# Kinetic Study of Dimethyltrimethylene Intermediates by the Triplet Mercury ($6^3P_1$) Photosensitization of Dimethylcyclobutanones[1]

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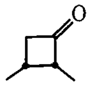
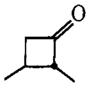
**Abstract:** Hg($6^3P_1$, 112.7 kcal/mol) photosensitization of *cis*- and *trans*-2,3-dimethylcyclobutanone (**1** and **2**) and *cis*- and *trans*-2,4-dimethylcyclobutanone (**3** and **4**) at room temperature gave decomposition products which are formed by two distinct pathways. Formation of a dimethyltrimethylene biradical ("triplet") *via* efficient decarbonylation accounts for 0.8 of the products, while formation of an excited singlet dimethylcyclobutanone accounts for 0.2 of the products. The *hot* biradical intermediate can undergo: (1) ring closure to give *cis*- and *trans*-dimethylcyclopropanes; (2) 1,2-hydrogen shift to give pentenes; or (3) dissociation to give 2 monoradical fragments. The lifetime of the hot biradical intermediate can be estimated as $\sim 10^{-9}$ sec, upon examination of the quenching effects of inert Ar gas on the dissociation process. In contrast, the biradicals produced in the benzene ($^3B_{1u}$, 84.5 kcal/mol) photosensitization undergo only ring closure. The similarities as well as the differences in the kinetic behavior of "triplet" trimethylene biradicals produced by various experimental methods are discussed.

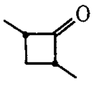
Significant mechanistic insight has recently been gained into the stereochemistry of concerted ring fission and decarbonylation processes by studying direct photolytic, ($^3B_{1u}$) benzene-photosensitized, and pyrolytic decomposition of *cis*- and *trans*-2,3- and 2,4-dimethylcyclobutanones (DMCB).[2]



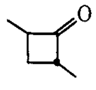
1 (*cis*-2,3-DMCB)



2 (*trans*-2,3-DMCB)



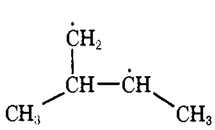
3 (*cis*-2,4-DMCB)



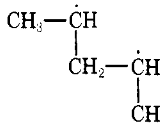
4 (*trans*-2,4-DMCB)

These studies have been extended to include Hg($6^3P_1$) photosensitization in order to better understand the differences in kinetic behavior of the proposed biradical intermediates. The product stereochemistry can give insight into the effects of (a) electronic spin states (singlet and triplet) and (b) vibrational energy on the reaction intermediates. The results obtained here with the four DMCB isomers will be compared to the results obtained in the Hg($6^3P_1$)-photosensitized decomposition of cyclobutanone for which the amount of singlet sensitization was estimated to be 10.5%.[3]

The proposed 1,2-dimethyltrimethylene biradical (1,2-DMTM) (**5**) generated from *cis*- and *trans*-2,3-DMCB will be compared to the triplet 1,2-DMTM generated in the addition of triplet methylene to *cis*- or *trans*-2-butene[4-6] and to the analogous biradical 1,3-DMTM (**6**) generated from *cis*- and *trans*-2,4-DMCB. These biradicals give *cis*- and *trans*-dimethylcyclopropanes (**7** and **8**) upon ring closure.



5 (1, 2-DMTM)



6 (1, 3-DMTM)

7 (*cis*-DMCP)

8 (*trans*-DMCP)

## Experimental Section

Samples of *cis*- and *trans*-2,3-DMCB and *cis*- and *trans*-2,4-DMCB prepared for the earlier studies[2] in this laboratory were used. The hydrocarbon impurities were present in less than 0.005%, while the geometric isomer impurity was present in an amount (<1%) insignificant for the present study. Cyclobutanone was obtained from Aldrich Chemical Co., and was used without further purification as the impurities were less than 0.005%. Whenever necessary, a small correction for the hydrocarbon impurity present in the sample prior to photolysis was made. Ar (Baker Chemical Co.) and $O_2$ (Air Products) were used without purification.

The photolysis cell was a cylindrical quartz vessel of 30.5 ml volume with a flat end window (25 mm o.d.). It was equipped with a greaseless valve having a Viton diaphragm (Springham). While in use the valve was heated above 50° with a heat gun in order to reduce the amount of the parent ketones absorbed by the diaphragm. Mercury vapor was provided by a small droplet of mercury in the vessel at room temperature (23 ± 2°). The samples were handled in a grease-free, glass vacuum line equipped with glass–Teflon valves (Fisher-Porter). The pressure measurement was made with a diaphragm gauge (Consolidated Vacuum, GHD-100) to an accuracy of 10% or 0.2 Torr, whichever is greater. A combination of a low-pressure mercury resonance lamp (Ultraviolet Products, Mineralight R-51), a Corning CS 7-54 filter, and a 10-mm thick $D_3P$ filter solution[7] provided monochromatic radiation at 2537 Å. Normal photolysis time was 10 sec, although one photolysis of 240-sec duration was carried out in which the intensity was reduced 20-fold with a set of collimator plates. Typical conversion was <1%.

After photolysis, samples were transferred on the vacuum line to an evacuated sample loop (14.2 ml) immersed in liquid nitrogen.

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[1] This research has been supported by a National Science Foundation grant and a Petroleum Research Fund grant administered by the American Chemical Society.

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

[3] D. C. Montague and F. S. Rowland, *ibid.*, **91**, 7230 (1969).

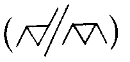
[4] (a) H. M. Frey, *Progr. React. Kinet.*, **2**, 131 (1964); (b) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; (c) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

[5] C. McKnight, P. S. T. Lee, and F. S. Rowland, *J. Amer. Chem. Soc.*, **89**, 6802 (1967).

[6] (a) D. C. Montague and F. S. Rowland, *J. Phys. Chem.*, **72**, 3705 (1968); (b) a Hg($6^3P_1$) sensitization study to be published.

[7] (a) C. L. Braga and M. D. Lumb, *J. Sci. Instrum.*, **43**, 341 (1966); (b) R. G. Shortridge, Jr., and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 2228 (1970).

**Table I.** Hydrocarbon Product Distribution in Hg($^3P_1$) Sensitization of *cis*- and *trans*-2,4-DMCB[a]

| | Pressure, Torr | | | Products,[b] mol % | | | | |
|---|---|---|---|---|---|---|---|---|
| Run no. | *cis*-3 | *trans*-4 | Additive |  |  |  |  (c) |  |
| 54 | 1.0 | | | 12.5 | 0.8 | 48.1 | 38.7 | 1.24 |
| 55 | 1.0 | | ~0.2 ($O_2$) | 15.6 | 0.7 | 46.3 | 37.4 | 1.24 |
| 56 | 1.0 | | 0.3 ($O_2$) | 15.8 | 0.3 | 46.9 | 36.9 | 1.26 |
| 33 | 1.0 | | | 12.4 | 0.6 | 47.9 | 39.1 | 1.22 |
| 38 | 1.0 | | 77 (Ar) | 7.9 | 0.2 | 50.2 | 41.1 | 1.20 |
| 36 | 1.0 | | 250 (Ar) | 6.6 | 0.2 | 50.9 | 42.1 | 1.21 |
| 43 | 1.0 | | 560 (Ar) | 4.7 | 0.1 | 52.3 | 42.8 | 1.22 |
| 35 | 1.0 | | 580 (Ar) | 5.2 | 0.1 | 52.1 | 42.6 | 1.22 |
| 31 | | 1.0 | | 12.3 | 0.5 | 48.0 | 39.3 | 1.22 |
| 45 | | 1.0 | 540 (Ar) | 4.2 | 0.2 | 52.5 | 43.1 | 1.22 |

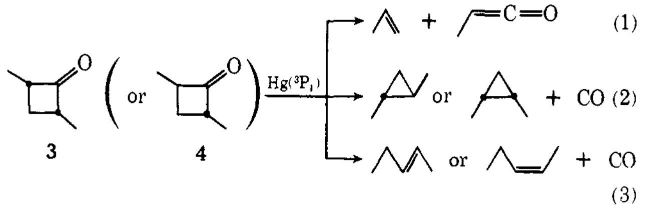
[a] Samples were irradiated for 10 sec, except in runs 54–56 (20 sec). [b] Probable error for the product yield is ±0.2. [c] Includes a small amount of unseparated *cis*-2-pentene, probably less than the amount of *trans*-2-pentene.

Noncondensable gaseous products (chiefly CO) were not collected by this sampling procedure. The sample in the loop was injected into a 25 ft × 0.25 in. o.d. dimethylsulfolane column (30% by weight of DMS on Chromosorb P) at room temperature, and it was analyzed with a flame ionization detector (Perkin-Elmer F-11). The $C_1$–$C_5$ hydrocarbon product distribution was then obtained by correcting the gc peak areas (ball and disk integrator) for their calibrated molar sensitivity. Separation of *cis*-2-pentene from *cis*-dimethylcyclopropane was not possible on the DMS column, and thus the sum of the two was measured. Unfortunately, several samples were contaminated with minor but undetermined quantities of nonphotolytic *cis*-2-butenes, and thus the *cis*-2-butene yields were not evaluated (Table II). Analysis of $CH_4$ and CO was not possible using the normal sampling technique because they were removed as noncondensable gases. Determinations of $CH_4$ present were made from runs when the noncondensable gases were not removed, and it was found to be present in a minor quantity, <0.1 of the amount of $C_2H_6$ present.

Occasionally, 0.2 Torr of $O_2$ was added to scavenge the long-lived free radicals. It is estimated that the triplet energy transfer from Hg($^3P_1$) to the ketones at 1.0 Torr pressure is reduced by ~7% by the $O_2$ addition.

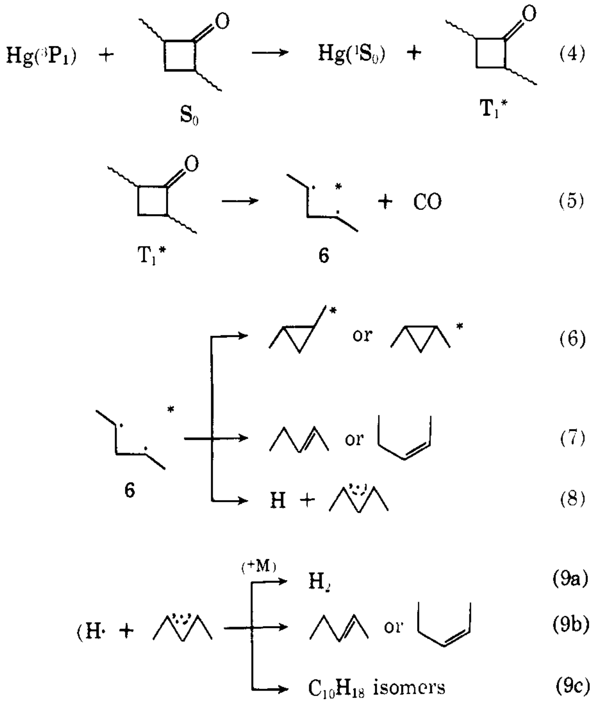
## Results and Discussion

**A.** ***cis*- and *trans*-2,4-DMCB (3 and 4).** The Hg($6^3P_1$) photosensitized decomposition of 1.0 Torr of *cis*- or *trans*-2,4-DMCB gave products which are largely accountable for by the following three pathways (eq 1–3). The product yields are shown in Table I and there appears to be no significant difference between the product yields from the cis or trans isomers.



The trans/cis ratio for the DMCP (**8**/**7**) is constant at 1.23 ± 0.03, the same, within experimental error, as the value obtained in the ($^3B_{1u}$) benzene photosensitization of 2,4-DMCB but unlike in the direct photolysis of 2,4-DMCB.[2b] The DMCP yields are unaffected by the addition of small quantities of $O_2$, as a free-radical scavenger, and Ar, as an inert deactivating gas, whereas the yields of the minor products, propylene and the 2-pentenes, are affected.

The probable precursor of propylene is an excited singlet state of 2,4-DMCB as found in the Hg($^3P_1$)–cyclobutanone system[3] and it will be discussed later in part B. The most probable precursor of dimethylcyclopropane is the triplet state of 2,4-DMCB which decomposes to a biradical **6**. The following mechanistic scheme seems adequate (eq 4–9c). Since neither 3-methyl-1-butene nor 2-methyl-2-butene[8] is found as a product in this sytem, the structural isomerization of the hot dimethylcyclopropanes produced in eq 6 must be negligible. It was not practical to measure the yields of $H_2$ and $C_{10}H_{18}$ isomers in these samples, and the $O_2$ scavengeable yield of 2-pentenes provides the estimate of the unimolecular H elimination process (eq 8), because 0.2 Torr of $O_2$ is sufficient to scavenge entirely H atoms and 1,3-dimethylallyl radicals. The precursor responsible for the relatively slow H elimination process must be the vibrationally hot biradical **6** which is degraded in energy by the deactivating collisions with Ar.



**B.** ***cis*- and *trans*-2,3-DMCB (1 and 2).** The Hg($^3P_1$)-photosensitized decomposition of 1.0 Torr of 2,3-DMCB gave a product distribution more complex than that obtained from the Hg($^3P_1$)–2,4-DMCB system. Table II shows no serious, unaccountable effect of the

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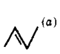
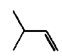
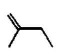
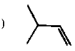
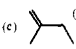
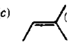
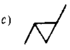
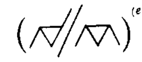
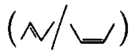
(8) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc., Ser. A*, 260, 424 (1961).

**Table II.** Effects of Photolysis Time, Intensity, and Pressure Variation on the Product Distribution [Hg($^3P_1$) + *trans*-2,3-DMCB(**2**)]

| Run no. | Time, sec | *P*, Torr | Conv, % | C–C |  |  [a] |  |  |  |  |  |  [b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 6 | 1.0 | 0.17 | 7.2 | 8.0 | 5.5 | 1.2 | 1.4 | 0.4 | 0.5 | 48.4 | 26.4 |
| 7 | 10 | 1.0 | 0.33 | 6.3 | 7.8 | 6.3 | 1.6 | 1.6 | 0.4 | 0.8 | 47.5 | 26.7 |
| 8 | 20 | 1.0 | 0.67 | 5.9 | 7.5 | 6.9 | 2.1 | 2.4 | 0.6 | 0.5 | 46.5 | 26.4 |
| 19[c] | 240 | 1.0 | 0.27 | 3.9 | 8.4 | 6.5 | 0.3 | 0.3 | 0.7 | 0.6 | 51.0 | 27.5 |
| 6 | 10 | 0.5 | 0.50 | 6.5 | 7.6 | 6.8 | 1.7 | 2.0 | 0.5 | 0.9 | 46.4 | 25.8 |
| 5 | 10 | 3.0 | 0.21 | 5.7 | 7.5 | 5.8 | 1.8 | 1.7 | 0.4 | 0.6 | 48.7 | 27.2 |

[a] The *cis*-2-butene yield was estimated as ~1% in all cases. [b] Includes a small amount of unseparated *cis*-2-pentene. [c] Intensity was reduced by 20-fold.

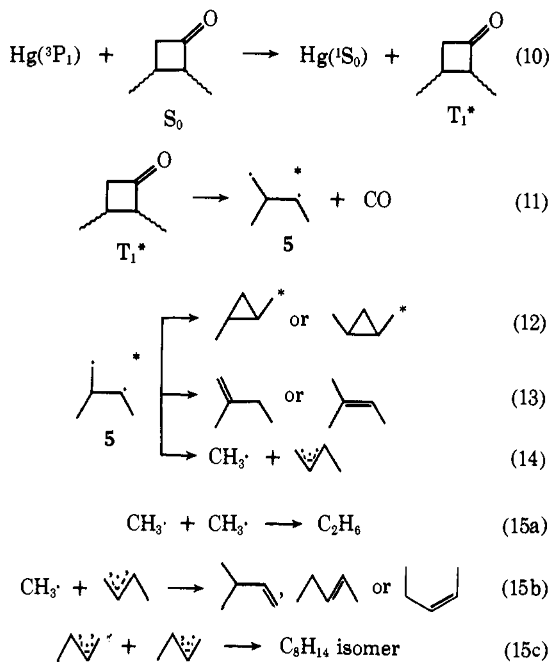
**Table III.** Hydrocarbon Product Distributions in Hg($^3P_1$) Sensitization of *cis*- and *trans*-2,3-DMCB[a]

| Run no. | Pressure, Torr *cis*-**1** | Pressure, Torr *trans*-**2** | Additive | Products, mol % C–C |  |  |  [b] |  |  [c] |  [c] |  [c] |  |  [d] |  [e] |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 9 | 1.0 | | | 6.2 | 9.9 | 1.3 | 6.2 | 1.1 | 0.9 | 0.3 | 0.6 | 46.6 | 27.2 | 1.75 | 0.2 |
| 29 | 1.0 | | 580 (Ar) | 0.8 | 4.4 | (0.7) | (3.4) | 0.3 | 0.3 | 0.3 | 0.3 | 60.0 | 28.3 | 2.12 | |
| 49 | | 1.0 | 0.2 ($O_2$) | | 8.5 | 7.9 | 0.9 | | | 0.4 | 0.5 | 53.6 | 27.7 | 1.93 | 9 |
| 47 | | 1.0 | | 6.2 | 7.4 | 6.9 | 0.8 | 1.7 | 1.5 | 0.5 | 0.4 | 48.4 | 26.5 | 1.90 | 9 |
| 11 | | 1.0 | 44 (Ar) | 4.8 | 6.7 | 6.3 | (0.8) | 1.0 | 0.7 | 0.4 | 0.2 | 51.2 | 28.0 | 1.86 | |
| 12 | | 1.0 | 89 (Ar) | 3.2 | 6.2 | 5.8 | (0.7) | 0.7 | 0.5 | 0.5 | 0.4 | 53.2 | 28.8 | 1.87 | |
| 13 | | 1.0 | 213 (Ar) | 1.7 | 4.5 | 4.8 | (0.6) | 0.4 | 0.2 | 0.4 | 0.5 | 57.1 | 29.8 | 1.93 | |
| 46 | | 1.0 | 540 (Ar) | 1.9 | 2.7 | 3.8 | 0.5 | 0.8 | 0.6 | 0.4 | 0.4 | 60.6 | 28.2 | 2.18 | 8 |
| 28 | | 1.0 | 580 (Ar) | 1.7 | 3.0 | 3.3 | (0.4) | 0.3 | 0.3 | 0.4 | 0.7 | 62.3 | 27.7 | 2.26 | |
| 20 | | 1.0 | 620 (Ar) | 1.8 | 2.4 | 3.4 | (0.4) | 0.8 | 0.6 | 0.3 | 0.3 | 62.5 | 27.5 | 2.30 | |

[a] All samples were irradiated for 10 sec. [b] Amounts of *cis*-2-butene in parentheses were estimated. [c] Probable error for the product yield is ±0.2. [d] Includes a small amount of unseparated (*cis*-2-pentene) ≈ 0.7 × (*trans*-2-pentene). [e] Corrected for the *cis*-2-pentene as indicated in footnote *d*.

parent pressure variation on the per cent conversion and the product distribution,[9] but it shows clearly a substantial effect of the photolysis time and photolytic intensity. The relative yields of 3-methyl-1-butene and *trans*-2-pentene are reduced by short photolysis time, while that of ethane increases. Reduction of the photolytic intensity also reduces the yields of these products, the yields of the 2-pentenes being reduced more than that of ethane. The results obtained to show the effects of $O_2$ scavenger and inert gas pressure are shown in Table III.

The major products, *cis*- and *trans*-dimethylcyclopropanes, and the minor products, 2-methyl-1-butene and 2-methyl-2-butene, are probably the result of ring closure of the biradical **5** and 1,2-H migration in the biradical **5**, respectively, as observed analogously in 2,4-DMCB's (eq 10–15c). The trans/cis ratio for dimethylcyclopropane from 1.0 Torr of *cis*-2,3-DMCB (**1**) is ~1.75 and that from 1.0 Torr of *trans*-2,3-DMCB (**2**) is ~1.90, showing only a slight difference. This ratio, at 580 Torr Ar pressure, is also nearly the same from both parent isomers, 2.1 *vs.* 2.3, which is considerably higher than that obtained at low pressure but is appreciably lower than that obtained in the benzene ($^3B_{1u}$) photosensitization of 1,2-DMCB, ~2.6[2a] or 2.4 as in ref 10. Furthermore, the trans/cis ratio for dimethylcyclopropane produced from the triplet $CH_2$ addition to *trans*- or *cis*-2-butene is 1.58 at the total pressure of 50 Torr (2-butene + ketene), and it also increases with the increasing pressure.[6]



An average amount of the internal energy transferred to cyclobutanone from the benzene ($^3B_{1u}$, 84.5 kcal/mol) photosensitization of cyclobutanone has been found to be 80–85 kcal/mol,[11] while that from the Hg($6^3P_1$, 112.7 kcal/mol) has been found to be ~105 kcal/mol.[3] Therefore, one could estimate that the hot cyclopropane resulting from the benzene ($^3B_{1u}$) and the Hg($^3P_1$) sensitization have <75 and <100 kcal/mol of internal excitation energy, respectively.[12]

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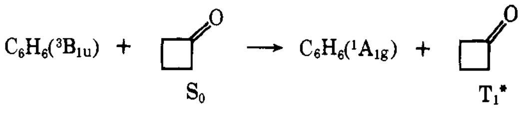
(9) The extent of the conversion in runs 5–7 follows a Stern–Volmer relationship for the quenching of Hg($^3P_1$) by 2,3-DMCB.

(10) More accurate trans/cis ratios for dimethylcyclopropane determined recently in the benzene ($^3B_{1u}$) sensitization of *cis*- and *trans*-2,3-DMCB are 2.37 and 2.42, respectively.[2a]

(11) H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, **90**, 3628 (1968).

(12) The value of $\Delta H$ for the decarbonylation of the ground-state cyclobutanone is +6.7 kcal/mol.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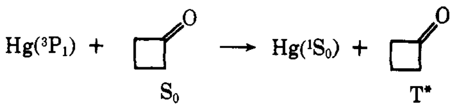
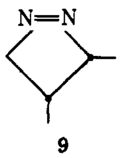

(17)

For the case of the DMCB, only a very small fraction of the excess energy should be partitioned to CO in the decarbonylation process, if the energy partitioning would be statistical to an approximation. Therefore, we estimate that the most probable excess energies of the hot dimethylcyclopropanes resulting from the benzene ($^3B_{1u}$) and Hg($^3P_1$) sensitization of 2,3-DMCB are ~65 and ~90 kcal/mol, respectively, while the excess energy of the hot dimethylcyclopropanes resulting from the triplet $CH_2$ addition to 2-butenes must be ~92 kcal/mol.[13] These three values are consistent with the interpretation that the trans/cis ratio for dimethylcyclopropanes increases with the decreasing internal excess energy of dimethylcyclopropane, nearing a lower energy value of ~2.4.[10,14] The four minor products, ethane, 3-methyl-1-butene, *cis*- and *trans*-2-pentene, are eliminated by addition of 0.2 Torr of $O_2$, reduced by the lower photolytic intensity, and reduced by an addition of Ar as an inert quencher. These observations are consistent with a mechanism in which a vibrationally hot biradical **5** decomposes unimolecularly by an allylic $CH_3$ elimination[15] and subsequent recombinations of $CH_3$ and butenyl (methylallyl) radicals give rise to the above products. Although the $C_8$ diolefins resulting from the recombination reactions of two butenyl radicals were not analyzed due to the limitation in the gas chromatographic analysis,[16] there is no reason to suspect their absence in the photolytic samples. The $CH_3$ elimination reaction (eq 14) has been observed also in the triplet $CH_2$ addition reactions to 2-butenes where slightly greater extent of the decomposition is observed due to a greater excess energy present in the 1,2-DMTM biradical **5** thus generated.[6]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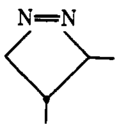
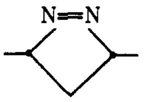
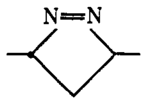

**10**


**11**


**12**

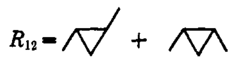
The ratio of $R_{15a}/R_{15b}$ decreases with the increasing photolysis time at normal intensities indicating that the $CH_3$ radical reaches its steady-state concentration more rapidly than the butenyl radical. This is to be expected as the rates of recombination of the allyl radical, which contains a similar radical stabilization from a double bond as the butenyl radicals, recombine at about a quarter of the rate of methyl radicals.[17] The products from reactions 15a and 15b decrease when the intensity of radiation is reduced 20-fold indicating that a large fraction of radicals may be removed by processes other than recombination reactions. This implies that the yield of the $CH_3$ elimination reaction 14a determined from the experimental results may be too small. With the assumptions[18] that the *cis*-2-pentene yield is 0.7 times the *trans*-2-pentene yield, the minimum $CH_3$ yield is

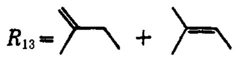
$$R(CH_3) = R_{14} \geq 2R_{15a} + R_{15b} \qquad (18)$$

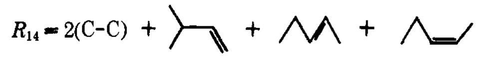
We estimate from runs 7–9 that ~19% of the 1,2-DMTM biradical **5** decomposes *via* $CH_3$ elimination process 14 at 1.0 Torr. The per cent decomposition of the biradical **5** decreases with the increasing Ar pressure as shown in Table IV. Since a trace amount of $O_2$ impurity present in the Ar-pressurized samples could easily lower the radical yields, the values of $R_{14}$ shown in Table IV must be regarded as the lower limit.

**Table IV.** Estimates of Relative Radical Yields in Hg($^3P_1$)–*trans*-2,3-DMCB Samples

| Runs | Pressures, Torr Parent | Ar | $R_{12}{}^a$ | $R_{13}{}^b$ | $R_{14}{}^c$ | % $R_{14}$ |
|---|---|---|---|---|---|---|
| 4 | 1.0 | | 73.8 | 0.9 | 18.2 | 19.6 |
| 7 | 1.0 | | 73.1 | 1.2 | 16.9 | 18.5 |
| 8 | 1.0 | | 71.2 | 1.1 | 18.0 | 19.9 |
| 47 | 1.0 | | 73.9 | 0.9 | 14.9 | 16.6 |
| 11 | 1.0 | 44 | 78.7 | 0.6 | 11.8 | 13.0 |
| 12 | 1.0 | 89 | 81.6 | 0.9 | 8.0 | 8.8 |
| 46 | 1.0 | 540 | 88.4 | 0.8 | 5.7 | 6.0 |
| 20 | 1.0 | 620 | 89.6 | 0.6 | 5.5 | 5.7 |

[a]


[b]


[c]


If the vibrationally hot biradical **5** produced in the decarbonylation process (eq 9) were monoenergetic and thus had a unique value of unimolecular decomposition lifetime or a specific rate constant, $k_E$, for reactions 12–14, a Stern–Volmer plot of (1/% $R_{14}$) *vs.* Ar pressure should be linear. The fact that it gives a downward curvature implies an initial wide distribution of $k_E$ values and thus energy photopartitioning in process 9 as expected.[19,20] Of course, an energy spread in the triplet energy transfer process 10 must be considered quite probable.

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(13) (a) S. W. Benson and H. E. O'Neal (*Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 21 (1970)) give the following $\Delta H_f{}^\circ{}_{298}$ values: *cis*-2-butene, −1.7 kcal/mol; *trans*-2-butene, −2.7; *cis*-DMCP, −0.3; *trans*-DMCP, −1.3; (b) R. W. Carr, Jr., T. W. Eder, and M. G. Toper (*J. Chem. Phys.*, **53**, 4716 (1970)), give $\Delta H_f{}^\circ{}_{298}$ = 95 ± 1 kcal/mol for triplet $CH_2$.

(14) For comparison, see R. Moore, A. Mishra, and R. J. Crawford, *Can. J. Chem.*, **46**, 3305 (1968). Similar values of 2.63 and 2.73 were obtained in the benzophenone (triplet) sensitized decomposition of *cis*- and *trans*-3,4 dimethylpyrazoline (11 and 12) in solution.

(15) The $CH_3$ elimination process (eq 14) proceeds much more rapidly than the analogous H elimination process (eq 8), since the latter process requires 15 kcal/mol more energy than the former.

(16) Particularly, identification of six possible $C_8$ diolefins (*cis,cis*-, *cis,trans*-, and *trans,trans*-2,6-octadienes, *cis*- and *trans*-1,6-heptadienes, and 2,3-dimethyl-1,5-hexadienes) would be difficult when the conversion is so low.

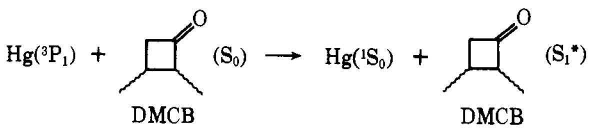
(17) (a) A. B. Callear and H. E. Van Den Berg, *Trans. Faraday Soc.*, **66**, 2681 (1970); (b) R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

(18) Trans/cis ratio for 2-pentene in the $CH_3$-butenyl recombination is 0.7 [see R. F. Kubin, B. S. Rabinovitch, and R. E. Harrington, *J. Chem. Phys.*, 37, 937 (1962)]. Relatively unimportant radical disproportionation reactions are neglected here.

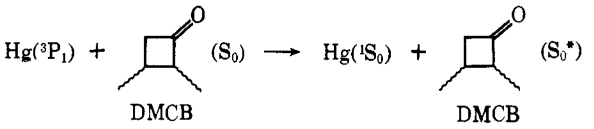
(19) (a) R. J. Campbell, E. W. Schlag, and B. W. Ristow, *J. Amer. Chem. Soc.*, **89**, 5098 (1967); (b) R. J. Campbell and E. W. Schlag, *ibid.*, **89**, 5103 (1967).

(20) N. E. Lee and E. K. C. Lee, *J. Chem. Phys.*, **50**, 2094 (1969).

**C. "Singlet" Sensitization.** Now a mechanistic discussion of the propylene yield from the Hg($^3P_1$)–2,4-DMCB system and the propylene–*cis*- and *trans*-2-butene yields from the Hg($^3P_1$)–2,3-DMCB system must be presented. In the latter system, the trans/cis ratio for 2-butene show a strong stereoretention (see Table III) as in the direct photolysis.[2] This observation is consistent with the earlier report that "singlet" sensitization by Hg($^3P_1$) is a minor but important process,[3] and we propose the following process to account for most of the "singlet" yield

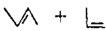

(18)

A significant fraction of $S_1^*$ DMCB's undergoes an internal conversion process *via* a chemical mechanism,[2b] and thus the $S_0^*$ DMCB's are generated rather efficiently. An overall process[21] such as


(19)

must contribute to some extent, but the present study does not permit any quantitative evaluation of its contribution. Table V summarizes the yields of "singlet products," on the assumption that some DMCP's are generated through an $S_1$ mechanism (eq 18). The "singlet yield" estimated in this manner can be as much as 16–19%. It should also be noted that "singlet" contribution from the direct photolysis was estimated to be less than 0.6% of the total decomposition.

Table V. Relative Yield of "Singlet Products" at Low Pressure (1.0 Torr of Parent)

| |  I |  II III | $\Sigma C_5$[a] | Singlet total |
|---|---|---|---|---|
| *cis*-2,4-DMCB (**3**) | 12.4 | | 3.3 | 15.7 |
| *trans*-2,4-DMCB (**4**) | 12.3 | | 3.6 | 15.9 |
| *cis*-2,3-DMCB (**1**) | 9.9 | ~7.5 | 2.8 | 18.9[b] |
| *trans*-2,3-DMCB (**2**) | 7.4 | 7.7 | 2.6 | 16.5[b] |

[a] ($\Sigma C_5$)/I are 0.27, 0.29, 0.28, and 0.35 in order of listing at 281-nm direct photolysis, where 102 kcal/mol of energy is absorbed. [b] The total "singlet" contribution evaluated as the sum of I, II, III, and $\Sigma C_5$ above is 20.2 for **3** and 17.7 for **4**. A correction must be made for the $CH_3$ yield (2 × $C_2H_6$) at 1.0 Torr pressure, which makes the nominal value of the total decomposition yield to be ~107.

The yields of propylene and 2-butenes are pressure quenched as expected,[2] but the internally converted precursor DMCB's ($S_0^*$) have considerable energy and $k_E$ distributions due to the initial intermolecular energy transfer process 18. The extent of the pressure quenching by added Ar observed in the Hg($^3P_1$)–*cis*-2,3-DMCB system is comparable to that found in the direct photolysis of *cis*-2,3-DMCB at 280 nm. Therefore, the amount of the energy transferred in the singlet energy transfer process (eq 18) is 100–110 kcal/mol, similar to that found in the Hg($^3P_1$)–cyclobutanone system.[2]

**D. Ring Closure in Biradicals.** The values of the trans/cis ratio for dimethylcyclopropane resulting from various triplet sensitizer–acceptor systems are summarized in Table VI. In general, the values obtained in the benzophenone–DMPZ system[14] in solution are greater by +0.3 than those obtained in the benzene–DMCB system[2,10] in the gas phase. But this difference is rather insignificant, and the DMTM biradicals generated in the two low-energy sensitizer systems are correspondingly similar in their kinetic behavior. It is interesting to note that the trans/cis ratio for dimethylcyclopropane in the Hg($^3P_1$)–2,3-DMCB system is clearly lower at lower pressures and it approaches, only at high Ar pressures, the trans/cis ratio obtained for the vibrationally relaxed 1,2-DMTM biradical **5**, while the trans/cis ratio in the Hg($^3P_1$)–2,4-DMCB system is, even at low pressures, very close to the ratio obtained for the vibrationally relaxed 1,3-DMTM biradical **6**.

Table VI. The Trans/Cis Ratio for Dimethylcyclopropane (**8**/**7**) from Various Sources

| | Triplet sensitizer | | |
|---|---|---|---|
| | $(C_6H_5)_2CO$ | $C_6H_6(^3B_{1u})$ | Hg($^3P_1$) |
| $E_T$, kcal/mol | 69 | 84.5 | 112.7 |
| Reference | 14, liquid | 2,13 | This work |
| Acceptors | 3,5-DMPZ[a] | 2,4-DMCB | 2,4-DMCB |
| Cis parent | 1.55 | 1.23 | 1.24 (1.22)[b] |
| Trans parent | 1.58 | 1.24 | 1.22 (1.22)[b] |
| Acceptors | 3,4-DMPZ[a] | 2,3-DMCB | 2,3-DMCB |
| Cis parent | 2.63 | 2.37 | 1.75 (2.1)[b] |
| Trans parent | 2.77 | 2.42 | 1.90 (2.3)[b] |

[a] DMPZ = dimethylpyrazolines (**9**, **10**, **11**, or **12**). [b] Values in parentheses are obtained with 540–580 Torr of Ar.

The lifetime of the vibrationally excited 1,2-DMTM biradical **5** estimated from the collisional quenching of the $CH_3$ elimination process (eq 14) is a few times $10^{-9}$ sec. This indicates that the rate of ring closure ($k_{10}$) for the 1,2-DMTM biradical **5** is in the range of $10^8$–$10^9$ sec$^{-1}$, and the time scale for the ring closure is too slow to be that expected of a "singlet" biradical.[4] Therefore, the rate-determining step for the ring closure for the 1,2-DMTM biradical **5** may be its triplet–singlet intersystem crossing. Also, it is reasonable to assume $k_6 \approx k_{10} \approx 10^{8-9}$ sec$^{-1}$.

It is likely that the triplet DMTM biradicals have undergone numerous internal rotations before their crucial transformation to the singlet DMTM biradicals and thus the resulting singlet DMTM biradicals no longer remember from which geometric isomer of the DMCB parent they resulted. Hence, the trans/cis ratio for dimethylcyclopropane must be rationalized on the basis of the *structure* (1,2-DMTM or 1,3-DMTM) and the *excess internal energy* of the resulting singlet biradical. The $C_1$–$C_2$ bond length for the 1,2-DMTM biradical must be close to a normal C–C single bond length (1.54 Å), and the two $CH_3$ groups are close enough to each other to suffer a moderate steric hinderance constantly. Thus, the 1,2-DMTM biradical begins to ring close at the $C_1$–$C_3$ position, aware of a moderate steric interference between the two adjacent

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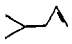
(21) In light of a recent report on the quenching of the triplet $CF_3COCH_3$ by the ground-state Hg($^1S_0$) (C. Pearce and D. A. Whytock, *J. Phys. Chem.*, 75, 439 (1971)), it is conceivable that the physical separation of the products in the triplet energy transfer steps 4 and 10 is slow enough to effect a $T_1 \rightsquigarrow S_0$ intersystem crossing of DMCB aided by the product Hg($^1S_0$) atom. This is certainly equivalent to the overall process (eq 20).

Table VII. Hydrocarbon Product Distribution in Hg($^3P_1$) Sensitization of Cyclobutanone

| Run no. | Time, sec | P, Torr |  | Products, mol % |  |  |  |  |  |  |  | % conv |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | CB | $O_2$ | $C_2H_4$ |  |  |  |  |  |  |  |  |
| 64 | 30 | 0.95 |  | 10.9 | 0.05 | 55.7 | 33.0 |  |  |  | 0.3 | 1.3 |
| 65 | 60 | 1.0 |  | 11.1 | 0.15 | 53.5 | 33.4 | 0.08 | 0.16 | 0.7$_3$ | 0.8$_3$ | 3.5 |
| 66 | 90 | 1.0 |  | 10.8 | 0.25 | 53.7 | 33.2 | 0.09 | 0.22 | 0.9$_5$ | 0.8$_4$ | 4.6 |
| 67 | 90 | 0.9$_5$ | 0.2 | 11.9 |  | 52.8 | 35.2 |  |  |  |  | 3.8 |

$CH_3$ groups, and a preference for the formation of *trans*-dimethylcyclopropane over the cis isomer is likely to result on the energetic grounds. Of course, such an energetically controlled preference plays an important role in favoring the high ratio of trans/cis isomers at lower internal energies, while the preference diminishes at higher energies, confirming the observed results in the triplet 1,2-DMTM biradical transformation. On the other hand, the two $CH_3$ groups in the 1,3-DMTM biradical can afford a distance of separation too far for a strong steric interference, and thus the biradical begins to ring close at the $C_1$–$C_3$ position aware of a negligible steric interference between the two conformationally free $CH_3$ groups. Consequently, *cis*-dimethylcyclopropane should be formed just about as readily as *trans*-dimethylcyclopropane, confirming the observation for the triplet 1,3-DMTM biradical transformation. Furthermore, no significant effect of the excess internal energy was found as expected.

**E. Reexamination of the Hg($^3P_1$)-Cyclobutanone System.**[3] It should be apparent by now that the vibrationally hot trimethylene biradical **13**, $\cdot CH_2CH_2CH_2\cdot$, generated by the Hg($^3P_1$) sensitization of cyclobutanone, should decompose unimolecularly to give a H atom and an allyl radical, as observed in the Hg($^3P_1$)–$CD_2CO$–$C_2H_4$ system[22] and as observed analogously in the Hg-($^3P_1$)-2,4-DMCB system.

The results of a reexamination of the Hg($6^3P_1$)-photosensitized decomposition of cyclobutanone, under conditions favoring the production of radical products, are listed in Table VII.

All of the radical products, which can be scavenged by 0.2 Torr of $O_2$ as expected, are formed from $CH_3$, $C_2H_5$, *i*-$C_3H_7$, and allyl radicals. H atoms, produced from the hot trimethylene decomposition, add to the olefinic primary products and form many of the above radicals. Since a similar radical mechanism has been suggested earlier for the Hg($^3P_1$) cyclopropane system,[23] no further discussion of mechanism seems necessary.

The extent of the H elimination process (eq 22) from the trimethylene biradical **13** is in the order of 3–4%, as compared to the H elimination process (eq 8) from the 1,3-DMTM biradical **6** estimated at ~0.2%. The endothermicity of the H elimination process (eq 22) is ~25 kcal/mol,[13a] and the excess vibrational energy of the hot biradical **13** cannot be more than ~40 kcal/mol. Ineffectiveness of the unimolecular H elimination process 8 in the 1,3-DMTM biradical **6** as compared to the energetically comparable process (eq 22) in the trimethylene biradical **13** is certainly due to the increased number of oscillators upon substituting two $CH_3$ groups for two terminal hydrogens in trimethylene (**13**).

**Acknowledgment.** We appreciate the helpful discussions of the methylene reactions with Robert Russell, Derek Montague, and Professor F. S. Rowland.

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[22] R. J. Cvetanović, H. E. Avery, and R. S. Irwin, *J. Chem. Phys.*, **46**, 1993 (1967).

[23] O. P. Strausz, P. J. Kozak, G. N. C. Woodall, A. G. Sherwood, and H. E. Gunning, *Can. J. Chem.*, **46**, 1317 (1968).