benzoin alkyl ethers are about 10^5 times more reactive toward α cleavage than deoxybenzoin. Substituents capable of stabilizing an adjacent positive charge are far more effective in accelerating α cleavage than are substituents capable of stabilizing free radical centers. It is concluded that the transition state for α cleavage has considerable ionic character and does not resemble the free radical products.

Benzoin,[3-5] benzoin ethers,[5-9] and benzoin esters[10] undergo photochemical α cleavage to form a benzoyl-substituted benzyl radical pair (eq 1). The photochemical α cleavage of benzoin acetate is a relatively slow triplet-state reaction[10] as is the α cleavage of deoxybenzoin ($k_\alpha = 1.6 \times 10^6$ sec^{-1}).[11] In contrast, the α cleavage of benzoin ethers cannot be quenched by standard triplet quenchers[7-9] and must be either an exceptionally rapid triplet process ($k_\alpha > 10^{10}$ sec^{-1}) or a singlet process which competes efficiently with intersystem crossing.[12] γ-Hydrogen abstraction (eq 2), which is the predominant photochemical reaction for α-alkoxyacetophenones ($k_\gamma > 10^9$ sec^{-1}),[13] does not compete with the α-cleavage reaction of benzoin ethers.[7,9] Benzoin and benzoin ethers are widely used as initiators for photopolymerization.[14] Therefore elucidation of structure-reactivity relationships for the α cleavage of benzoin and its derivatives has practical as well as mechanistic consequences.



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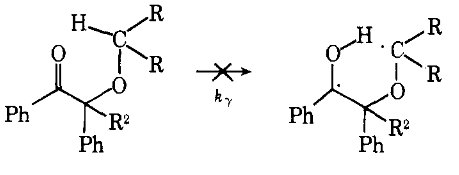

(2)

Results and Discussion

Benzoin Ethers. Irradiation of the benzoin ethers **1–4** in benzene solution results in the formation of benzaldehyde, benzil, and an equimolar mixture of diastereomeric pinacol ethers. Isolated yields of the pinacol ethers are 60–70%. All

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