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Photolytic and Triplet Benzene-Sensitized Decomposition of *cis*- and *trans*-2,3- and -2,4-Dimethylcyclobutanones[1]

Howard A. J. Carless, John Metcalfe, and Edward K. C. Lee*

Contribution from the Department of Chemistry,
University of California, Irvine, California 92664.
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Abstract: Direct photolytic (λ_{ex} 254, 281, 313, 325, and 334 nm) and triplet benzene ($^3B_{1u}$) sensitized decompositions of cis and trans isomers of the 2,3- and 2,4-dimethylcyclobutanones (DMCB) have been studied in detail. It is shown that from a series of pressure-dependence studies at λ_{ex} 325 nm, *ca.* three-fourths of the DMCB (S_1) internally converts to the hot ground state, DMCB (S_0*), while the remainder decomposes to an olefin (C_3 or C_4) plus a ketene (C_2 or C_3) or to a dimethylcyclopropane (DMCP) plus CO. At higher photoexcitation energies, the $S_1 \rightsquigarrow S_0$ internal conversion yield drops slightly and the decomposition (*via* singlet biradical) yield gradually increases. Only at 334 nm does the $S_1 \rightsquigarrow T_1$ intersystem crossing become distinct to the extent of $\Phi(S_1 \rightsquigarrow T_1) \approx 0.1$. The DMCB ($T_1$*) formed *via* C_6H_6 ($^3B_{1u}$) sensitization gives the decarbonylation products, *cis*- and *trans*-dimethylcyclopropane (DMCP), with complete loss of stereochemistry of the parent ketone; the *trans*-DMCP/*cis*-DMCP ratios are 2.4 from the *cis*- and *trans*-2,3-DMCB's and 1.24 from the *cis*- and *trans*-2,4-DMCB's. On the other hand, the *trans*-DMCP/*cis*-DMCP ratios obtained in the direct photolyses indicate predominant inversion of stereochemistry in the decarbonylation process. These results are discussed in terms of biradical intermediates whose lifetimes are long or short compared to the time scale of internal rotations. The results of direct photolyses at 325 nm in the liquid phase indicate that the predominant singlet mechanism operative in the gas phase at $\lambda_{ex} \leq 325$ nm can largely account for the product formation observed in the liquid phase, recognizing that virtually all of the DMCB (S_0*) is quenched out. The observed differences in kinetic behavior of the biradicals produced from *singlet* and *triplet* precursors are discussed.

Recent studies on the direct photochemical[2] and the benzene ($^3B_{1u}$)- and the mercury (6^3P_1)-sensitized[3] decomposition as well as on the fluorescence excitation spectroscopy[4] of cyclobutanone (CB) have led to a greater understanding of the decomposition pathways open to an excited cyclobutanone molecule. It was found in the earlier studies that the vibrationally hot, ground electronic state CB (S_0*) obtained in thermolysis[5] decomposed mainly to ethylene and ketene and that direct photolyses in the first $S_0 \rightarrow S_1$ electronic absorption band resulted in the formation of C_2H_4, CH_2CO, cyclopropane (propylene), and CO.[2] From the recent benzene ($^3B_{1u}$) sensitization study,[3a] it was observed that the triplet CB (T_1) decomposed mainly to cyclopropane and CO, and from the study of pressure dependence and wavelength dependence of the product formation in direct photolysis,[2b] it was found that ethylene (ketene) alone was quenched at high pressure but less effectively at shorter excitation wavelength. These results were interpreted as evidence for the presence of a vibrationally hot CB (S_0*) precursor, whose unimolecular lifetime for decomposition is comparable to the mean intervals of gas kinetic collisions, as well as for the presence of a short-lived triplet CB (T_1) precursor in direct photolysis.[2b] At that time, it was not possible to rule out unequivocally the alternative that the precursor of the vibrationally hot cyclopropane (plus CO) in direct photolysis is an electronically excited singlet CB (S_1). But, for the sake of maintaining simplicity in the mechanism it was proposed that CB (T_1) was solely responsible for the photodecarbonylation products.[2b] It is now clear[4b,c] that

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[2] (a) S. W. Benson and G. B. Kistiakowsky *J. Amer. Chem. Soc.*, 64, 80 (1942); (b) N. E. Lee and E. K. C. Lee, *J. Chem. Phys.*, 50, 2094 (1969); (c) ref 5–10 contained in ref 2b.

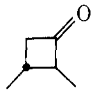
[3] (a) H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, 90, 3628 (1968); (b) D. C. Montague and F. S. Rowland, *ibid.*, 91, 7230 (1969); (c) J. Metcalfe and E. K. C. Lee, *ibid.*, 94, 7 (1972).

[4] (a) R. G. Shortridge, Jr., C. F. Rusbult, and E. K. C. Lee, *ibid.*, 93, 1863 (1971); (b) J. C. Hemminger, C. F. Rusbult, and E. K. C. Lee, *ibid.*, 93, 1867 (1971); (c) J. C. Hemminger and E. K. C. Lee, *J. Chem. Phys.*, 54, 1405 (1971); (d) J. C. Hemminger, H. A. J. Carless, and E. K. C. Lee, submitted for publication.

[5] (a) M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, *J. Amer. Chem. Soc.*, 76, 6271 (1954); (b) A. T. Blades, *Can. J. Chem.*, 47, 615 (1969).

such a simplified mechanism involving the $S_1 \rightsquigarrow T_1$ intersystem crossing is only acceptable near the threshold of the $S_0 \rightarrow S_1$ absorption (>320 nm); most of the photoproducts observed in the rest of the $S_0 \rightarrow S_1$ absorption band (240–313 nm) must arise from the decomposition of CB (S_1*) and CB (S_0*), because the molecular predissociation process predominates over the $S_1 \rightsquigarrow T_1$ intersystem crossing when CB (S_1) has more than 3 kcal/mol of excess vibrational energy.[4b,c]

The present study was undertaken in the hope of gaining a greater insight into the photochemical mechanism of competitive unimolecular decompositions. The rates of various decomposition modes influenced by the stereochemical restrictions present in four geometric and structural isomers of dimethylcyclobutanone (DMCB, **1**–**4**) were measured. Pressure and wavelength dependence of the product quantum yields (Φ) obtained in the direct photolysis will be compared with those obtained in the triplet sensitization,[3] in order to understand the influence of the electronic spin multiplicity and the vibrational energy content on the excited state chemistry. Some interesting preliminary results have been reported already on the DMCB systems,[6a,b] and the study of the 2-*n*-propylcyclobutanone system[6c] has provided some key observations germane to the discussion of the present work. The fact that cis or trans geometry of the 2,3-DMCB isomers dictates the stereochemical structure of the 2-butene product and that all four isomers of DMCB likewise dictate the stereochemical outcome of the dimethylcyclopropane (DMCP) products is extremely valuable, despite the fact that the product distributions are apparently complex.



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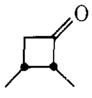

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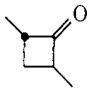

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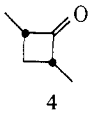

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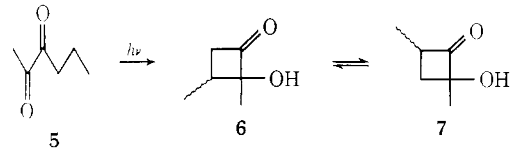
Experimental Section

Preparation of the Dimethylcyclobutanones (1–4). A solution of hexane-2,3-dione (**5**, 56 g, Aldrich) in benzene (310 ml) was irradiated in a cylindrical reactor for 6.5 hr using a 450-W mercury lamp insert, a Pyrex probe, and a 1-cm thickness of filter solution (6 *M* aqueous $NaNO_3$) to prevent absorption of light by the photoproduct. The solution was deoxygenated by nitrogen bubbling for 0.5 hr before and throughout the irradiation. The *cis*- and *trans*-cyclobutanols (**6c** and **6t**) derived from intramolecular hydrogen abstraction and ring closure of the resulting biradical[7] undergo a facile intramolecular alkyl shift[8] to give a complex mixture of **6c**, **6t**, **7c**, and **7t**. Vpc (SE-30, 100°) showed 93% of the starting diketone had reacted and the appearance of two product peaks which were isolated as a mixture; reduced pressure distillation gave a liquid fraction, bp 62° (1.1 mm) (35.8 g 64%), identified as a mixture of the 2-hydroxy-2,3-dimethylcyclobutanone (**6**) and 2-hydroxy-2,4-dimethylcyclobutanone (**7**) isomers: ir (film) 3390 s (OH), 2985 s, 1770 s (cyclobutanone C═O), 935 s cm⁻¹; nmr (60 MHz, CCl_4) τ 5.75 (broad singlet, 1 H), 6.75–8.5 (complex, 3 H), 8.7–9.1 (several peaks, 6 H).



The mixture of hydroxy ketones **6** and **7** (14 g) was dissolved in pentane (200 ml), and zinc dust (20 g, Mallinckrodt analytical) was added. The mixture was stirred at 0° while concentrated hydrochloric acid (35 ml) was added in 2-ml portions over 10 min. After standing at 0° overnight, the pentane layer was separated and washed in turn with water, 10% aqueous sodium carbonate, and water. Drying ($MgSO_4$) and distillation gave a fraction of bp 120–143° (750 mm) (5.6 g, 46%). Vpc (TCEP, 55°) showed this fraction as a mixture of the four possible DMCB isomers, separated by preparative vpc: *trans*-2,4-DMCB (30%), *cis*-2,4-DMCB (30%), *trans*-2,3-DMCB (15%), and *cis*-2,3-DMCB (25%) in order of elution.

Preparative vpc separation of the 2,3-DMCB isomers was carried out on a fluorosilicone oil (QF 1) column (125°); the order of elution of the products was (i) a mixture of *trans*- and *cis*-2,4-DMCB, (ii) *trans*-2,3-DMCB, and (iii) *cis*-2,3-DMCB. Samples of *trans*- and *cis*-2,3-DMCB (>95% pure) were collected; recycling the collected material gave samples of *trans*-2,3-DMCB (>99.5%) and *cis*,2,3-DMCB (≥98%). The 2,4-DMCB isomers were not separated on this column and were collected as a mixture. Preparative vpc on another column (TCEP, 55°) allowed the separation of the 2,4-DMCB isomers; recycling the collected material gave samples of *trans*-2,4-DMCB (>98%) and *cis*-2,4-DMCB (>97%) containing only small quantities of the alternative 2,4-DMCB isomer as impurities.

The dimethylcyclobutanones have been prepared previously by the rearrangement of cyclobutane epoxides[9a] and the ring expansion reactions of diazoethane with ketene.[9b] The assignments of the structures of the *trans*- and *cis*-2,4-DMCB isomers were readily made, since the CH_2 protons of the cyclobutanone ring show as a simple triplet for the trans isomers (A_2B_2-like system) but are nonequivalent for the cis isomer (A_2BC-like system). Conia and Salaün have applied this distinction to the *trans*- and *cis*-2,4-di-*tert*-butylcyclobutanones.[10] *trans*-2,3-DMCB (**1**): ir (film) 2940 s, 2915 s, 2874, 1773 s, 1450 s, 1397, 1372, 1340, 1167, 1033, 973, 865 s cm⁻¹; nmr (60 MHz, CCl_4) τ 6.5–8.0 (complex, 4 H), 8.97 (doublet, J = 7 Hz, 3 H), 9.04 (doublet, J = 7 Hz, 3 H). *cis*-2,3-DMCB (**2**): ir (film) 2950 s, 1776 s, 1453, 1393, 1374, 1239, 1209, 1143, 1096, 1031, 1012, 853, 837, 725 cm⁻¹; nmr (60 MHz, CCl_4) τ 6.9 max (multiplet, 2 H), 7.2–8.7 (multiplet, 2 H), 8.90 (doublet, J = 7 Hz, 3 H), 8.95 (doublet, J = 7 Hz, 3 H).

trans-2,4-DMCB (**3**): ir (film) 2940 s, 1773 s, 1450, 1366, 1300, 1238, 1104, 980, 957, 813, cm⁻¹; nmr (60 MHz, $CDCl_3$) τ 6.70 (broad quartet, $J \sim$ 7 Hz, 2 H), 8.17 (triplet, J = 7.5 Hz, 2 H), 8.78 (doublet, J = 7.5 Hz, 6 H). *cis*-2,4-DMCB (**4**): ir (film) 2976 s, 1776 s, 1450, 1372, 1227, 1117, 990, 952, 939, 877 cm⁻¹; nmr (60 MHz, $CDCl_3$) τ 6.82 (multiplet, 2 H), 7.45 (quartet, J = 10.5 Hz, 1 H), 8.90 (multiplet, 1 H), 8.86 (doublet, J = 7.5 Hz, 6 H).

The following vpc columns were used. QF 1 (28-ft 17% fluorosilicone oil FS 1265 on Chromosorb P); TCEP (30% tris-2-cyanoethoxypropane); SE-30 (6-ft silicone gum rubber).

Chemicals. The following gases were used directly without further purification, and the purity is that quoted by the manufacturers: Ar (99.995%, high purity grade, Matheson Co.), O_2 (99%, Air Products), and C_2H_4 (99.9%, research grade, Phillips).

The following hydrocarbons were also used after degassing: benzene (zone-refined grade, Litton Chemicals), *n*-heptane (chromatoquality, Matheson Coleman and Bell), and cyclohexane (spectrograde, Mallinckrodt, which was used after vpc purification on a di-*n*-decyl phthalate column).

Vacuum and Photochemical Apparatus. Samples were handled on a glass–metal vacuum line free from grease and mercury, and photolyses were carried out at room temperature in photolysis cells of 85.2- and 483-ml volume as described previously.[2b] Photolyses at 325.0 nm were carried out using a Spectra Physics He–Cd laser (Model 185, rated at 15 mW) which had a light intensity of 1.8×10^{16} quanta/sec after dispersing the beam with an f = 5 cm quartz lens and passing through a Corning CS 0–54 filter to remove any short uv radiation. Photolyses at 313 and 281 nm were carried out using a 200-W super pressure mercury arc lamp (HBO–200, Osram) operated by a stabilized dc power supply (Model 701–A, PEK, Inc.), the emissions being resolved by a high-intensity monochromator (uv–visible grating, 7.4 nm/mm reciprocal dispersion,

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[6] (a) H. A. J. Carless and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 4482 (1970); (b) *ibid.*, **92**, 6683 (1970); (c) *ibid.*, **94**, 1 (1972).

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[8] W. H. Urry, J. C. Duggan, and M. H. Pai, *ibid.*, **92**, 5785 (1970).

[9] (a) J. L. Ripoll and J. M. Conia, *Bull. Soc. Chim. Fr.*, 2755 (1965); (b) N. J. Turro and R. B. Gagosian, *J. Amer. Chem. Soc.*, **92**, 2036 (1970).

[10] J. M. Conia and J. Salaün, *Bull. Soc. Chim. Fr.*, 2751 (1965).

Table I. Pressure Dependence of the Hydrocarbon Product Distribution from the Photolyses of *cis*- and *trans*-2,3-DMCB at 325 nm

Run[a]	Pressure, Torr	Conversion, %	PR	*t*-2B	*c*-2B	*t*-DMCP	*c*-DMCP	2B *t*/*c*	DMCP *t*/*c*
				cis-2,3-DMCB					
92	0.1	1.4	522	71	304	51	53	0.23	0.97
97	0.1	2.9	517	74	303	52	53	0.25	0.98
88	0.5	2.0	522	67	305	52	54	0.22	0.96
90	1.5	1.7	502	65	314	58	60	0.21	0.97
91	3.0	1.5	473	62	328	67	69	0.19	0.97
94	5.5	2.7	417	62	351	84	87	0.17	0.96
95	8.0	1.3	385	58	362	96	96	0.16	0.98
151[b]	0.5	0.5	519	60	312	55	55	0.19	1.01
153[b]	0.5	3.2	518	61	312	54	55	0.19	0.97
152[b]	5.5	0.9	427	52	352	82	86	0.15	0.95
				trans-2,3-DMCB					
72[a]	0.15	2.4	419	451	30	81	20	15.5	3.96
68	0.5	6.8	408	452	30	86	23	14.8	3.65
74	0.5	3.2	408	451	31	87	22	14.5	3.95
70	1.0	1.9		460	31	98	25	14.6	3.92
71	1.5	1.3	364	466	33	110	28	14.2	3.91
66[a]	3.0	4.4	313	483	35	136	31	~14	4.02
69	5.0	0.8	266	499	35	160	39	14.4	4.07
67	8.0	3.5	217	519	35	182	45	14.6	4.02
73	11.5	1.6	181	526	36	206	50	14.4	4.12

[a] A large cell (483 ml) was used; otherwise an 85.2-ml cell was used. [b] Runs 151–153 were on a highly purified sample (>99.5% single isomer).

Bausch and Lomb No. 33-86-07). The light intensity at 313 nm was 5 × 10^{15} quanta/sec and that at 281 nm was 7 × 10^{14} quanta/sec at a spectral band pass of ~6 nm in each case. Photolyses at 334 nm were carried out similarly using the 450-W mercury arc lamp (HBO-450, Osram), the B and L monochromator, Corning CS-0-74 glass filter, and a 1-cm path length of 0.4 *M* KNO_3 (in H_2O) filter solution. Photolyses at 253.7 nm were carried out using a combination of a low-pressure mercury grid lamp (Mineralight R-51, Ultraviolet Products, Inc.), a Corning CS 7-54 filter, and a 1.0-cm thick D_3P filter solution.[11] The light intensity at 253.7 nm was 7.5 × 10^{15} quanta/sec. Light intensity was monitored using a phototube (RCA 935) which had been calibrated using chemical actinometry. The relative intensity fluctuation of the three light sources used was less than 10% throughout the period of a day.

Liquid-Phase Photolyses (325 nm). Known amounts of the ketone (0.36 mg) and *n*-heptane (6.8 mg) were measured out on the vacuum line, condensed, degassed, and sealed into a capillary tube. The liquid samples were irradiated by placing them in the path of the 325-nm laser beam for 30–45 min; analysis was done by injecting the entire contents of the tube into the vpc inlet at room temperature. As the geometry of the irradiation system was not reproducible, only relative yields of products could be measured. Blank runs showed that *n*-heptane impurities were not responsible for the observed products.

Product Analysis. Analysis of the photolysis products was carried out as described elsewhere,[6c] using a 25 ft × 0.25 in. o.d. dimethylsulfolane column (30% by weight of DMS on 30–60 mesh Chromosorb P) at room temperature and a flame ionization detector (Perkin-Elmer F-11). As separation of *cis*-2-pentene (*cis*-2P) from *cis*-dimethylcyclopropane (*cis*-DMCP) was not possible on the DMS column, a different analytical approach was taken: *cis*-2P and *cis*-DMCP peaks were separated on a 10 ft × 0.25 in. o.d. silver nitrate column (20% by weight saturated $AgNO_3$ in ethylene glycol on 30–60 mesh Chromosorb P-HMDS) in series with a 10 ft × 0.25 in. o.d. column (30% by weight of DMS on 30–50 mesh Chromosorb P). Separation was effected by performing a conventional analysis with the 25-ft DMS column until just before the combined *cis*-2P and *cis*-DMCP peak was eluted, then switching the combined $AgNO_3$–DMS column onto the end of the 25-ft DMS column using a four-way stopcock and allowing the peak to enter the $AgNO_3$–DMS column. As soon as the peak completed its entry into the combined column, the combined column was switched out again to allow elution of the 2-methyl-2-butene peak from the 25-ft DMS column. The combined column containing the two components was then switched in to elute the separated *cis*-2P and *cis*-DMCP peaks.[12]

Results

***cis*- and *trans*-2,3-DMCB.** The hydrocarbon products[13] obtained in the photolysis of *cis*- and *trans*-2,3-DMCB are, in their order of elution from the DMS column, propylene (PR), *trans*-2-butene (*trans*-2B), *cis*-2-butene (*cis*-2B), *trans*-dimethylcyclopropane (*trans*-DMCP), 2-methyl-1-butene (2M1B), *trans*-2-pentene (*trans*-2P), *cis*-2-pentene (*cis*-2P), *cis*-dimethylcyclopropane (*cis*-DMCP), and 2-methyl-2-butene (2M2B). The amount of PR and *cis*- and *trans*-2B was reduced in photolyses at higher pressures, the pressure increase necessary to quench out one-half of the precursor ($P_{1/2}$) increasing as the exciting wavelength (λ_{ex}) was decreased. The four pentene isomers mentioned above were not produced to any measurable extent in the photolyses at 325 nm (see Table I) and 313 nm, but they appeared in the 1.0-Torr ketone sample to the extent of ~3% of the C_5 products at 281 nm and ~9% at 254 nm (see Table II).

At 325 nm, the DMCP yields are independent of pressure, as confirmed by a study of the quantum yields of products in the absence and in the presence of C_2H_4 as a quencher (see Tables III and IV). It is therefore convenient to express the yields of PR and 2-B relative to DMCP as estimates of the relative quantum yields of products. A Stern–Volmer plot for the product quenching by C_2H_4 is shown for *trans*-2,3-DMCB in Figure 1. Quenching of propylene formation obeys the Stern–Volmer kinetics, in that the plot of DMCP/PR *vs.* pressure is linear, and this suggests the propylene arises purely from a single vibrationally excited precursor; $P_{1/2}$ is 2.2 ± 0.2 Torr of ketone at 325 nm. However, the plot of DMCP/2-B appears to level off at high pressure of ketone, suggesting a quenchable and an unquenchable component

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[11] C. L. Braga and M. D. Lumb, *J. Sci. Instrum.*, **43**, 341 (1966).

[12] (a) D. C. Montague and F. S. Rowland, submitted for publication; (b) *J. Chem. Soc., Chem. Commun.*, 193 (1972).

[13] No analysis of CO, ketene, methylketene, or DMCB isomers remaining after photolysis was undertaken. It was assumed that the quantity of ketene was equal to the amount of the 2-butenes formed and likewise methylketene to that of the propylene formed. The amount of DMCB remaining was assumed to be equal to the number of moles present at the beginning of the photolysis less the number of moles of the observed product formed.

Table II. Effect of Added Ar Pressure on the Photolysis Products of DMCB Isomers at 281 and 254 nm[a]

Run no.	Parent, Torr	Ar, Torr	PR	t-2B	c-2B	2M1B	2M2B	t-2P	c-2P	t-DMCP	c-DMCP	DMCP t/c
λ_{ex} 281 nm												
DB3	t-2,3 (1.01)		285	302	30.8	1.9	1.9	<0.1	<0.1	73.5	22.6	3.25
DB4	t-2,3 (1.09)	540	80	159	14.8	1.6	2.3			74.9	21.6	3.48
DB25	c-2,3 (0.99)		350	49	242	1.2	1.2	<0.1	<0.1	45.1	52.5	0.86
DB13	c-2,3 (1.06)	137	253	32	198	1.1	1.5			42.3	54.9	0.77
DB22	t-2,4 (1.07)		343			<0.1	0.1	1.5	1.0	54.8	42.6	1.29
DB23	c-2,4 (1.11)		371			0.2	0.2	1.4	0.9	63.2	34.1	1.85
DB20	c-2,4 (1.15)	166	187			<0.1	0.2	1.0	0.4	65.5	32.8	2.00
λ_{ex} 254 nm												
DM3	t-2,3 (1.0)		212	204	21.5	4.4	4.3	0.7	0.6	64.9	25.2	2.57
DM4	t-2,3 (1.0)	390	139	154	14.8	3.1	3.0			70.8	23.1	3.06
DM19	c-2,3 (1.01)		242	31.7	165	3.3	3.1	0.7	0.5	46.7	45.6	1.02
DM18	c-2,3 (1.02)	120	203	23.7	138	1.8	2.5	0.1	0.1	47.9	47.7	1.00
DM20	t-2,4 (1.04)		210			1.3	1.3	4.5	2.6	53.1	37.9	1.40
DM22	c-2,4 (0.96)		250			0.9	1.3	3.8	2.2	56.1	35.6	1.58

[a] Yields estimated at ΣC_5 product = 100 units.

Table III. Relative Moles of Products per Torr of *trans*-2,3-DMCB per Hour of Photolysis at 325 nm

Run	Pressure, Torr	PR	2B	DMCP
68	0.5	3.95	4.68	1.06
74	0.5	3.70	4.38	0.99
70	1.0		4.00	1.01
71	1.5	2.49	3.42	0.95
69	5.0	1.26	2.53	0.95
67	8.0	0.97	2.50	1.04

Table IV. Effect of C_2H_4 on the Product Distribution from *cis*- and *trans*-2,3-DMCB (0.5 Torr) at 325 nm

Run	Pressure C_2H_4, Torr	Conversion, %	PR	2B	DMCP	2B t/c	DMCP t/c
cis-2,3-DMCB							
153	0	3.2	5.18	3.77	(1.00)	0.19	0.97
106	2.0	2.2	4.07	3.12	(1.00)	0.19	0.97
107	5.0	1.8	3.47	2.87	(1.00)	0.19	0.97
108	12.0	1.4	2.41	2.32	(1.00)	0.17	0.99
111	25.2	1.5	1.53	1.94	(1.00)	0.18	1.00
109	50	0.8	~0.8	1.71	(1.00)	0.17	0.98
110	100	0.8	~0.6	1.29	(1.00)	0.19	1.02
trans-2,3-DMCB							
A78	0	2.9	3.80	4.40	(1.00)[a]	14.9	4.0
A75	14.6	1.3	0.92	2.31	0.96	13.8	4.1
A76	51.7	0.9		1.82	0.94	16.5	4.1
A77	97	0.9		1.74	0.94	17.6	4.1
B83	0	2.9	3.78	4.48	(1.00)[a]	14.7	4.2
B81	3.0	2.1	2.39	3.44	0.97	14.6	4.1
B80	7.8	1.6	1.43	2.66	0.96	14.6	4.0
B79	148	0.8		1.75	0.99	19.9	4.2
B82	201	0.8		1.61	0.93	20.1	4.1

[a] Two actinometer runs (A78 and B85) agreed within 5%, and the two series were run 1 hr each in a 85.2-ml cell.

are responsible for 2-butene formation. After subtraction of a certain unquenchable fraction of 2-butene, a Stern–Volmer plot of the *quenchable* 2-butene fraction gives a linear pressure dependence. The best Stern–Volmer plot is given by assuming an unquenchable 2-butene fraction of 33 ± 4%, for *trans*-2,3-DMCB, and the half-quenching pressure for the *quenchable* 2-butene fraction is then 2.6 ± 0.7 Torr of ketone. A similar kinetic analysis has been shown to be adequate in the photolytic decomposition study of 2-*n*-propylcyclobutanone,[6c] and was also applied to the *cis*-2,3-DMCB isomer.

In order to test whether the precursor could be scavenged as a free radical by O_2, a pressure dependence study was carried out with O_2 at 325 nm. The results indicated that O_2 quenched the products not as a free radical scavenger but as a vibrational deactivator, similar to C_2H_4. A Stern–Volmer plot for O_2 quenching is shown in Figure 2.

At higher photoexcitation energies, the *cis*- and *trans*-2P were completely quenched out by ~50 Torr of Ar added as an inert deactivating gas, while the yields of 2M1B and 2M2B were reduced by *ca.* one-third to an amount which was not further reduced by addition of higher pressure of Ar. The quantum yield of the total C_5 products did not seem to be affected by high pressure of Ar as seen from Table V; the observed variations in the total C_5 yield are within the experimental error of pressure measurement and light intensity. A similar invariance in the quantum yield of the total C_5 products with pressure was found at the other wavelengths except 254 nm. Addition of O_2 as a radical scavenger at λ_{ex} 254 nm apparently leads to a slight reduction of the total C_5 yield compared to the

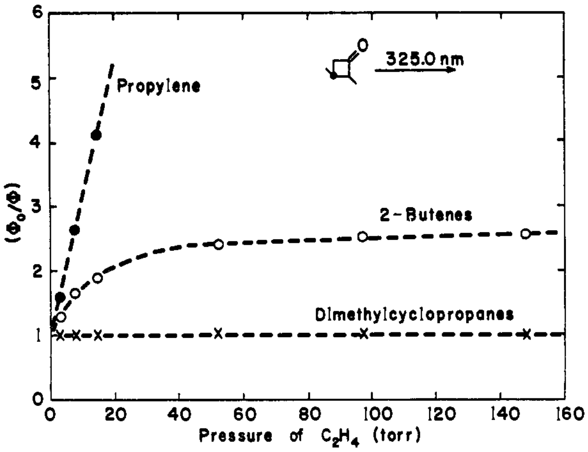

Figure 1. Stern-Volmer plots for product yields obtained from the photolyses of *trans*-2,3-DMCB (0.5 Torr, 325 nm) *vs.* pressure of C_2H_4, where Φ and Φ_0 are quantum yields of products in the presence and in the absence of C_2H_4, respectively.

Table V. Effect of Added Ar Pressure on the Photolysis Products of *trans*-2,3-DMCB at 281 and 254 nm

Run no.	Pressure, Torr *t*-2,3-DMCB	Ar	Conversion, % ΣC_3	PR	2B
		λ_{ex} 281 nm			
DB3	1.01	0	0.119	0.338	0.395
DB7	1.05	32	0.104	0.289	0.320
DB9	1.05	57	0.101	0.225	0.280
DB5	1.02	110	0.107	0.196	0.266
DB8	0.97	203	0.099	0.132	0.213
DB6	1.00	350	0.106	0.104	0.202
DB4	1.09	540	0.110	0.088	0.191
		λ_{ex} 254 nm			
DM3	1.0	0	0.148	0.314	0.335
DM11	1.0	21	0.142	0.301	0.318
DM5	1.0	38	0.139	0.311	0.331
DM7	1.0	60	0.149	0.309	0.327
DM10	1.0	93	0.138	0.275	0.298
DM8	1.0	140	0.146	0.277	0.303
DM12	1.0	229	0.140	0.230	0.263
DM6	1.0	303	0.137	0.207	0.241
DM4	1.0	390	0.133	0.198	0.240

Table VI. Effects of Added O_2 and Cyclohexane on the Photolysis Products of *trans*-2,3-DMCB at 254 nm

Run no.	Pressure, Torr Ketone	O_2	c-C_6H_{12}	Conversion, %[a] ΣC_3	PR	2B
DM30	1.93			0.212	0.533	0.441
DM31	1.97	1.3		0.213	0.524	0.422
DM26	1.00			0.245	0.584	0.480
DM27	0.99	1.2		0.211	0.541	0.441
DM28	0.23 ± 0.03			0.412	0.974	0.820
DM29	0.23 ± 0.03	1.1		0.439	1.096	0.910
DM38	1.05		0	0.220	0.463	0.523
DM39	1.07		4.8	0.195	0.446	0.522
DM36	1.01		9.8	0.198	0.454	0.508
DM37	1.01		20	0.195	0.429	0.467
DM35	1.04		40	0.203	0.400	0.406
DM40	1.03		58	0.182	0.340	0.364

[a] Irradiations of 30 min for DM26, -27, -30, and -31; 60-min irradiations for DM28 and -29.

olefin yields, as can be seen from Table VI. If O_2 only interfered as the vibrational deactivator of CB (S_0*), then the ratios of ΣC_3/PR and ΣC_3/2-B should have increased in the O_2-added samples. The opposite

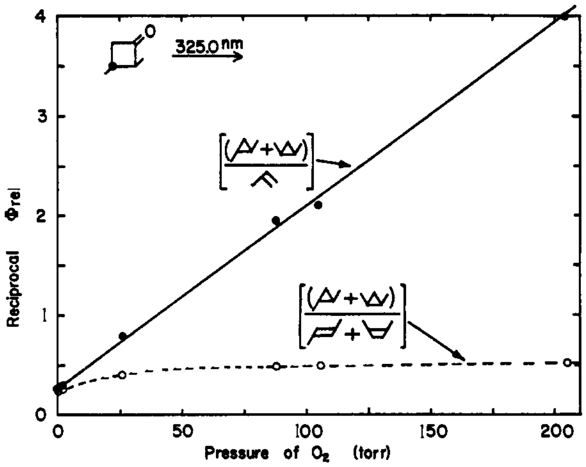

Figure 2. Stern-Volmer plots for pressure-dependent product yields (C_3H_6 and 2-C_4H_8) obtained from the photolyses of *trans*-2,3-DMCB (0.5 Torr, 325 nm) *vs.* pressure of O_2.

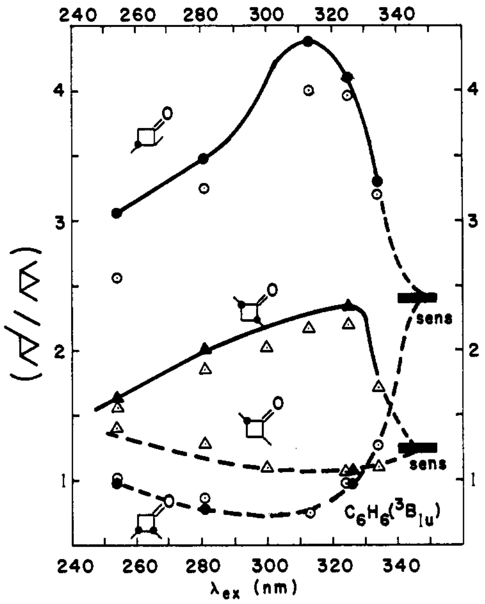

Figure 3. Ratio of *trans*-DMCP/*cis*-DMCP obtained from four isomers of DMCB *vs.* excitation wavelengths: open symbols, 1.0 Torr of DMCB; filled symbols, 1.0 Torr of DMCB + high pressure of deactivator gas (≥ 120 Torr of Ar).

observation indicates the presence of small amounts of long-lived radicals in the system.

At all photolytic wavelengths, the ratio of *trans*-DMCP/*cis*-DMCP from *trans*-2,3-DMCB increased with pressure, while that from *cis*-2,3-DMCB decreased slightly with pressure. Stereoretention at 1.0 Torr of ketone appeared to be somewhat greater at longer wavelengths except 334 nm, as can be seen from Figure 3. The ratios of *trans*-DMCP/*cis*-DMCP obtained from *cis*- and *trans*-2,4-DMCB are also shown in Figure 3.

***cis*- and *trans*-2,4-DMCB.** Photolysis products of *cis*- and *trans*-2,4-DMCB were the same as those produced in the photolysis of *cis*- and *trans*-2,3-DMCB except that virtually no 2-butenes[14] were produced. Addition

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[14] The amount present (<0.5% of the total products) was assumed to be produced from the photolysis of a very small (<1%) amount of one or both of the 2,3-DMCB isomers present as an impurity, and not from some internal rearrangement in the 2,4-DMCB's followed by decomposition. No attempt was made to verify it, since the difficulties in obtaining a very pure sample of the isomer were considerable.

of inert quenching gases reduced the propylene yield (see Table II) in a manner similar to the reduction of PR and 2-B in the photolysis of *cis*- and *trans*-2,3-DMCB (see Tables I and IV). The total C_5 product yields were again apparently unaffected by pressure at 325, 313, and 281 nm. *trans*- and *cis*-2P, 2M1B, and 2M2B were not produced to any measurable extent in the photolyses at 325 and 313 nm but were produced to the extent of ~3% of the total C_5 products at 281 nm and ~8% at 254 nm (see Table II) at 1.0 Torr of ketone pressure. The *cis*- and *trans*-2P yields were reduced by *ca.* one-half at high Ar pressures and remained constant at this level, while almost all of the 2M1B and 2M2B was quenched out at high Ar pressures.

It can be seen from Table VII that the *trans*-DMCP/*cis*-DMCP ratio shows an apparent stereoinversion. As the photolysis pressure is increased, this apparent stereoinversion also increases as shown in Figure 3.

Table VII. Pressure Dependence of the Hydrocarbon Product Distribution from the Photolyses of *cis*- and *trans*-2,4- DMCB at 325 nm

Run	Pressure, Torr	Conversion, %	PR/(*t*- + *c*-DMCP)	DMCP *t/c*
		cis-2,4-DMCB		
124	0.1	5.3	8.2	2.14
128	0.2	4.2	7.9	2.20
89	0.5	4.5	7.0	2.21
115	0.5	4.6	6.8	2.24
125	1.0	3.0	5.4	2.25
127	1.5	2.6	4.6	2.32
126	2.0	3.0	4.1	2.35
142	8.0	1.1	2.5	2.33
123	(0.5 + 30)[a]	1.4	2.0	2.38
		trans-2,4-DMCB		
135	0.1	5.6	7.1	1.02
131	0.2	9.0	6.5	1.05
93	0.5	3.7	5.6	1.07
98	0.5	5.5	5.5	1.06
132	1.0	4.1	4.1	1.06
134	1.5	3.0	3.4	1.06
133	2.0	2.7	3.0	1.07
141	(0.5 + 30)[a]	1.5	1.17	1.07

[a] Added to this was 0.5 Torr of 2,4-DMCB plus 30 Torr of C_2H_4.

Pressure Quenchable and Unquenchable Portions. As mentioned earlier, the total C_5 product yields (ΣC_5) were unaffected by pressure. "Relative" quantum yields (R) of PR and *cis*- and *trans*-2B at each pressure were obtained as the ratios of each observed C_3- or C_4-olefin yield to the ΣC_5 yield. It was not possible to pressure quench these olefins to any appreciable extent at 281 and 254 nm by increasing the parent ketone pressure to its vapor pressure limit. Thus, a series of photolyses of *trans*-2,3-DMCB were carried out using Ar as a quenching gas at 281 and 254 nm (see Table V).

Stern–Volmer plots ($1/R$ *vs.* P)[2b,c] from these pressure-quenching studies for the four DMCB isomers at 325 and 313 nm were made in order to determine the specific rate constants (k_E's) for formation of PR and *cis*- and *trans*-2B. In all cases, except the PR formation from the 2,3-DMCB's, the Stern–Volmer plots were curved downward. As discussed earlier this curvature reflects the presence of two precursors (or more) for each product olefin, the lifetimes of precursors for their unimolecular decompositions being sufficiently different from each other. The nature of the precursors are the same as those found in the 2-*n*-propylcyclobutanone system,[6c] namely (i) the S_1 state which yields the *pressure-unquenchable* portion (R_1) of these products and (ii) the S_0* state which yields the *pressure-quenchable* portion (R_0) of these products, where $R = R_0 + R_1$. In the photolyses of the 2,3-DMCB isomers, the Stern–Volmer plots of $1/R_0$ *vs.* pressure, where an appropriate *pressure-unquenchable yield* of *cis*- and *trans*-2B was subtracted from the observed yield by the relationship $R_0 = R - R_1$, gave straight lines.[15] Likewise, the PR yields from the 2,4-DMCB isomers were treated similarly. Table VIII shows the primary yields of pressure quenchable (R_0) and unquenchable (R_1) products obtained from each DMCB isomer.

Table VIII. Partitioning of Pressure Quenchable (R_0) and Unquenchable (R_1) Products

Product Olefins	Parent DMCB isomers			
	trans-2,3	*cis*-2,3	*trans*-2,4	*cis*-2,4
	λ_{ex} 325 nm			
$R_0(C_3H_6)$	4.44	5.4	7.2	7.23
$R_1(C_3H_6)$	~0	~0	0.8	1.54
$R_0(C_4H_8)$	3.3	2.29		
$R_1(C_4H_8)$	1.6	1.35		
	λ_{ex} 313 nm			
$R_0(C_3H_6)$	4.65	6.2	*a*	*a*
$R_1(C_3H_6)$	~0	~0	*a*	*a*
$R_0(C_4H_8)$	3.17	2.7		
$R_1(C_4H_8)$	1.8	1.5		

[a] Not measured.

A series of photolyses with *trans*-2,3-DMCB were carried out at 325 nm using Ar as the quenching gas, so that relative efficiency of Ar compared to the parent DMCB as the deactivator could be measured. The apparent efficiency of Ar compared to *trans*-2,3-DMCB was found to be 0.155 (pressure/pressure), from the comparison of the two Stern–Volmer plots, as outlined previously.[2b] When the Ar pressure quenching data in Table V were used to make the Stern–Volmer plots, in which the effective pressure, $P_{eff} = P_{ketone} + 0.155\ P_{Ar}$ was employed, a linear slope was obtained at 281 nm but a curved (upward) plot was obtained at 254 nm,[16] after correction for the pressure unquenchable products. To circumvent poor deactivating efficiency of Ar in collision with the hot DMCB (S_0*) produced at 254 nm, a comparative series of photolyses was performed with *trans*-2,3-DMCB using cyclohexane as the collisional deactivator, on the assumption that cyclohexane should be an efficient vibrational deactivator. Unfortunately, the result of this series of photolyses shows not only a reduction of the PR and *cis*- and *trans*-2B yields but also a slight reduction of the total C_5 yield (runs 35–40 in Table VI). Therefore, we were not able to produce a meaningful Stern–Volmer plot from this series of runs. It appears from this and the

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(15) In the case of the photolysis of the 2,3-DMCB isomers, the formation of two different products (PR and *cis*- and *trans*-2B) from the same intermediate, requiring the same half-quenching pressure ($P_{1/2}$) for each product, provides a convenient check on the accuracy and validity of this procedure. In all cases, the paired $P_{1/2}$ values were the same within the experimental error (see Table IV of ref 16).

(16) J. Metcalfe, H. A. J. Carless, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **94**, 7235 (1972).

Table IX. Product Ratios from the DMCB Isomers at λ_{ex} 334 nm

Run	Ketone	Pressure, Torr	Conversion, %	C_3/C_5	C_4/C_5	2B *t*/*c*	DMCP *t*/*c*
158	*c*-2,4	0.5	0.2	4.64			1.71
159	*t*-2,4	0.5	0.3	5.01			1.10
156	*c*-2,3	0.5	0.1	2.43	1.77	0.203	1.26
157	*t*-2,3	0.5	0.13	2.10	2.45	12.8	3.16
160	*t*-2,3	1.5	0.106	1.57	2.07	14.4	3.23
161	*t*-2,3	3.0	0.086	1.10	1.73	13.5	3.18
162	*t*-2,3	5.0	0.070	0.81	1.55	13.5	3.27
163	*t*-2,3	8.0	0.061	0.59	1.40	12.9	3.29
164	*t*-2,3	11.0	0.051	0.47	1.33	14.3	3.32

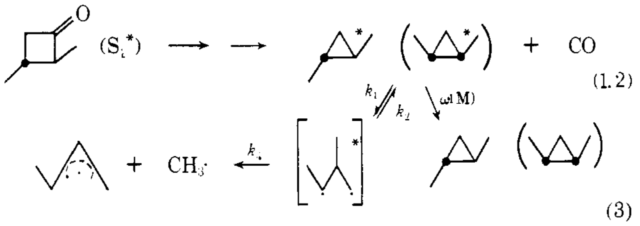
Table X. Product Distributions from the Benzene Photosensitization of the DMCB Isomers[a]

DMCB	Conversion,	Relative moles of product						
isomers	%	PR	*t*-2B	*c*-2B	*t*-DMCP	*c*-DMCP	Σolefins	DMCP*t*/*c*
cis-2,3	12	0.045	0.023	0.027	0.637	0.268	0.095	2.37
trans-2,3	10	0.046	0.041	0.017	0.634	0.262	0.104	2.42
cis-2,4	10	0.030			0.536	0.434	0.030	1.24
trans-2,4	12	0.021			0.541	0.438	0.021	1.23

[a] 0.034 Torr of ketone and 1.00 Torr of benzene were irradiated for 3-4 min in a 483-ml cell.

O_2-scavenger runs mentioned earlier that some of the highly vibrationally excited dimethylcyclopropanes have enough energy to decompose into two radical fragments, probably by Scheme I.

Scheme I



From the heats of formation known or estimated for the molecular species involved in Scheme I, it is possible to estimate empirically the activation energies for the processes 1–3.[17] By assuming reasonable Arrhenius preexponential factors,[17] the unimolecular rate constants, k_1, k_2, and k_3, can be estimated from the RRKM theory.[18] Such a calculation shows that $CH_3\cdot$ and $C_4H_7\cdot$ can be formed to an appreciable extent at 254 nm and that their involvement will be less important at 281 nm (<0.5 of that at 254 nm).

Direct Photolyses at 334 nm. Photolyses of the DMCB isomers were carried out at 334 nm, but a pressure-dependence study was made only with *trans*-2,3-DMCB. Product ratios obtained in these runs are shown in Table IX. It was also observed at this wavelength that the relative quantum yields of DMCP were gradually reduced by the increasing pressure of *trans*-2,3-DMCB. A Stern–Volmer plot of $1/\Phi$ *vs.* P_{DMCB} for each product was obtained as shown in Figure 4. The observed linearity for the propylene yield is consistent with the pressure quenching of the hot DMCB (S_0^*) precursor, while the observed positive slope for the DMCP yield is consistent with the pressure quenching of its biradical precursor[3c] as will be discussed later.

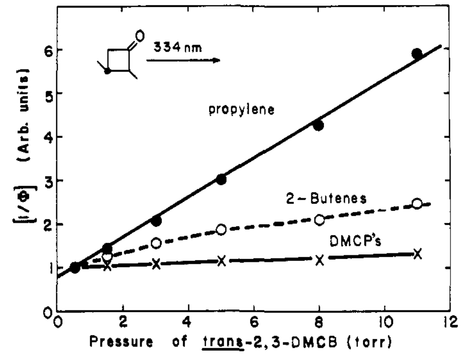


Figure 4. Stern–Volmer plots for pressure-dependent product yields obtained from the photolyses of *trans*-2,3-DMCB (334 nm) *vs.* pressure of ketone, where Φ is the quantum yield of product each normalized to the value obtained at 0.50 Torr of *trans*-2,3-DMCB.

Secondary Photolysis. At longer wavelengths and larger conversions, there is a possibility of secondary photodecomposition of the ketene product, since the excitation wavelength is close to the ketene and methylketene absorption maxima. We have been able to follow this ketene decomposition, since photolysis of methylketene gives ethylene and CO *via* an intramolecular hydrogen shift (in CH_3CH:).[19] A plot of ethylene yield *vs.* conversion for *trans*-2,3-DMCB at 325 nm is approximately linear (the C_2H_4/C_3H_6 ratio is 0.10 at ~7% conversion for a 0.5-Torr sample), as expected, and under our photolysis conditions the conversion is small enough that secondary photolysis of the methylketene is negligible. Also, methylene (CH_2) produced by secondary photolysis of ketene gives some *trans*-2-pentene and 2-methyl-2-butene, but no further discussion regarding the reaction mechanism will be given here.

Benzene Photosensitization (253.7 nm). The results of the triplet benzene ($^3B_{1u}$)-sensitized decomposition of the DMCB isomers at low ketone pressure are shown in Table X. The major observed products are DMCP's

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(17) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions," Report NSRDS-NBS 21, U. S. Government Printing Office, Washington, D. C., 1970.

(18) (a) See for a review, B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, 3, 1 (1964); (b) see ref 3a and 3c for examples.

(19) (a) G. B. Kistiakowsky and B. H. Mahan, *J. Amer. Chem. Soc.*, 79, 2412 (1957); (b) D. P. Chong and G. B. Kistiakowsky, *J. Phys. Chem.*, 68, 1793 (1964).

Table XI. Product Distributions in Liquid-Phase Photolysis (325 nm)

Run	DMCB isomers	Conversion, %	PR	*t*-2B	*c*-2B	*t*-DMCP	*c*-DMCP
			Moles of product ($\times 10^{-10}$)				
175	*cis*-2,3	16	287	468	3920	510	605
176	*trans*-2,3	9	106	2470	113	609	60
177	*cis*-2,4	11	3560			490	126
178	*trans*-2,4	11	2830			659	472

as expected,[3a] but the trans/cis ratio is very different from those obtained in direct photolysis.

Liquid-Phase Photolyses (325 nm). The results of the irradiations of the ketones in *n*-heptane are given in Tables XI and XII. The product distribution resembles that of the high-pressure, gas-phase results at 325 nm, and in general higher stereospecificity is observed in the 2-B and DMCP products.

Table XII. Product Ratios in Liquid-Phase Photolysis (325 nm)

DMCB isomer	*t*-DMCP/*c*-DMCP	*t*-2B/*c*-2B	PR/Σbutenes	Σcyclopropanes/Σolefins
cis-2,3	0.85	0.12	0.06/0.94	0.24
trans-2,3	10.2	22	0.04/0.96	0.25
cis-2,4	3.9			0.17
trans-2,4	1.4			0.40

Discussion

Triplet Benzene ($^3B_{1u}$, 84.4 kcal/mol) Sensitization. The major products of benzene photosensitization are the DMCP isomers (see Table X). The trans/cis DMCP ratio is nearly independent of the particular cis or trans starting isomer, suggesting the intermediacy of a long-lived, decarbonylated 1,3-biradical[3] with time for bond rotations before ring closure to cyclopropanes.

At the pressures used, singlet energy transfer is small, but will occur [using $P_{1/2}$(singlet transfer) = 3 Torr and $P_{1/2}$(triplet transfer) = 0.03 Torr, we expect ~3% singlet energy transfer].[3a,20] There is also <1% directly competing singlet absorption by the ketone. These two factors can explain the olefin formation (2–3%) observed for the 2,4-DMCB isomers, but do not explain the olefin formation (~10%) from the 2,3-DMCB isomers.[20]

Since the 2,3 and 2,4 isomers generate different biradicals (**8** and **9**, respectively) it might be expected


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9

that they would give different trans/cis DMCP ratios. One expects quite different interactions between the methyl groups both in the biradicals and in the transition-state for ring closure to dimethylcyclopropanes.[3c]

A comparison of the trans/cis DMCP ratio produced from the 2,3 isomers (2.4) and 2,4 isomers (1.23) should be made with the ratio obtained from (i) mercury photosensitization studies,[3c] (ii) triplet CH_2 addition to *cis*- and *trans*-2-butene, (iii) benzophenone-sensitized solution-phase photolysis of dimethyl-1-pyrazolines,[21] and (iv) thermolysis of DMCP's.[22] Since a reasonable amount of discussion regarding (i)–(iv) appears in ref 3c, a detailed discussion will not be repeated here. A pressure-dependence study for the benzene photosensitized decomposition of the DMCB isomers has not been carried out as yet, so we cannot ascertain the magnitude of the rate of the decarbonylation process for the triplet DMCB with low vibrational excitation energy.[23,24]

Direct Photolysis (≤325 nm). The S_1 state of DMCB's can react or be deactivated (described for *trans*-2,3-DMCB but applicable to the other isomers) as shown in Scheme II.

Scheme II

$$\textit{trans}\text{-2,3-DMCB}\ (S_0) + h\nu \longrightarrow \underset{\text{excitation}}{\textit{trans}\text{-2,3-DMCB}\ (S_1{}^*)} \qquad (4)$$

$$\textit{trans}\text{-2,3-DMCB}\ (S_1{}^*) \longrightarrow \underset{\text{fluorescence}}{\textit{trans}\text{-2,3-DMCB}\ (S_0) + h\nu_f} \qquad (5)$$

$$\longrightarrow \underset{\text{intersystem crossing}}{\textit{trans}\text{-2,3-DMCB}\ (T_1{}^*)} \qquad (6)$$

$$\xrightarrow{\omega(M)} \underset{\text{collisional deactivation}}{\textit{trans}\text{-2,3-DMCB}\ (S_0)} \qquad (7)$$

$$\longrightarrow (\alpha)\textit{trans}\text{-2,3-DMCB}\ (S_0{}^*) + (\beta)\textit{cis}\text{-2,3-DMCB}\ (S_0{}^*);\ \text{internal conversion} \qquad (8)$$

$$\xrightarrow{a} \underset{\text{cleavage}}{CH_3CHCO + C_3H_6}$$

$$\xrightarrow[b]{} CH_2CO + (\alpha')\textit{trans}\text{-2B} + (\beta')\textit{cis}\text{-2B} \qquad (9)$$

$$\longrightarrow (\alpha'')\textit{trans}\text{-DMCP}^* + (\beta'')\textit{cis}\text{-DMCP}^* + CO;\ \text{decarbonylation} \qquad (10)$$

It has been demonstrated[4d] that the quantum yield of fluorescence emission process 5 (Φ_F) from the DMCB (S_1*) at λ_{ex} 325 nm is very low ($\leq 10^{-4}$), so process 5 plays no significant mechanistic role. The $S_1 \rightsquigarrow T_1$ intersystem crossing process 6 is also considered to play a minor mechanistic role ($\Phi_{ISC} \leq 0.04$) at all wavelengths studied here (except at 334 nm) due to the rapid predissociation of S_1*,[4d] by analogy with cyclobuta-

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(20) The $P_{1/2}$ values for the singlet energy transfer to *cis*- and *trans*-2,4-DMCB are 1.0 and 1.1 times, respectively, the $P_{1/2}$ value for cyclobutanone (G. M. Breuer and E. K. C. Lee, unpublished results). While no such data are available now for the 2,3-DMCB isomers, we expect them to be similar. The $P_{1/2}$ values for the triplet energy transfer to *cis*-2,3-, *trans*-2,3-, *cis*-2,4-, and *trans*-2,4-DMCB are 0.03, 0.03, 0.03, and 0.02 Torr, respectively (J. Metcalfe and E. K. C. Lee, unpublished results). It should be noted that, at high conversions, the olefinic products from the sensitization could quench the triplet benzene in competition with the parent ketone, and hence lower the yield of the *triplet products*. This effect would be more important for the 2,3-DMCB isomers than for the 2,4-DMCB isomers, since 2-butenes are twice as effective as propylene in quenching the triplet benzene.[5a]

(21) R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, 46, 3305 (1968).

(22) (a) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc., Ser. A*, **257**, 122 (1960); (b) *ibid.*, 260, 424 (1961).

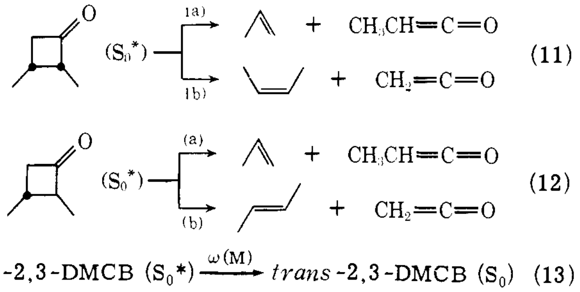
(23) The energies of the lowest triplet state of the DMCB isomers are not known, but they should be 80–85 kcal/mol above S_0, if a small singlet–triplet splitting for the $n\pi^*$ configuration of ~1500 cm^{-1} is assumed.[24]

(24) (a) D. C. Moule, *Can. J. Phys.*, 47, 1235 (1969); (b) W. D. Chandler and L. Goodman, *J. Mol. Spectrosc.*, **35**, 232 (1970); (c) H. E. Howard-Lock and G. W. King, *ibid.*, **36**, 53 (1970).

none.[4,25] The ratios of *trans*-DMCP/*cis*-DMCP obtained in direct photolysis (Figure 3) bear no resemblance to the ratios obtained in the triplet-sensitized decomposition (benzene[6] and Hg[3c]) which show virtually no memory of the cis or trans stereochemistry of the parent ketone. Thus, the DMCB (S_1*) or an *intermediate*, which is neither a DMCB (T_1*) nor a DMCB (S_0*), gives rise to all of the pressure-unquenchable ring cleavage products *via* process 9 and *nearly all* of the decarbonylation products *via* process 10. Again, the lifetime consideration of the DMCB (S_1*), *e.g.*, $\tau_F \leq 3 \times 10^{-10}$ sec,[4d] emphasizes the negligible contribution made by the collisional deactivation process 7 at ordinary pressures.

The pressure-quenchable ring fission products are produced by the unimolecular decomposition of the long-lived DMCB (S_0*) with stereoretention (*trans*-2B from *trans*-2,3-DMCB and cis-2B from *cis*-2,3-DMCB), and a detailed discussion of its kinetics shown in Scheme III is presented in the following paper.[16]

Scheme III

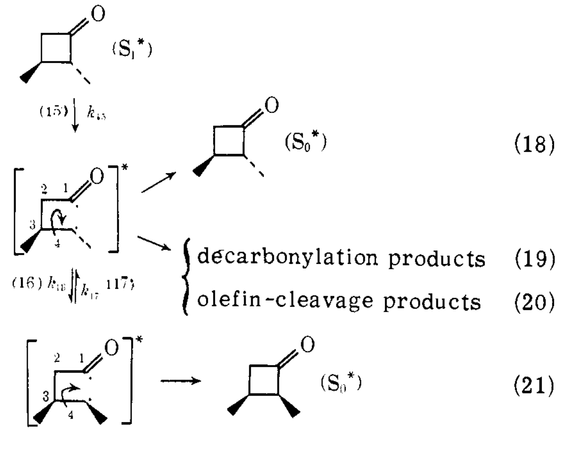


$$trans\text{-}2,3\text{-DMCB }(S_0{*}) \xrightarrow{\omega(M)} trans\text{-}2,3\text{-DMCB }(S_0) \quad (13)$$

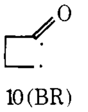
$$cis\text{-}2,3\text{-DMCB }(S_0{*}) \xrightarrow{\omega(M)} cis\text{-}2,3\text{-DMCB }(S_0) \quad (14)$$

(i) **Biradical Precursor.** It should be recalled that a ring-opened, *vibrationally hot biradical* intermediate (**10**)[6,26] was postulated to account for the minor yield of *cis*-2B produced from *trans*-2,3-DMCB and likewise for that of *trans*-2B from *cis*-2,3-DMCB in photolyses shown in Scheme IV.

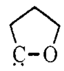
Scheme IV



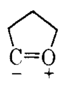
Since an oxacarbene (**11**) has been shown to be formed in the solution photolysis of cyclobutanones,[27] we must look for evidence of its role in the gas-phase photolysis.



10(BR)



11(OX)



12(YD)

13(PZ)

It is interesting to note that a ylide-like five-membered ring intermediate (**12**) should be analogous electronically to 1-pyrazoline (**13**), and it is a resonance form of the oxacarbene **11**. Particularly, comparisons of photolysis and thermolysis between cyclobutanones and 1-pyrazolines suggest the intermediacy of **11** and **12** in addition to (or instead of) the intermediacy of **10** in the gas phase, since **11** has been shown to ring-contract to cyclobutanone in a recent study.[28] How the oxacarbene intermediates might be produced are now considered. As discussed earlier, $k_6 \approx 2 \times 10^8$ sec^{-1} for $S_1 \rightsquigarrow T_1$,[4d,25] and probably k_{15} is $>10^{10}$ sec^{-1} where DMCB's predissociate.[4d] The vibrational excitations, especially the O-atom in-plane wagging vibration, in conjunction with (i) the nonplanar equilibrium geometry, (ii) the lengthened C=O bond by ~0.1 Å in the excited singlet state,[24] and (iii) the more electrophilic O-atom in the $n\pi^*$ state, probably aid the formation of the oxacarbene. The substitution of CH_3 groups at the α position could significantly enhance the ring expansion and the ring opening rates.[4d]

(ii) **Decarbonylation Process.** It is amazing that the *trans*-DMCP/*cis*-DMCP ratios obtained for the four isomers of DMCB given in Figure 3 are very similar to those obtained for the *cis*- and *trans*-3,4- and 3,5-dimethyl-1-pyrazolines (DMPZ) in photolyses.[21] The 2,4-DMCB isomers photodecarbonylate with *predominant stereoinversion*, and a similar stereoinversion is found for the N_2 extrusion process in 3,5-DMPZ. This inversion could occur from a ring-opened biradical intermediate,[21,29] or a concerted $[{}_\sigma 2_s + {}_\sigma 2_a]$ process,[30] which could lead to stereoinversion at one center. Unfortunately, the extent of the involvement of the biradical and the concerted processes cannot be determined at present. Since the necessity of postulating both mechanisms has been discussed in literature,[29] we will not pursue it further. However, we emphasize the notion that the similarity of the electronic structure of the ylide-like oxacarbene (**12**) and pyrazoline (**13**) might be responsible for the similar decomposition patterns observed in the photolyses of the DMCB isomers and in the photolyses of the DMPZ isomers.

A "restricted biradical" mechanism can also be used to explain the observed stereochemical results for the DMCP formation. Rotation about the C_3–C_4 bond (or C_1–C_2 bond) is assumed to be somewhat slower than rotation about the C_2–C_3 bond. The observed stereoinversion in the DMCP product from the 2,4-DMCB isomers can only be rationalized if these assumptions

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(25) G. M. Breuer and E. K. C. Lee, *J. Phys. Chem.*, **75**, 989 (1971). For cyclobutanone, $\tau_F = 4.7$ nsec and $\Phi_F \cong 0.002$ below its predissociation limit;[4c] furthermore, $k_F = \Phi_F/\tau_F = 4 \times 10^5$ sec^{-1}, and $k_{ISC} \cong 2 \times 10^8$ sec^{-1}.

(26) ΔH_f (25°) for BR (**10**) is estimated to be 30 kcal/mol, compared to that for cyclobutanone of −20 kcal/mol.[17] Thus the excess vibrational energy of BR (**10**) produced at 325 nm must be ≤40 kcal/mol.

(27) (a) N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967); (b) D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4349 (1970); (c) N. J. Turro and D. M. McDaniel, *ibid.*, **92**, 5727 (1970); (d) N. J. Turro and D. R. Morton, *ibid.*, **93**, 2567 (1971).

(28) W. C. Agosta and A. M. Foster, *Chem. Commun.*, 433 (1971).

(29) See, for example, (a) A. Mishra and R. J. Crawford, *Can. J. Chem.*, **47**, 1515 (1969); (b) R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969); (c) P. B. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971).

(30) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

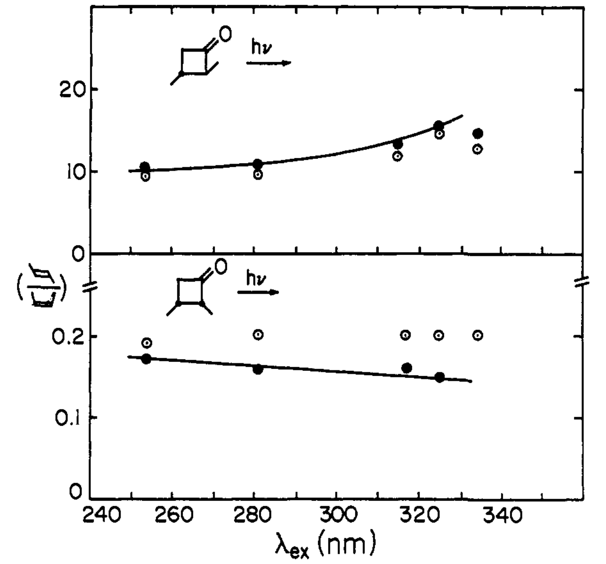
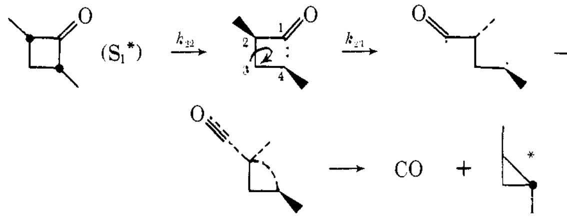


Figure 5. Ratio of *trans*-2B/*cis*-2B obtained from the 2,3-DMCB isomers *vs.* excitation wavelength: open symbols, 1.0 Torr of DMCB; filled symbols, 1.0 Torr of DMCB + high pressure of deactivating gas (Ar $\geq$ 120 Torr at 254 and 281) or 6–12 Torr of DMCB (313, 325, and 334 nm).

Scheme V



(22, 23)

are made, as illustrated in Scheme V. The stereoretention observed from the 2,3-DMCB isomers can also be rationalized, on this basis, because the center of inversion is at the unsubstituted C_2 carbon for the α-cleaved biradical (with CH_3 substitutions at C_4 and C_3 carbons) predominantly produced from the 2,3-DMCB (S_1*). We attribute the increased stereospecificity of the DMCP products at higher pressures (accompanying higher photoexcitation energy) to the collisional deactivation of the vibrationally hot DMCP's which might otherwise isomerize unimolecularly.[22] The diminishing stereospecificity in the decarbonylation process with the increasing photoexcitation energy (see Figure 3) may be an indication of the faster randomizing internal rotations in the biradical before the loss of CO.

The pressure-unquenchable portion of the pentenes (2M1B and 2M2B from the *cis*- and *trans*-2,3-DMCB isomers and *cis*- and *trans*-2P from the *cis*- and *trans*-2,4-DMCB isomers) observed at λ_{ex} 281 and 254 nm are probably formed from the vibrationally hot biradical intermediates (similar to **10**) *via* intramolecular H-atom migration, since these pentenes are also formed in much greater yields in the photolyses (and thermolyses) of the analogous DMPZ isomers.[21] As expected, the pressure-quenchable pentenes are formed from the structural isomerization of the vibrationally hot DMCP's and correspond to the products observed in the decomposition of the thermally excited[22] and chemically activated[31] *cis*- and *trans*-DMCP's.

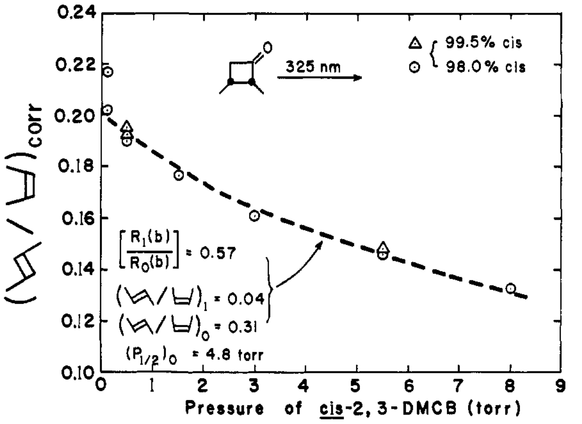


Figure 6. Pressure dependence of the *trans*-2B/*cis*-2B ratio from *cis*-2,3-DMCB at 325 nm. The ratio has been corrected for the presence of a small *trans*-2,3-DMCB impurity. Broken line indicates the ratios calculated for production of 24% *trans*-2,3-DMCB (S_0*) and 76% *cis*-2,3-DMCB (S_0*).

The maximum amounts of energy available for the internal excitation of CO and DMCP are ~95 kcal/mol at 281 nm and ~106 kcal/mol at 254 nm. The chemically activated *cis*-DMCP[31] with an average excitation energy of ~105 kcal/mol undergoes cis-trans isomerization with $k_g = 1 \times 10^8$ sec^{-1} and structural isomerization with $k_s = 1 \times 10^7$ sec^{-1}. These rate constants correspond to a mean collision frequency at 10 and 1.0 Torr of ketone pressure, respectively. The pressure dependence of the pentene yields and of the *trans*-DMCP/*cis*-DMCP ratio indicates that the DMCP has 90–100 kcal/mol excess vibrational energy at λ_{ex} 254 nm. No detailed analysis of the results will be attempted here, but it is interesting to note that the ring-opened biradical obtained from the 2,3-DMCB isomers by breaking the C_1–C_4 bond will give the stereoinverted DMCP's upon rotation of the C_2–C_3 bond.

(iii) **Cyclization Process.** The *trans*-2B/*cis*-2B ratios shown in Table I for the 325-nm photolyses of the *trans*- and *cis*-2,3-DMCB isomers show a significant pressure dependence only with the cis ketone, although the stereospecificity for both ketones increases with the increasing pressure as shown in Figure 5. Since even a small amount of the impurity ketone isomer affects this ratio substantially, it was necessary to correct the observed ratios for the presence of the opposite isomer in the photolytic samples. There were 0.5 and 2.0% *trans*-2,3-DMCB in the two separate, purified *cis*-2,3-DMCB samples used. A correction for the *trans*-2,3-DMCB impurity was made with the runs listed in Table I, and the corrected *trans*-2B/*cis*-2B ratios are plotted as a function of pressure in Figure 6.

A broken line in Figure 6 was calculated for the conditions that the trans/cis ratio for the unquenchable 2-butene fraction (R_1) is 0.04 ± 0.01 (high stereoretention), the trans/cis ratio for the quenchable 2-butene fraction (R_0) is 0.31 ± 0.02 ($P_{1/2}$ = 4.8 Torr of ketone), and $[R_1(2B)/R_0(2B)] = 0.57$. The fit of the experimentally observed points to the calculated curve is quite good, implying that *ca.* one-fourth of the internally converted 2,3-DMCB (S_0*) is of the trans isomer, when the cis isomer is photoexcited at 325 nm. Further-

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(31) See, for example, (a) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, 40, 1425 (1962); (b) J. W. Simons and G. W. Taylor, *J. Phys. Chem.*, 73, 1274 (1969).

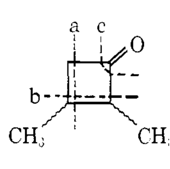
more, the extent of the stereoretention in the photocleavage process of *cis*-2,3-DMCB is ~96%, comparable to (or better than) the extent of the stereoretention in the photocleavage process of *trans*-2,3-DMCB, ≥94% (see Table I).[32] This interpretation is valid only if the ring fission process 11 and 12 for the 2,3-DMCB (S_0*) proceeds by pure stereoretention as in Scheme III, and there is no strong evidence against it.[16]

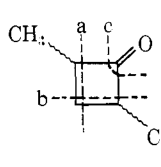
On the assumption that the above analysis is meaningful, we can proceed to examine the mechanism in detail. The ratio of k_{17}/k_{21} is about five times the ratio of k_{16}/k_{18} in Scheme IV, since ~24% of the 2,3-DMCB (S_0*) is of trans isomer from photoexcitation of *cis*-2,3-DMCB and ~5% of the 2,3-DMCB (S_0*) is of cis isomer from photoexcitation of *trans*-2,3-DMCB. If $k_{18} \approx k_{21}$ can be assumed, the k_{16}/k_{17} ratio would be ~0.2, although $k_{18} \geq k_{21}$ might be more realistic. Clearly, a strong driving force in favor of the trans biradical over the cis biradical is provided by the steric hindrance between two CH_3 groups at the C_4 and C_3 carbon atoms (see Scheme IV).

The wavelength dependence of the internal conversion yield (*via* cyclization) *vs.* the decarbonylation yield indicated by the $[R_1(c)/R_0(a + b)]$ ratio is shown for *trans*-2,3-DMCB in Table XIII.

Table XIII. Wavelength Dependence of the Primary Decomposition Yield (Extrapolated to Zero Pressure) in *trans*-2,3-DMCB

	λ_{ex}, nm		
	325	313	281
Quenchable			
R_0(a)	4.44	4.65	2.78
R_0(b)	3.3	3.17	2.17
$[R_0(trans\text{-}2B)/R_0(cis\text{-}2B)]$	14.4	11.6	9.1
Unquenchable			
R_1(a)	~0	~0	0.40
R_1(b)	1.6	1.8	~1.45
R_1(c)	(1.00)	(1.00)	(1.00)
$[R_1(trans\text{-}2B)/R_1(cis\text{-}2B)]$	16.0	13.0	10.8
$R_1(a + b)/R_1(c)$	1.6	1.8	1.85
$[R_1(c)/R_0(a + b)]$	0.13	0.13	0.20
$[R_1(a + b)/R_0(a + b)]$	0.21	0.23	0.37
$[R_1(a + b + c)/R_0(a + b)]$	0.33	0.36	0.57





This ratio, an approximate measure of k_{19}/k_{18}, increases with the increasing photoexcitation energy: 0.13 at 325 nm; 0.13 at 313 nm; 0.20 at 281 nm. This result can be rationalized with the lower Arrhenius *A* factor and the higher activation energy for the photodecarbonylation process 19 than for the cyclization process 18.[33]

One should now note a lesser degree of stereoretention observed in the DMCP products (see Figure 3) compared to the degree of stereoretention observed in the cyclization; *trans*-DMCP/*cis*-DMCP = 4 *vs.* *trans*-2,3-DMCB (S_0*)/*cis*-2,3-DMCB (S_0*) = 15–20 for the 325-nm photolysis of *trans*-2,3-DMCB. A similar correlation is observed also in the 325-nm photolysis of *cis*-2,3-DMCB; *trans*-DMCP/*cis*-2,3-DMCP = 1.0 *vs.* *trans*-2,3-DMCB (S_0*)/*cis*-2,3-DMCB (S_0*) = 0.33. Additional correlations can be obtained by examining the contents of Table XIV in which efficiencies of various competing processes are summarized for all four DMCB isomers at varying wavelengths.

Table XIV. Quantum Yields of the Primary Photochemical Processes (Extrapolated to Zero Pressure) from the DMCB Isomers

	cis-2,4	*trans*-2,4	*cis*-2,4	*trans*-2,3
λ_{ex} 334 nm				
Φ_1(DMCP)	0.177	0.166	0.192	0.180
λ_{ex} 325 nm				
$\Phi_1(S_0^*)$	0.74	0.80	0.77	0.75
Φ_1(PR)	0.16	0.09	0.00	0.00
Φ_1(2-B)	0.00	0.00	0.13	0.15
Φ_1(DMCP)	0.10_3	0.11_1	0.09_9	0.09_6
λ_{ex} 313 nm				
$\Phi_1(S_0^*)$			0.78	0.74
Φ_1(PR)			0.00	0.00
Φ_1(2-B)			0.23	0.17
Φ_1(DMCP)			0.09	0.09_4
λ_{ex} 281 nm				
$\Phi_1(S_0^*)$				0.63
Φ_1(PR)				0.05
Φ_1(2-B)				0.19
Φ_1(DMCP)	0.21	0.23	0.14	0.13
λ_{ex} 253.7 nm				
Φ_1(DMCP)	0.29	0.33	0.19	0.19

(iv) Olefin Cleavage Processes. The degrees of stereoretention observed here for the decarbonylation *vs.* the cyclization process are not consistent with the simple one biradical precursor mechanism which requires both of them to be identical. In order to account for this discrepancy, we need a second kind of biradical, which does not efficiently rotate about the C_2–C_3 bond (of the biradical) and consequently has very low probability for the decarbonylation process with the stereoinversion center at the C_2 position of the biradical.

In the foregoing discussion, it was established that the stereoretention in the *unquenchable* 2-butenes is very high (≥94%) while the stereoretention in the DMCP's and in the 2,3-DMCB (S_0*) is relatively low (<70%) if *cis*-2,3-DMCB is photolyzed at 325 nm. This observation is *also* incompatible with the simple one biradical precursor mechanism, since the degree of stereoretention expected for the olefinic cleavage products should be nearly identical with that observed for the cyclization product (S_0*), if a common biradical precursor is involved.

We are now led to postulate *two distinguishable* biradical precursors: (i) $(BR)_\perp$ having a favorable chance for the C_2–C_3 rotation (k_{23} in Scheme V) compared to the C_3–C_4 rotation (k_{16} or k_{17} in Scheme IV), and (ii) $(BR)_\parallel$ having a rather unfavorable chance for the C_2–C_3 rotation compared to the other processes such

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[32] Although *trans*-2,3-DMCB was better than 99% pure, the impurity *cis*-2,3-DMCB can give enough *cis*-2-butene (~1%) to lower the *trans*-2B/*cis*-2B ratio.

[33] The activation energies of decarbonylation process 19 and cyclization process 18 should be less than 10 kcal/mol, and ΔS_{act} for the former must be more negative than that for the latter.[17] Since the biradical produced here possesses 30–50 kcal/mol, a small energy dependence for the k_{19}/k_{18} is expected from the RRKM theory of unimolecular reaction rates.[18]

as ring closure to give a S_0* ($k_{23} \ll k_{18}$ and $k_{23} \ll k_{21}$). The second biradical, $(BR)_{\parallel}$, must maintain a high stereospecificity and give rise to the cyclization products (S_0*) and the olefinic cleavage products. Furthermore, it is conceivable that it is correlated with oxacarbene (OX, **11**) and ylide-like oxacarbene (YD, **12**) and that it is generated through the skeletal *in-plane* vibrational motions in the vibrationally hot S_1*. The first biradical, $(BR)_{\perp}$, must favor the formation of the decarbonylation products with inversion at the C_2 carbon (of BR). It also permits time sufficient for the inversion at the C_4 carbon (of BR) and an eventual formation of the stereoinverted olefinic cleavage and cyclization (S_0*) products to a minor extent. $(BR)_{\perp}$ is probably formed through the skeletal *out-of-plane* vibrational motions in the vibrationally hot S_1*. The initially prepared photoexcited CB (S_1*) is known to have predominantly *out-of-plane* O-atom wagging vibrations,[4c] because this mode makes the electronically forbidden $\pi^* \leftarrow n$ transition allowed through the vibronic mixing[24] and the progression for the out-of-plane C=O wagging vibration is strong in the optical absorption spectra. If a similar situation prevails with the DMCB (S_1*) species, then one should expect that $(BR)_{\parallel}$ is derived from the initially prepared (DMCB) (S_1*) with *out-of-plane* vibrations through intramolecular vibrational energy transfer processes (or by intermolecular processes in a dense medium).

The precursor for most of the unquenchable olefinic products at λ_{ex} 325 nm could be either DMCB (S_1*) or perhaps the ylide-like oxacarbene (**12**). The fact that the olefin cleavage products are formed with high stereoretention from DMPZ *only* in photolysis[21] encourages us to think that the similar electronic structures of the ylide-like oxacarbene (**12**) and the photoexcited PZ ($n\pi^*$) are responsible for their analogous kinetic behavior in decomposition. There is also the possibility that the photoexcited PZ ($n\pi^*$) might undergo a ring-contraction process (in addition to a ring-opening process) as OX (**11**) has been shown to become CB,[28] although the ring-contraction process for PZ ($n\pi^*$) would be energetically less favorable. It should be noted that the ring-expansion process *via* a bond migration at the α-substituted carbon for the photoexcited, substituted CB (S_1) proceeds with high stereoretention in solution.[27] It is obvious that further studies are required to elucidate the exact nature of the intermediates.

The fact that some pressure-unquenchable propylene is produced from the 281-nm excitation of the 2,3-DMCB (see Table XIV) implies that either or both (a) the C_1–C_4 bond is cleaved to give a hot biradical similar to **10** which decomposes to give PR in addition to DMCP; (b) the bond migration of the unsubstituted α carbon occurs to give the corresponding ylide-like oxacarbene (**12**) or direct cleavage from the S_1 state. A similar observation has been made in the photolyses of 2-*n*-propylcyclobutanone at high photoexcitation energies.[8c]

Direct Photolysis (334 nm). Figure 3 shows that the 334-nm photolysis appears to give an anomalous value of the trans/cis ratio of the DMCP product. This can be rationalized if the increasing importance of the $S_1 \rightsquigarrow T_1$ intersystem crossing at this photoexcitation wavelength is recognized, since the vibronic energy of the DMCB (S_1*) must be very small. If the values of $\Phi(S_1 \rightsquigarrow T_1)$ estimated as [Φ_1(DMCP); 334 nm) − Φ_1(DMCP; 325 nm)] were in the range of 0.06–0.09, then the values of $\Phi(S_1 \rightarrow$ DMCP) in the range of 0.10–0.11 (see Table XIV for the 325-nm values) could account for the observed trans/cis ratios at 334 nm.[4d] A similar interpretation regarding the importance of the $S_1 \rightsquigarrow T_1$ has been given for cyclobutanone near its $S_0 \rightarrow S_1$ absorption threshold.[4b–d] A slight pressure quenching of the DMCP product is also reminiscent of the pressure quenching of the cyclopropane observed in the photolysis of cyclobutanone at 334 nm.[4b]

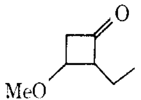
The $P_{1/2}$ value of 1.7 ± 0.2 Torr observed for the propylene yield from *trans*-2,3-DMCB at 334 nm is slightly lower than the $P_{1/2}$ value of 2.2 ± 0.2 Torr observed at 325 nm, indicating that the 2,3-DMCB (S_0*) produced at 334 nm is slightly less excited than that produced at 325 nm.

Liquid-Phase Photolysis (325 nm). In view of the involvement of vibrationally excited species in the photoreactions of the DMCB isomers, it seemed important to examine solution-phase photolyses, since these represent conditions where vibrational relaxation by collision becomes very fast, and the results should be comparable to those in the high-pressure gas phase.

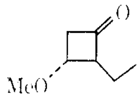
Broadly, the solution-phase data do correspond to those expected from examination of the gas-phase results at the high pressure. In particular, the solution-phase data for the 2,3-DMCB isomers (Table XI) show little propylene formation ($\leq 6\%$ compared to 2-butenes); this agrees well with the observations made in the photolysis of the 2,3-DMCB isomers at high gas pressures. Such preferred cleavage of the ring in α-substituted cyclobutanones has been observed previously in solution.[27]

The *trans*-2B/*cis*-2B ratio from the 2,3-DMCB isomers agrees well with that obtained in the gas studies: photolysis of the *cis*-2,3-DMCB gives 2-butenes of which 4–10% is *trans*-2-butene either in solution or in the high-pressure gas-phase results. Likewise, photolysis of *trans*-2,3-DMCB gives 2-butenes, of which ~4% and ~6% are *cis*-2-butene in solution and in the gas phase, respectively.

Turro and McDaniel[27c] have suggested that in the photolysis of the cyclobutanones **14** and **15** in benzene or methanol, the reactions to give olefin cleavage products or decarbonylation products are entirely stereospecific, and the per cent of nonstereospecific product observed is a result of contamination of the starting cyclobutanone with the alternative isomer. Our results with the isomerically pure and related 2,3-disubstituted cyclobutanones show that there does appear to be a few per cent of nonstereospecific reaction in the cleavage process in the photolysis of the DMCB isomers. A more important difference in our results is that the formation of dimethylcyclopropanes (at least for *cis*-2,3-DMCB and the *cis*- and *trans*-2,4-DMCB isomers) has a large nonstereospecific component. Nevertheless, the partition between *trans*/*cis*-DMCP is broadly in agreement with our results in the gas phase,

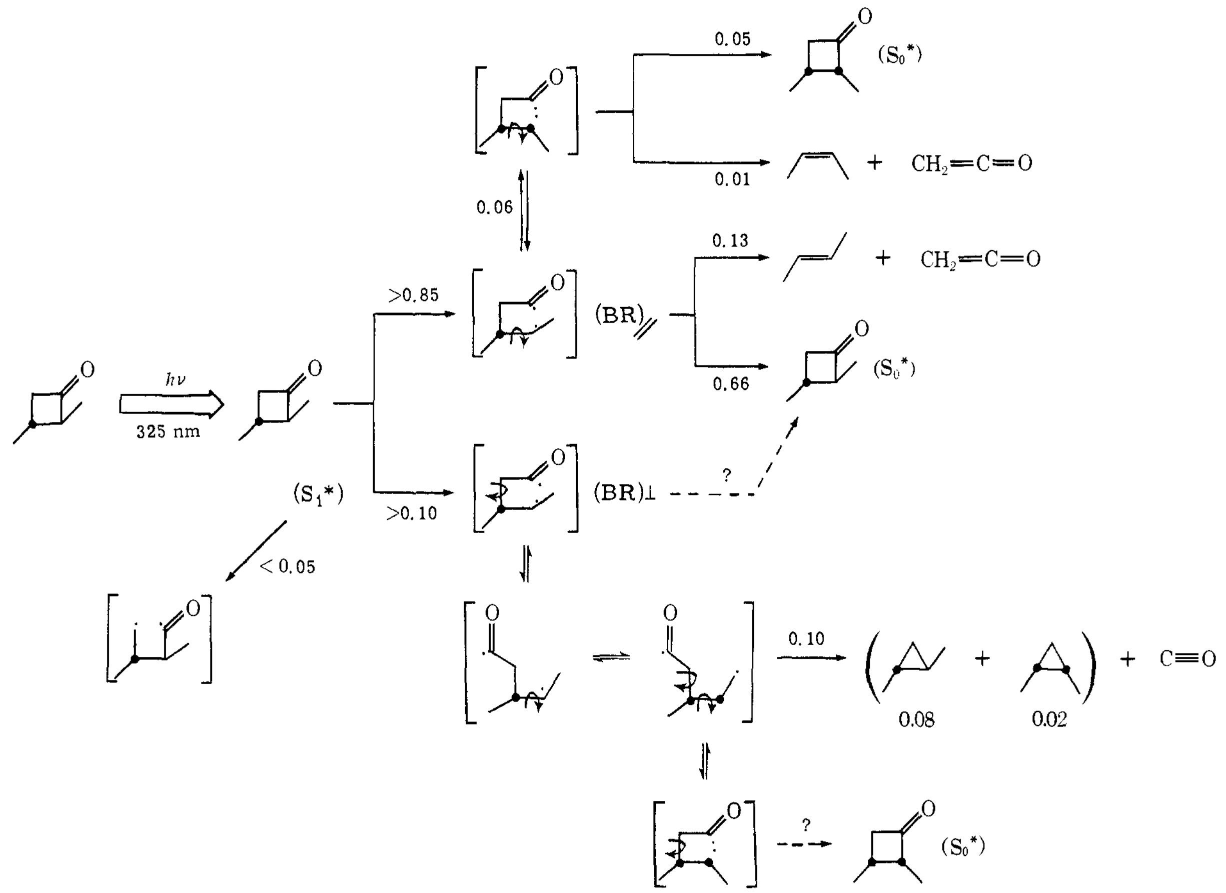


14



15

Scheme VI



suggesting there is no great change of mechanism from gas phase to *n*-heptane solvent. The percentages of the *trans*-DMCP in the total DMCP are as shown below.

	cis-2,3	*trans*-2,3	*cis*-2,4	*trans*-2,4
Gas, %	49	80	70	51
Soln, %	46	91	80	58

The total amounts of cyclopropanes relative to olefins (0.17–0.40) are 2.5–4 times lower than in the gas phase, and suggest the phase change does have some consistent effect on the partitioning of an intermediate between olefins and cyclopropanes, favoring olefin formation in the liquid. This could be ascribed to a cage-like effect hindering the rotation required to bring about a radical attack at the acyl C–C bond with elimination of CO as shown in Scheme V, whereas cleavage to olefin (and ketene) requires no such displacement. It is also conceivable that the ring-opened biradicals might ring-close to give an ylide-like oxacarbene (**12**) in the liquid cage, and as a result the stereoretention in the 2-butene product obtained in the solution-phase photolysis of *cis*-2,3-DMCB is lower by ~5% than that obtained in the gas-phase photolyses at 325 nm.

Overall Mechanism. Scheme VI gives a summary of the various competing photochemical transformation processes and their yields for *trans*-2,3-DMCB as an example. Similar information for the other DMCB isomers can be obtained from Table XIV.

Role of Electronic Spin Multiplicity. The mechanistic role of the electronic spin multiplicity has been questioned and discussed extensively in the literature.[34] In order to discuss the possible mechanistic role of the biradical spin states, we follow the suggestion of Cvetanović[35] and use an operational definition of "singlet" or "triplet" whose origin is traceable to the spin state of the precursor of the biradical. We are specifically concerned with the tetramethylene and trimethylene biradicals and their analogs.

We have produced the DMCB isomers in their S_1 and T_1 states having comparable vibrational excitation energies *via* direct and triplet-sensitized transitions. Clearly, the former gives a short-lived (< 10^{-10} sec) *singlet* 1,4-biradical of type **10** which undergoes competitively (i) cyclization (ii), decarbonylation, and (iii) bond rotation with rates $k_{\mathrm{i}} > k_{\mathrm{ii}} \geq k_{\mathrm{iii}}$, whereas the latter gives a long-lived (> 10^{-9} sec) *triplet* 1,3-biradical (**8** or **9**) and CO either directly or *via* intermediacy of a fleeting *triplet* 1,4-biradical of type **10** which fails to cyclize, $k_{\mathrm{i}} \ll k_{\mathrm{ii}}$. Evidence accumulated in the nπ^* photolysis of cyclopentanone[4a,36] and substituted cyclopentanones[37,38] is certainly in favor of a mechanism that the S_1 state of the cyclopentanones mainly undergoes the $S_1 \rightsquigarrow T_1$ intersystem crossing process.[25] Vi-

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(34) See, for example, (a) F. A. Matsen, *J. Amer. Chem. Soc.*, **92**, 3525 (1970); (b) F. A. Matsen and D. J. Klein, *Advan. Photochem.*, **7**, 1 (1969); (c) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); (d) L. M. Stephenson and J. I. Brauman, *ibid.*, **93**, 1988 (1971).

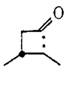
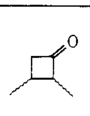
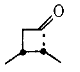
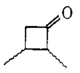
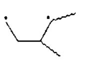
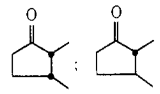
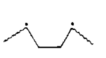
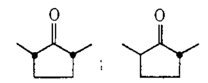
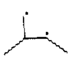
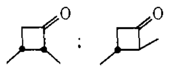
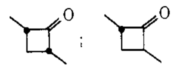
(35) R. J. Cvetanović, *J. Phys. Chem.*, 74, 2730 (1970).

(36) One of the latest studies includes a brief review of the earlier literature: A. T. Blades, *Can. J. Chem.*, **48**, 2269 (1970).

(37) (a) H. M. Frey and D. H. Lister, *J. Chem. Soc. A*, 627 (1970); (b) H. M. Frey and I. C. Vinall, *ibid.*, 3010 (1970).

(38) R. Lande and E. K. C. Lee, an unpublished photolysis study of *cis*-2,5- and *trans*-2,5-dimethylcyclopentanone in the gas phase. The trans/cis ratios for dimethylcyclobutane from 1.0 Torr of trans ketone at 23° are 1.00 ± 0.07 at 334 nm, 1.00 ± 0.08 at 313 nm, and 1.08 ± 0.08 (1.00 ± 0.08 for 5.0 Torr of trans ketone) at 254 nm. An identical product distribution was obtained with cis ketone. The olefin cleavage/decarbonylation ratios $[C_3H_6/2C_6H_{12}]$ were ~1.6, 1.6, and 2.4, respectively, at the three photolysis wavelengths.

Table XV. Ratio of Trans/Cis Observed in the Ring-Closed Products from Various Sources

	Precursor	Product	Trans/cis	Ref
 (S)		 (S_0*)	~20	This work
 (S)		 (S_0*)	~0.33	This work
 (T) from		 (S_0*)	3.9[a]	37a
 (T) from		 (S_0*)	1.0	38
 (T) from		 (S_0*)	2.4	This work, 3c
 (T) from		 (S_0*)	1.23	This work, 3c

[a] All measurements were made at 23°, except for this measurement at 100°

brationally hot T_1 species then decompose to give the olefinic and cyclobutane products (and CO) in favor of the low-energy 4-pentenal products. The precursors of the dimethylcyclobutanes are presumably *triplet* dimethyltetramethylene biradicals (**16** from 2,3-dimethylcyclopentanone[37a] and **17** from 2,5-dimethylcyclopentanone[38]). We will consider then that *singlet* dimethyltetramethylenes (**16** and **17**) are produced in *thermolysis* of *cis*- and *trans*-dimethylcyclobutanes.[17,39]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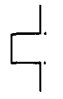
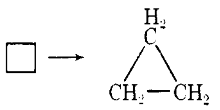
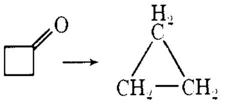

17

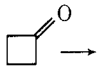
Enthalpies (at 23°) of decomposition processes involving cyclobutane and cyclobutanones will be similar to those involving dimethyl-substituted molecules. So, we will compare energetics of the following processes using the unsubstituted molecules.[17]

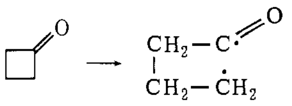
If it can be assumed that the rates of decomposition are mainly controlled by the enthalpy changes involved, and that electronic spin is conserved, we can rationalize from the values of enthalpy change why (i) singlet biradical **10** from DMCB (S_1) decomposes in favor of the decarbonylation process (19 in Scheme IV, or 26) over the olefin-cleavage process (20 in Scheme IV, or 27); (ii) singlet biradicals **16** and **17** from thermolysis[39] decompose only to olefins *via* C_2–C_3 bond rupture; (iii) triplet biradical **10** from DMCB (T_1) decomposes almost entirely *via* a decarbonylation process rather than *via* an olefin cleavage process;[3c,6ab] (iv) triplet biradicals **16** and **17** from 2,3-dimethylcyclopentanones[37a] and 2,5-dimethylcyclopentanones[38] (respectively) decompose *via* an olefin cleavage process.

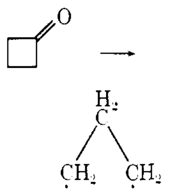

$\longrightarrow C_2H_4 + C_2H_4 \quad \Delta H = 18$ kcal/mol (24)


$+ \ CH_2 \quad \Delta H \approx 100$ kcal/mol (25)


$+ \ CO \quad \Delta H = 6$ kcal/mol (26)


$\longrightarrow CH_2CH_2 + CH_2CO \quad \Delta H = 18$ kcal/mol (27)


$\Delta H = 56\text{–}60$ kcal/mol (28)


(T) + CO $\Delta H = 65\text{–}75$ kcal/mol (29)

The fact that relatively stereospecific cyclization products result from the singlet C_4 biradicals while nonstereospecific cyclization products result from the triplet C_3 and C_4 biradicals is indicative of much *faster* ring closure *vs.* internal C–C bond rotation in the singlet species as compared to the ring closure *vs.* rotation in the triplet species. Furthermore, the trans conformation of the 1,2-dimethyl biradicals is favored consistently over the cis conformation for them, but such difference is minor for the 1,3- or 1,4-dimethyl biradicals (see Table XV). Varying degrees of steric interferences between two CH_3 groups in trans and cis conformers of the 1,2-DMTM biradical (**8**) are illustrated in Figure 7. van der Waals radius for the CH_3 group was taken to be 2.1 Å (as in CH_4), and a circle of this radius was drawn in. Conformational energy dependence calculated for the rotation angle ϕ from

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(39) (a) H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, **83**, 3935, 4883 (1961); (b) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968).

the trans conformation in *n*-butane[40] is also shown. The second minimum corresponding to $\phi = 112.5°$ (close to cis conformation) occurs $\sim$0.6 kcal/mol above the trans conformation ($\phi = 0$), and the Boltzmann factor at 300°K for the ratio of trans conformer/cis conformer is 2.7. Since the relaxed triplet 1,2-DMTM biradical (**8**), which lives long enough to achieve rotational (internal) equilibrium at room temperature, gives the *trans*-DMCP/*cis*-DMCP ratio of 2.4, it is likely that the conformer ratio for the DMTM biradical determines the *trans*-DMCP/*cis*-DMCP ratio, on the assumption that the biradical conformational and the *n*-butane conformational interactions are similar. It is also clear that steric interference between the two CH$_3$ groups in the *trans,trans*-1,3-DMTM biradicals (**9**) is nearly nonexistent, and hence the *trans*-DMCP/*cis*-DMCP ratio is near unity, $\sim$1.23. We believe similar arguments apply also in the case of triplet dimethyltetramethylene biradicals **16** and **17**. We should, however, note that the trans/cis ratio obtained for the cyclized dimethylcyclobutane from the biradical **16** is 3.9, indicating the possibility that an additional instability exists for the cis conformer of the 1,2-dimethyltetramethylene.

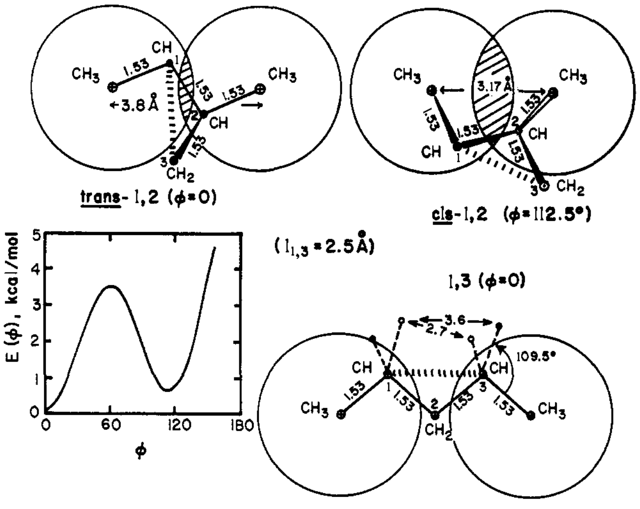

Figure 7. Projections of various geometries of model dimethyltrimethylenes having normal C–C and C–H bond distances. Steric interference between the two CH$_3$ groups is indicated by 2.1-Å circles corresponding to the van der Waals radius of the CH$_3$ group. Conformational energies of *n*-butane *vs.* the angle of deviation from the plane of the trans conformer is shown after Flory (ref 40).

In conclusion, we emphasize that the most important difference between the singlet and triplet biradicals is the short and long lifetime, respectively, with respect to cyclization. The long lifetime ($\sim$10^{-8} sec)[4c] of the triplet biradicals (slow ring closure) may be due to the slow spin-forbidden $T \rightsquigarrow S$ intersystem crossing which may precede the final act of coupling of the two radical centers.

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(40) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, pp 51, 141.

Decomposition of *cis*- and *trans*-2,3- and -2,4-dimethylcyclobutanones from the Vibrationally Excited Ground States. Thermal and Photochemical Activation[1]

John Metcalfe, Howard A. J. Carless, and Edward K. C. Lee*

Contribution from the Department of Chemistry,
University of California, Irvine, California 92664. *Received November 12, 1971*

Abstract: The unimolecular decomposition pathways of vibrationally hot cis and trans isomers of 2,3- and 2,4-dimethylcyclobutanone (DMCB) have been studied. Effects of geometric isomerism, position of CH$_3$ group substitution, and internal excitation energies (50–104 kcal/mol) on the decomposition rates are measured. Rates are significantly enhanced by high excitation, α,β rather than the α,α' substitution, and cis geometry of the 2,3-DMCB isomers. An attempt is made to rationalize these and other rate variations, by assuming steric interference in the critical configurations of the twisted cyclobutanone ring. It is found that specific rate constants calculated from the RRKM unimolecular rate theory agree well with the observed rate values. Collisional efficiencies (relative) of Ar, O$_2$, C$_2$H$_4$, and *trans*-2,3-DMCB in deactivating vibrationally hot *trans*-2,3-DMCB (S$_0$*, 91 kcal/mol) have been found to be 0.22, 0.26, 0.62, and 1.00. The probable mechanism of a minor thermal decarbonylation process (<0.2%) and its implication in cyclobutanone chemistry are briefly discussed.

It has been recently shown that vibrationally hot ground state cyclobutanones (S$_0$*) decompose in a concerted manner.[2] Likewise, the reverse reaction of cycloaddition of ketene and olefins has been found to be stereospecific (with retention of the configuration of the olefin) in several cases.[3] The present work on the *cis*- and *trans*-2,3- and -2,4-dimethylcyclobutanones (DMCB) was undertaken to investigate further the unimolecular rate processes involved in the decomposi-

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(1) This research has been supported by National Science Foundation Grant GP-28010X.

(2) (a) H. A. J. Carless and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 4482, 6683 (1970); (b) *ibid.*, **94**, 1 (1972).

(3) (a) R. Huisgen, L. Feiler, and G. Binsch, *Angew. Chem., Int. Ed. Engl.*, **3**, 753 (1964); (b) J. C. Martin, V. W. Goodlett, and R. D. Burpitt, *J. Org. Chem.*, **30**, 4309 (1965); (c) R. Montaigne and L. Ghosez, *Angew. Chem., Int. Ed. Engl.*, **7**, 221 (1968); (d) G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Lett.*, 4497 (1968); (e) T. Do Minh and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 1766 (1970).