Physical and Inorganic Chemistry

Photolysis and Pyrolysis of 2-n-Propylcyclobutanone in the Gas Phase[1]

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Abstract: Direct photolysis of 2-n-propylcyclobutanone (PrCB) at 325 nm gives C_2H_4, 1-C_5H_{10}, and n-propylcyclopropane as hydrocarbon products. Triplet benzene ($^3B_{1u}$) sensitization of PrCB gives only n-propylcyclopropane, while pyrolysis of PrCB at $\sim350°$ gives only C_2H_4 and 1-C_5H_{10} favoring the former product over the latter by a factor of 3.8. The most important primary process for the disappearance of the PrCB (S_1^*) is a chemical route for the $S_1^* \longrightarrow S_0^{**}$ internal conversion, involving biradical intermediates. The observed unimolecular lifetime of the hot ground-state PrCB (S_0^{**}) with ~88 kcal/mol of excess vibrational excitation energy is ~0.3 μsec, which compares well with the lifetime of ~0.1 μsec calculated from an RRKM approximation. The nature of the short-lived biradical intermediates as well as the nature of the pyrolytic intermediates undergoing "concerted" fission processes are compared. How the energetic and steric constraints influence the various reaction rates are discussed.

Recent studies of photolysis and pyrolysis of cis and trans isomers of 2,3- and 2,4-dimethylcyclobutanones in the gas phase have provided extremely interesting insight into the transformation mechanisms of the hot ground state as well as the electronically excited state.[2] While a thorough study of these model cyclobutanone systems was in progress, a similar study of a simpler model system, 2-n-propylcyclobutanone (PrCB), was undertaken. As expected, pyrolysis of PrCB at 350° gave ethylene and 1-pentene as the major hydrocarbon products (in 3.8:1 ratio), while direct photolysis of 2.0 Torr of PrCB at 325.0 nm gave ethylene, 1-pentene, and n-propylcyclopropane as the hydrocarbon products (in 0.16:1:0.58 ratio). Triplet benzene ($^3B_{1u}$) sensitization of PrCB gave only n-propylcyclopropane (and CO). The large difference in the ethylene–1-pentene ratios observed between the pyrolysis and the collisionally stabilized photolysis systems is significant. Consequently, we favor the interpretation that the cleavage of the α bond (C_1–C_2) at the posi-

tion of n-propyl substitution, giving a ring-opened biradical PrĊHCH₂CH₂ĊO, is favored in the excited singlet state (n, π^*) whereas the concerted ring fission mode, giving ethylene plus n-propylketene, is favored in the hot ground state due to the "steric" consideration in reaching the critical configuration. The discussion in support of this interpretation and other kinetic aspects of the study shall be presented in this paper.

Experimental Section

Preparation of 2-n-Propylcyclobutanone. A solution of n-heptanal (20 g) in benzene (210 ml) was deoxygenated by nitrogen flushing, sealed in a cylindrical reactor containing a Pyrex probe, and irradiated for 34 hr using a 200-W medium-pressure mercury arc. Vpc on a Carbowax 20 M column at 165° showed that >90% of the n-heptanal had reacted. Several products with retention times shorter than that of n-heptanal were evident, and there were two major partly resolved products (~2:1 ratio) of longer retention time. Rotary evaporation and distillation gave a 4.5-g fraction (bp 180–210°) consisting mainly of the long retention time products, the 2-n-propylcyclobutanol isomers. A sample was purified by preparative vpc (Carbowax 20 M, 150°) to give 1.4 g of 2-n-propylcyclobutanol (cis–trans mixture): ir (film) 3350 s (O–H), 1105 s, 1081 cm⁻¹ s; nmr (60 MHz, CCl₄) τ 5.86 (triplet) and 6.49 (five lines) (together 1 H, CHOH), 6.02 (broad singlet, D₂O exchangeable, 1 H, OH), 7.5–9.2 (complex, ~12 H).

(1) This research has been supported by National Science Foundation Grants GP-11390 and GP-28010X.

(2) (a) H. A. J. Carless and E. K. C. Lee *J. Amer. Chem. Soc.*, **92**, 4482 (1970); (b) *ibid.*, **92**, 6683 (1970).
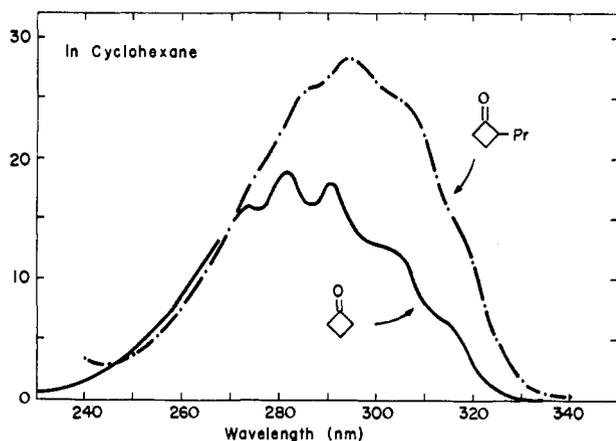
Figure 1. Comparison of the absorption curves for 2-*n*-propyl-cyclobutanone and cyclobutanone: molar absorptivity (ϵ in l. mol^{-1}cm^{-1}) vs. exciting wavelength (nm).

A solution of CrO$_3$ (0.62 g) in H$_2$O (2 ml) and H$_2$SO$_4$ (0.6 ml) was added dropwise with stirring to a solution of 2-*n*-propylcyclo-butanol (1.00 g) in acetone (2 ml), keeping the temperature of the mixture at 15–20°. After standing overnight, the organic layer was decanted. Vpc (40-ft Carbowax 20 M, 160°) showed the production of a new product, which was collected (260 mg) by preparative vpc and assigned the structure 2-*n*-propylcyclobutanone (>99% vpc pure): ir (film) 1775 cm^{-1} s (cyclobutanone ring); uv λ_{max} (cyclohexane) 295 nm (ϵ 28). The samples for use in experiments were further purified by preparative vpc (20-ft tris(2-cyanoethoxy)propane, 120°), and analytical vpc of the sample showed no detectable impurities on three columns. The 2-*n*-propylcyclobutanone was degassed and stored *in vacuo* at −196°, and the sample was degassed immediately before each use.

Vacuum, Photochemical, and Pyrolysis Apparatus. Samples were handled on a glass–metal vacuum line free of grease and mercury, and two photolysis cells (85.2 and 483 ml) with 50-mm diameter Suprasil windows were used as described elsewhere.[3] The photolyses at 325.0 nm were carried out with a Spectra Physics He–Cd laser (Model 185, ∼15 mW), and the benzene sensitization runs at 253.7 nm were carried out with a low-pressure mercury lamp (Mineralight) equipped with isolation filters.[3]

Pyrolysis was carried out in a quartz vessel (8.3 ml) inserted into a tubular furnace kept at ∼350°. Neither the accuracy of the temperature nor the uniformity of the temperature throughout the vessel was carefully controlled, since the product distribution alone was of interest here.

Product Analysis. The sample containing the decomposition products was transferred on a vacuum line to an evacuated sample loop immersed in liquid nitrogen, and the content was injected into a 0.125 in. o.d. × 20 ft dimethylsulfolane column at room temperature for separation of the hydrocarbon products. The products were analyzed initially with a thermistor detector (Carle Instrument, Model 1000) and later with a flame ionization detector (Perkin-Elmer, F-11). Carbon monoxide, ketenes, and 2-*n*-propyl-cyclobutane were not analyzed by this method. The observed peak areas were corrected for the molar sensitivity of each product component.

Results

Pyrolysis. Two pyrolysis runs were made to ∼30% conversion at ∼350°, and the results are tabulated in Table I. Slight traces of propylene and *n*-propylcyclo-

Table I. Pyrolysis of 2-*n*-Propylcyclobutanone (∼620°K)

Pressure, Torr	C$_2$H$_4$	1-C$_5$H$_{10}$	C$_3$H$_6$	PCP
	Product distribution (mol fraction)			
2.1	0.778	0.215		∼0.006
2.1	0.797	0.197	∼0.005	

(3) R. G. Shortridge, Jr., and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 2228 (1970).

propane (PCP) were found, and we will ignore them as being unimportant in pyrolysis. The ratio of the two major hydrocarbon products, C$_2$H$_4$/1-C$_5$H$_{10}$, is 3.8 as an average of two runs. We assume that this ratio represents the ratio of rate processes a/b in the concerted fission (eq 1).[2]

$$C_2H_4 + PrCH=C=O \quad (1a)$$
$$1\text{-}C_5H_{10} + CH_2=C=O \quad (1b)$$
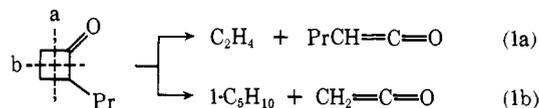
Direct Photolysis. 2-*n*-Propylcyclobutanone not only absorbs more strongly than cyclobutanone in the singlet n → π* band but also starts to absorb ∼6 nm to the red of cyclobutanone as shown in Figure 1. However, no such effect of α substitution has been found in 2-methyl- or 2-ethylcyclopentanone as compared to cyclo-pentanone (in cyclohexane solution), and clearly a study of this inadequately understood variation is in order. The results obtained from a systematic pressure-dependence study are shown in Table II. One direct photolysis run at 253.7 nm was made at 2.5 Torr pressure of 2-*n*-propylcyclobutanone, and the following product ratio was obtained: C$_2$H$_4$-1-C$_5$H$_{10}$-PrCP = 1.8 : 1.4 : 1.0.

Benzene ($^3B_{1u}$) Sensitization. Benzene photosensi-tization runs made at ∼0.2 Torr of 2-*n*-propylcyclo-butanone gave *n*-propylcyclopropane in >99% yield with a trace amount of 1-pentene, as expected. At this acceptor ketone pressure, the contribution from the benzene ($^1B_{2u}$) sensitization should be very small compared to the benzene ($^3B_{1u}$) sensitization.[4]

Discussion

A. Pressure Dependence. The observation at λ_{ex} = 325.0 nm confirming the pressure quenching of the olefinic products leads us to propose a hot ground-state precursor, 2-*n*-propylcyclobutanone (S$_0$**), as found earlier in other cyclobutanone systems.[2,5,6] On the other hand, we propose the precursor of the pressure unquenchable *n*-propylcyclopropane at λ_{ex} = 325.0 nm to be singlet *biradicals* **1** and **2**, derived from
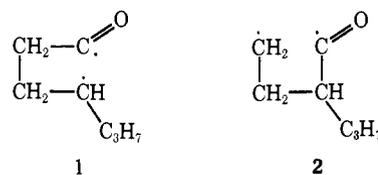
the first excited singlet state of 2-*n*-propylcyclobutanone (S$_1$*). We consider this S$_1$* species to be very shortlived (τ < 10^{-10} sec), because its "predissociation"[6] to a biradi-cal predominates over the S$_1$ —⤳→ T$_1$ intersystem cross-ing. The following mechanistic scheme which neglects the S$_1$ —⤳→ T$_1$ intersystem crossing step entirely is thus proposed for the unimolecular photochemical transfor-mations as in the case of *trans*-2,3-dimethylcyclobuta-none (Scheme I).[2b]

(4) (a) H. O. Denschlag and E. K. C. Lee, *ibid.*, **90**, 3628 (1968); (b) M. W. Schmidt and E. K. C. Lee, *ibid.*, **92**, 3579 (1970).
(5) N. E. Lee, and E. K. C. Lee, *J. Chem. Phys.*, **50**, 2094 (1969).
(6) (a) J. C. Hemminger, C. F. Rusbult, and E. K. C. Lee, *J. Amer. Chem. Soc.*, **93**, 1867 (1971); (b) J. C. Hemminger, and E. K. C. Lee, *J. Chem. Phys.*, **54**, 1405 (1971).

Table II. Effect of Pressure on the Hydrocarbon Product Yields (λ_{ex} = 325.0 nm, t = 23°)

Run no.[a]	Pressure, Torr PrCB	Pressure, Torr Add.	Product yields, 10^{-10} mol C_2H_4 (α)	1-C_5H_{10} (β)	PCP (γ)	Φ_{rel} ($R_2 = \alpha/\gamma$)	($R_5 = \beta/\gamma$)
180	0.028		169.4	160.7	58.9	2.88	2.72
181	0.05		39.1	34.8	13.5	2.90	2.58
182	0.06		43.5	44.0	17.2	2.53	2.56
170	0.10		5.98	6.20	2.50	2.40	2.48
A 175	0.10		55.4	57.1	23.5	2.36	2.43
169	0.20		12.2	17.7	8.4	1.45	2.11
179	0.20		70.6	97.6	45.8	1.54	2.13
166	0.5		23.6	52.6	26.8	0.88	1.97
167	1.0		14.1	51.3	28.1	0.50	1.83
168	2.0		12.5	80.2	46.6	0.27	1.72
B 177	0.10		49.0	44.7	19.3	2.54	2.32
A 176	0.10	100 (O_2)	1.7	35.4	23.0	0.07	1.54
B 178	0.10	100 (O_2)	1.4	33.4	20.8	0.07	1.60
C 201	0.10		43.4	52.1	23.0	1.88	2.26
C 202	0.10	10 (MeOH)	3.9	29.2	17.0	0.23	1.72

[a] The absolute product yields are meaningful only for comparison between the pair of runs with the identical prefix letters.

Scheme I
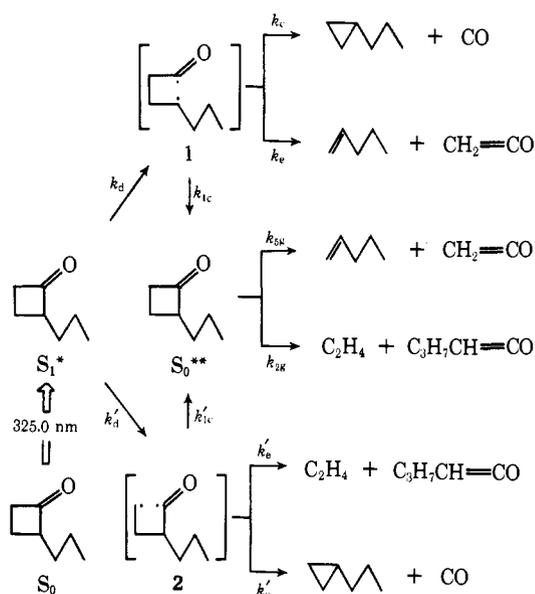
The lifetimes of the vibrationally hot biradicals **1** and **2** are too short to be quenched at ordinary gas pressures,[7] and the internally converted PrCB (S_0^{**}) is produced by a collision-free process. We will consider its unimolecular decomposition with a specific rate constant $k_{2g}(E)$ and its collisional stabilization with a pressure-dependent rate $\omega(M)$

$$\text{PrCB} (S_0^{**}) + M \xrightarrow{\omega(M)} \text{PrCB} (S_0) + M \quad (2)$$

It can then be shown that

$$\frac{1}{R_2} = \frac{1}{R_2^0}\left[1 + \frac{\omega(M)}{k_{2g}}\right] \quad (3)$$

where R_2 and R_2^0 are relative quantum yields of C_2H_4 at a given pressure of the collision partner M and at the zero pressure limit of M, respectively.

In a few sets of runs for which the light intensity and the photolysis time were well controlled, it was found that the relative quantum yield of PCP was pressure independent in the range of 0.03–2.0 Torr of PrCB (see

(7) O_2 (100 Torr) had no effect on the PCP yield (see Table II). A similar observation was made also with dimethylcyclobutanones.[2] See the scavenging of the vibrationally cold biradicals in P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5724 (1970).

Table II). Thus, for convenience, relative quantum yield were evaluated relative to the PCP yield in each run to an accuracy of ±0.02 unit. The Stern–Volmer plot shown for C_2H_4 in Figure 2 is linear, and the as-
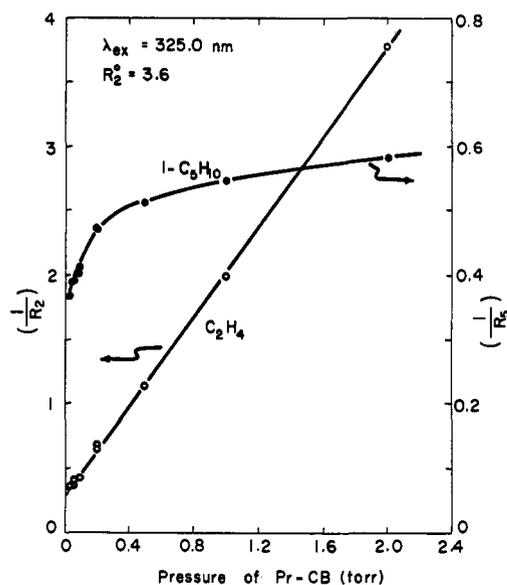
Figure 2. Stern–Volmer plots for the reciprocal yield $(1/R)$ *vs.* pressure of the quenching gas (see eq 3): left, C_2H_4; right, 1-C_5H_{10}.

sumption of one precursor (S_0^{**}) mechanism for C_2H_4 is verified. The contribution from the pressure-unquenchable C_2H_4 elimination process, *via* the biradical **2**, R_e', is negligible; $R_e' < 0.1$ and $R_2^0 = R_{2g}^0 + R_e' = 3.5_8$.

For the 1-pentene yield, a direct application of the one-precursor mechanism giving an expression similar to eq 3 for C_2H_4 cannot account for the observed result; the Stern–Volmer plot for the 1-pentene yield (R_5) shown in Figure 2 is not linear and curved downward. One plausible reason for this behavior is that there could be a substantial yield (R_e) from the pressure-unquenchable 1-pentene elimination process with a rate constant k_e *via* the unimolecular decomposition of the biradical **1**. Consequently, one should expect to obtain a linear Stern–Volmer plot if the 1-pentene yield resulting only

Figure 3. Corrected Stern–Volmer plot for the reciprocal yield of the pressure-quenchable 1-C_5H_{10} ($1/R_5 - R_e$) vs. pressure of the quenching gas, when $R_e = 1.65$ is assumed (see eq 4).

from the hot S_0^{**} precursor is considered, e.g., $R_{5g} = R_5 - R_e$

$$\frac{1}{R_{5g}} = \frac{1}{(R_5 - R_e)} = \frac{1}{(R_5^0 - R_e)}\left[1 + \frac{\omega(M)}{k_{5g}}\right] \quad (4)$$

where R_5^0 is the relative quantum yield of 1-C_5H_{10} at the zero pressure limit of M. Treating the value of R_e as a variable parameter, we have obtained a linear Stern–Volmer plot which best fits eq 4 as shown in Figure 3, when $R_e = 1.65 \pm 0.05$ was assumed. This implies that the 1-pentene yield from the hot S_0^{**} precursor at very low pressures is $R_{5g}^0 = R_5^0 - R_e = 1.22$. Hence the intramolecular competition ratio for the two ring fission processes, a/b, in the hot S_0^{**} generated at 325.0 nm is

$$\left[\frac{k_{2g}}{k_{5g}}\right]_{325\,nm} = \left[\frac{R_{2g}^0}{R_{5g}^0}\right]_{325\,nm} = \frac{\sim 3.5}{1.22} \cong 2.9 \quad (5)$$

B. Photolytic Biradical Precursors. The analysis of $R_2^0 \approx R_{2g}^0$ implies $k_{1c} \ll k_{1c}'$, $k_e' \ll k_{1c}'$, or $k_d' \ll k_d$. We favor the last alternative, because the energetic requirement favors the formation of the secondary biradical 1 over the formation of the primary biradical 2 from the slightly hot S_1^* precursor generated at 325.0 nm.[8] Another justification for choosing the last alternative is that $k_{1c}/k_e/k_c$ should be roughly comparable to $k_{1c}'/k_e'/k_c'$ and thus $k_d \approx k_d'$ cannot be compatible with the observation of $R_e = 1.65$ vs. $R_e' < 0.1$. Of course, this conclusion favoring $k_d \gg k_d'$ is entirely consistent with the earlier observation made with cis- and trans-2,3-dimethylcyclobutanone in that practically all of propylene arises from the corresponding hot S_0^{**}.[2] It is expected that the ratio of k_d'/k_d would increase with the increasing excitation energy, and its further study should be made.

One important consequence of accepting $k_d' \ll k_d$, e.g.

$$\left[\frac{k_d'}{k_d}\right]_{325\,nm} \leq 0.06 \quad (6)$$

is that practically all of the observed PCP is formed from the biradical 1. Therefore, we obtain for the ratio of decarbonylation to 1-pentene elimination from the biradical 1

$$\left[\frac{k_c}{k_e}\right]_{325\,nm} = \left[\frac{1}{R_e}\right]_{325\,nm} = 0.61 \quad (7)$$

(8) The 0–0 band of the $S_0 \rightarrow S_1$ absorption for cyclobutanone is at 330.0 nm[6b] and that for 2-n-propylcyclobutanone is estimated at $\sim$337 nm from Figure 1. Therefore, $\Delta E(S_1 - S_0)$ is $\sim$85 kcal/mol.

In view of the recent results obtained with $Hg(^3P_1)$-sensitized decomposition of 2,3- and 2,4-dimethylcyclobutanones and 2-n-propylcyclobutanone,[9] we must regard the "singlet" biradicals 1 and 2 obtained from the "predissociation" of S_1^* to be distinguishable kinetically from the biradical precursors generated by the $Hg(^3P_1)$ sensitization or by the benzene ($^3B_{1u}$) sensitization; the "triplet" cyclobutanones (T_1) decarbonylate very efficiently to give a "triplet" trimethylene-like biradical 3

which is sufficiently long-lived to lose the stereochemical specificity of the parent CB.

C. Photolytic Hot Ground-State Precursor (S_0^{**}). The half-quenching pressures ($P_{1/2}$) for the hot S_0^{**} obtained from Figures 2 and 3 are 0.18 ± 0.02 Torr of PrCB for quenching C_2H_4, and 0.16 ± 0.04 Torr of PrCB for quenching 1-C_5H_{10}. Ideally, these two values must be equal, since the precursor is identical. For the lifetime computation, the $P_{1/2}$ value of 0.18 Torr with more reliability will be used. Assuming an efficient and complete collisional deactivation by the parent PrCB molecule in process 2 and a gas kinetic collision diameter of $\sim$8 Å, a unimolecular rate constant $k(E) = k_{2g}(E) + k_{5g}(E) = 3.8 \times 10^6$ sec^{-1} at $E = 91.7$ kcal/mol or the unimolecular lifetime $\tau_E = 1/k(E) = 2.6 \times 10^{-7}$ sec is found. The value of $k(E)$ for $s = 54$, calculated from an approximation based on the RRKM formulation,[5,10] is 1.0×10^7 sec^{-1}, if the values of $A = 10^{14.56}$ sec^{-1} and $E_{act} = 52.0$ kcal/mol determined in the thermal unimolecular decomposition of cyclobutanone[11] and the estimated values of $E_z = 110.6$ kcal/mol, $E_{th} = 3.7$ kcal/mol, and "a" = 0.85^{12} were adapted for the calculation. The observed value of the unimolecular lifetime τ_E is only $\sim$3 times greater than the calculated value, and the agreement is quite satisfactory in view of the simplifying assumptions made in estimating the specific rate constant $k(E)$.

D. Pyrolytic Precursor. The major products of cyclobutanone pyrolysis have been found to be ethylene and ketene.[11a] Benson and O'Neal have proposed that "the biradical mechanism is consistent with the kinetics with ring opening being rate determining,"[13a] and have established the Arrhenius parameters on the basis of a mechanism involving the β-cleaved intermediate biradical 4.[13b] From a study of a minor pyrolysis prod-

(9) (a) See the accompanying paper: J. Metcalfe and E. K. C. Lee. J. Amer. Chem. Soc., 94, 7 (1972); (b) unpublished, preliminary results,

(10) (a) See, for a review, B. S. Rabinovitch and D. W. Setser, Advan. Photochem., 3, 1 (1964). (b) $k(E) = A'[(E - E_0 + a^+E_z^+)/(E + aE_z)]^{s-1}$ used by D. W. Setser and B. S. Rabinovitch (Can. J. Chem., 40, 1425 (1962)) was taken with further approximations of $A' = A^{11}$ and $E_0 = E_{act},^{11} a = a^+$, and $E_z = E_z^+$.

(11) (a) M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, J. Amer. Chem. Soc., 76, 6271 (1954). (b) Pyrolysis rate of PrCB is $\sim$4 × the rate of cyclobutanone at 660–690°K (ref 8b).

(12) (a) E_z of PrCB was estimated as E_z of cyclobutanone (57.8 kcal/mol)[5] plus the contribution due to the (CH₂)₃ substituent, 3 × 17.6 kcal/mol. (b) E_{th} of PrCB was estimated as the average vibrational energy content at a 296°K thermal bath, and $E = E_{h\nu} + E_{th}$. (c) "a" = 0.85 at $\epsilon' = E/E_z = 0.80$ ($\lambda_{ex} = 325.0$ nm) was chosen from G. Z. Whitten and B. S. Rabinovitch, J. Chem. Phys., 38, 2466 (1963).

(13) (a) S. W. Benson and H. E. O'Neal, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 21, 283 (1970); (b) S. W. Benson and H. E. O'Neal, J. Phys. Chem., 72, 1866 (1968).

4   **5**

uct, cyclopropane (0.5% yield), Blades[14] has suggested that β cleavage of the cyclobutanone ring could be responsible for ethylene and ketene production, while α cleavage could lead to the biradical **5**, and hence cyclopropane (and CO) formation. It was also suggested[14] that the latter decomposition mode had a 6 kcal/mol higher activation energy than the former decomposition mode and that the decarbonylation process would become increasingly important at higher energies. The fact that the yield of n-propylcyclopropane is not quenched at all by the addition of 100 Torr of O_2 (see Table II) whereas the yield of ethylene is reduced by a factor of 40 by the O_2 addition provides *strong evidence* that the hot PrCB (S_0^{**}) with 91 kcal/mol vibrational energy gives no detectable amount ($<0.5\%$) of n-propylcyclopropane (and CO) as the high-energy product in its unimolecular decomposition. Particularly, recent evidence[15] that there is no resonance energy in the acetonyl radical, $CH_3COCH_2\cdot$, throws Blade's proposal into doubt. Blades found the ratio of the thermal A factors for the α vs. β cleavage to be 0.65. Therefore, the precursor of cyclopropane in pyrolysis and photolysis cannot be subjected to the same RRKM treatment given to the energized cyclobutanone (S_0^*).

The Woodward–Hoffmann rules[16] would allow a *concerted* process for the thermal decomposition of cyclobutanone (described as $_\sigma 2_s + _\sigma 2_a$) or cycloaddition of an olefin to a ketene ($_\pi 2_s + _\pi 2_a$) with the olefin as the suprafacial component and the ketene as the antarafacial component. The Woodward–Hoffmann rules cannot, of course, rule out the possibility of a biradical pathway for decomposition or cycloaddition. It is relevant that thermal decomposition of *cis*- or *trans*-2,3-dimethylcyclobutanone has been shown to produce *cis*- or *trans*-2-butene with stereospecific retention[2a] in agreement with a *concerted* pathway or an extremely short-lived biradical. Likewise, the reverse reaction—that of cycloaddition of ketene to an olefin—has been found to be stereospecific in several cases.[17] Relatedly, β-lactams decompose thermally in a stereospecific manner.[18] It is notable, however, that such a stereospecific and possibly concerted process cannot account for the results of Frey and Isaacs[19] in which cycloaddition of dimethylketene to *trans*-2-butene is interpreted as a coplanar approach to reactants with a two step (biradical) mechanism for addition. Dowd, Gold, and Sachdev[20] have shown that the biradical **5** arising from α cleavage of photoexcited cyclobutanone can be trapped with 1,3-butadiene at $-78°$,

(14) A. T. Blades, *Can. J. Chem.*, 47, 615 (1969).

(15) K. D. King, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, 92, 5541 (1970).

(16) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

(17) (a) R. Huisgen, L. Feiler, and G. Binsch, *ibid.*, 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).

(18) L. A. Paquette, M. J. Wyvratt, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, 92, 1763 (1970).

(19) H. M. Frey and N. S. Isaacs, *J. Chem. Soc. B*, 830 (1970).

(20) P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, 92, 5724 (1970).

while their experiments provided no evidence for the biradical **4** arising from β cleavage.

If a biradical were involved in the thermal fragmentation of 2-n-propylcyclobutanone, it is difficult to rationalize the observed ethylene-1-pentene ratio of ~ 3.8, since cleavage of the PrCB ring would be expected to occur between the most substituted bonds to give the biradical **1** which would lead to a predominance of 1-pentene in the final cleavage products. However, a concerted fission to give a ($_\sigma 2_s + _\sigma 2_a$) decomposition in the Woodward–Hoffmann manner would guide us to rationalize the observed ethylene-1-pentene ratio in the thermal fragmentation. Decomposition would occur from a *critical configuration* involving severe ring puckering of the PrCB, in which the incipient olefin and ketene components are perpendicular to each other.[16,21] Nonplanarity of the PrCB ring leads to *pseudoequatorial* and *pseudoaxial* grouping as shown in Scheme II. Further distortion of these conformations

Scheme II
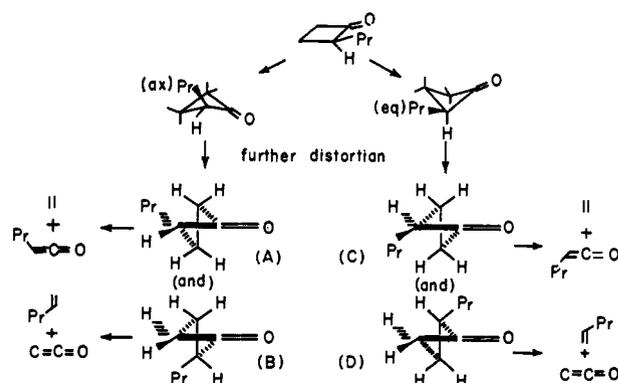
gives, from the pseudoaxial propyl conformer, the critical configurations shown as A or B. Critical configuration A is strongly disfavored, since it involves severe interference between the large propyl group and the incipient olefinic fragment. Critical configuration B is also disfavored, since it involves interaction of the large propyl group with the C_4 hydrogen of the incipient ketene fragment. We might therefore not expect ring puckering involving a pseudoaxial propyl group to lead to a favorable critical configuration for thermal decomposition.[21]

The situation is very different for the ring-puckering motion which places the propyl group in a pseudoequatorial position. Further distortion leads to the two possible critical configurations C and D. *The former configuration C is most favored*, since it places the propyl group of the incipient propylketene in a direction pointed away from the incipient olefin, and there should be least steric interference: hence decomposition to ethylene and propylketene predominates. Although there is some interaction between the propyl group and the carbonyl oxygen atom in critical configuration D, decomposition to 1-pentene and ketene can still occur favorably.

E. Competitive Rates. The intramolecular competitive ring fission ratio of $k_{1a}/k_{1b} = 3.8 \pm 0.1$ in pyrolysis can be rationalized with an activation energy difference (ΔE_{act}) between modes a and b of ~ 1.6 kcal/mol, if the Arrhenius preexponential factors

(21) T. Do Minh and O. P. Strausz, *ibid.*, 92, 1766 (1970).

(A) are assumed to be equal. If the assumptions of $A_{2g}/A_{5g} = 1$ and $\Delta E_{act} = E_{act(5g)} - E_{act(2g)} = 1.6$ kcal/mol are made accordingly for photoactivation at 325 nm, the k_{2g}/k_{5g} ratio calculated from the RRKM rate approximation is only ~1.4, far short of the observed ratio of 2.9 ± 0.2. Since the photolytic S_0^* has ~40 kcal/mol more vibrational energy than the pyrolytic S_0^*, the rate difference due to the activation energy difference is very minor as expected. Therefore, it is reasonable to attribute the major factor favoring the fission mode 1a over mode 1b for the hot ground-state PrCB (S_0^{**}) to the Arrhenius preexponential factors, or specifically the entropy of activation which becomes more negative in the critical configurations in which the propyl group interferes sterically.

F. Primary Processes at Low Pressures (325.0 nm). It is reasonable to assume that the quantum yield of the photochemical decomposition processes in this system is unity at zero pressure limit. Then, the following estimates of the unimolecular quantum yields from the first excited singlet state can be made, recognizing $k_d \gg k_d'$: $\Phi(S_0^{**}) = 0.65$; Φ(unquenchable 1-C_5H_{10}) = 0.22; and Φ(PCP) = 0.13. The quantum yield of the $S_1 \longrightarrow S_0$ internal conversion process for PrCB is slightly lower than that observed for cyclobutanone at 313 nm, ~0.72.[5] Certainly, the recyclization of the biradical 1 cannot proceed as efficiently as in cyclobutanone because of the propyl substituent. Furthermore, the 1-pentene elimination process (k_e) is ~1.65 times more efficient than the decarbonylation process (k_c), and hence the PCP yield is substantially lower for PrCB as compared to the cyclopropane yield of 0.28 for cyclobutanone.[5] A detailed comparison with the dimethylcyclobutanones, which is forthcoming, should be very interesting.

Turro, *et al.*, have trapped ring expansion products from several cyclobutanone derivatives in good yield by irradiating in methanol solution, and has suggested oxacarbene intermediates in cyclobutanone photolysis.[22] Our gas-phase experiment (runs C 201–202 in Table II) suggests that appreciable trapping of an oxacarbene intermediate does not occur at the pressures we have used. As long as the vibrationally hot oxacarbene intermediates are extremely short-lived, as the hot biradicals 1 and 2 are, we cannot intercept them readily; it might even be that the former is a precursor of 1 and 2. In any case, the product ratio obtained in the methanol-containing samples indicates that methanol quenches the olefinic products with $P_{1/2} \approx 0.68$ Torr as a vibrational deactivator.

The total absence of the expected type II product, propylene, could mean the extreme short lifetime of the S_1^* or T_1^* or the unfavorable geometrical factor present in the excited state.

G. Triplet Products. Triplet benzene sensitization gives exclusively *n*-propylcyclopropane (and CO), and it suggests that a triplet biradical precursor 6, PrCH-CH$_2$CH$_2$, is produced *via* an efficient decarbonylation process (8). Since singlet biradical precursors 1 and 2 do also give *n*-propylcyclopropane (and CO) as shown in Scheme I, it is difficult to assess unequivocally the $S_1 \longrightarrow T_1$ intersystem crossing yield on the basis of the observed *n*-propylcyclopropane yield ($\Phi = 0.13$) in the 325.0-nm direct photolysis, but it cannot exceed a value of 0.13. In view of the predominant retention of stereospecificity in the 1,2-dimethylcyclopropanes resulting from the 325.0-nm photolysis of *cis*- and *trans*-2,3-dimethylcyclobutanone, and the lack of sterospecificity in the triplet benzene sensitized decomposition,[2a] it is reasonable to suggest that the $S_1 \longrightarrow T_1$ intersystem crossing yield in 2-*n*-propylcyclobutanone is relatively unimportant, $\Phi_{ISC} < 0.05$.

(22) D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Amer. Chem. Soc.*, 92, 4349 (1970).