

of Moss and Gerstl<sup>32</sup> and Moore and Levine<sup>33</sup>) also resulted in a 6.3% yield of product.

**1-Chloro-1-fluoro-2-*p*-nitrophenylcyclopropane (9).** A 1:1 mixture of **10** and **12** was nitrated using the method of Ketcham, *et al.*,<sup>6</sup> for the nitration of phenylcyclopropane.

To 11.5 ml of acetic anhydride in a 100-ml flask was added dropwise 3.5 ml (0.075 mol) of fuming nitric acid at  $-40^{\circ}$ . To this rapidly stirred mixture was added 4.0 g (0.023 mol) of the mixture of **10** and **12** at a rate such that the temperature did not exceed  $-30^{\circ}$ . The mixture was stirred for 0.5 hr at  $-30$  to  $-15^{\circ}$  and then slowly added to warm water and extracted with ether. The ether layer was washed with 25 ml of warm water and two 25-ml portions of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The ether was removed *in vacuo* and the product distilled to give 3.4 g (69.5%) of a yellow liquid, bp  $117-120^{\circ}$  (0.2 mm). Compound **9** crystallized and upon recrystallization from ethanol gave white needles, mp  $74.5-75.5^{\circ}$ , having infrared bands at 7.59, 8.15, 8.74, 11.71, 11.89, and  $14.60 \mu$ , and having ultraviolet absorption at 216 and  $274 m\mu$  ( $\epsilon$  8900, 10,000).

*Anal.* Calcd for  $C_9H_7ClFNO_2$ : C, 50.12; H, 3.27. Found: C, 50.02; H, 3.11.

The crude nitration mixture from this experiment was examined by  $^{19}F$  nmr and found to have three sets of peaks with relative area ratios of 2:1:1 at 124.8, 146.4, and 143.8 ppm. Crystalline **9** had a  $^{19}F$  resonance centered at 124.8 ppm and had a proton spectrum that displayed the characteristic  $A_2B_2$  pattern for aromatic protons, indicative of para substitution. In a separate experiment a sample of **12** was nitrated to give a 1:1 mixture of products having  $^{19}F$  resonance patterns at 146.3 and 148.3 ppm and having an aromatic proton spectrum indicative of a mixture of ortho and para isomers.

(32) R. Moss and R. Gerstl, *J. Org. Chem.*, **32**, 2268 (1967).

(33) R. A. Moore and R. Levine, *ibid.*, **29**, 1883 (1964).

This mixture had infrared bands at 7.51, 7.90, 8.80, 11.60, 11.71, and  $14.40 \mu$  and ultraviolet absorption at 225 and  $274 m\mu$  ( $\epsilon$  8500 and 9600). Attempts to separate this mixture on QF-1 and Carbowax gas chromatography columns were unsuccessful as was column chromatography on silica gel and activated alumina.

**1-Chloro-1-fluoro-2-*p*-aminophenylcyclopropane (11).** This compound was prepared from **9** according to the general procedure of Woodward<sup>7</sup> for the reduction of *p*-nitrobenzaldehyde.

A 25-ml flask was charged with 0.738 g (0.003 mol) of finely powdered stannous chloride dihydrate and 2 ml of concentrated hydrochloric acid. The mixture was cooled with stirring to  $0^{\circ}$  and 0.232 g (0.001 mol) of **9** was added in one portion; the mixture was then refluxed under nitrogen at  $110^{\circ}$  for 2 hr followed by gradual cooling. It was dissolved in water, made slightly basic with a 10% sodium hydroxide solution, and extracted with ether. The ether extract was acidified with dilute hydrochloric acid and dried, and the solvent was evaporated. There was no evidence of unreacted nitro compound. The aqueous layer was made slightly basic, extracted with ether, washed with two 25-ml portions of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure to give an orange oil, having significant infrared bands at 2.95-3.05, 3.45-3.39, 6.20, 7.9, 8.10, 8.70-8.80, 9.00, 11.80, 12.20, and  $13.50 \mu$  and ultraviolet absorption at 216, 243, and  $292 m\mu$  ( $\epsilon$  5100, 5600, and 360).

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## Type I and Type II Photochemical Reactions of Some Five- and Six-Membered Cycloalkanones<sup>1</sup>

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J. A. Barltrop, and J. D. Coyle

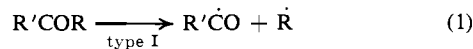
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**Abstract:** The type I and type II photochemical reactions of a series of cyclopentanones and cyclohexanones have been studied. Quantum yields and rate constants for the various processes were determined. The results from the type I reactions show that  $\alpha$  cleavage occurs predominantly from the triplet excited state, whereas the type II reactions occur from both the singlet and triplet excited states. Although the reactivities toward intramolecular  $\gamma$ -hydrogen abstraction of singlet and triplet states seem to be comparable, the triplet appears to be much more reactive than the singlet toward the  $\alpha$  cleavage process. The efficiency of type II reaction from the singlet is generally higher than that from the triplet of the same molecule. These results are discussed in the light of other recent investigations in the field.

Since Norrish<sup>6</sup> in the 1930's discovered the type I (eq 1) and type II (eq 2) photochemical reactions of ketones, there have been numerous studies on both types of reactions. Both alkyl ketones<sup>7,8</sup> and aryl

alkyl ketones<sup>8</sup> have undergone extensive and intensive investigation.

The type I cleavage of medium-ring alkanones is believed to result from photochemical production of a



(1) (a) Molecular Photochemistry, XLVIII. Paper XLVII: R. R. Hautala and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 5595 (1971).

(2) NIH Predoctoral Fellow, 1966-1970.

(3) NATO Postdoctoral Fellow, 1969-1971.

(4) Alfred P. Sloan Fellow, 1966-1970; Columbia University.

(5) NIH Predoctoral Fellow, 1966-1969.

(6) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1945), and references therein.

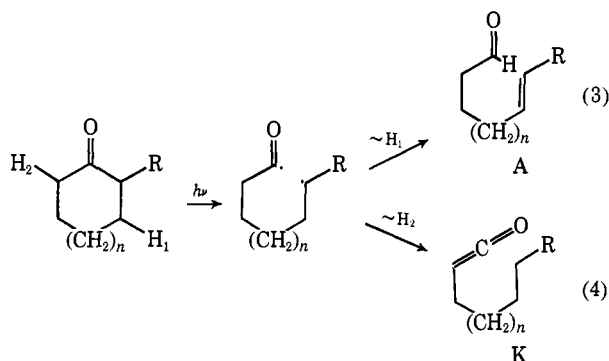
(7) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970).

(8) For reviews of recent work see (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967; (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966; (c) N. J. Turro, *et al.*, Ed., "Annual Survey of Photochemistry," Vol. I-III, Wiley-Interscience, New York, N. Y., 1967-1969; (d) N. J. Turro, *Tech. Org. Chem.*, **14**, 133 (1969).



biradical intermediate which rearranges to isomeric enals and/or ketenes<sup>9-14</sup> (Scheme I). Photodecar-

### Scheme I



bonylation<sup>15</sup> and other reactions<sup>16-18</sup> can sometimes compete with photoisomerization for stabilization of this biradical intermediate. There have only been a few reports<sup>19-24</sup> of the type II photoelimination from cyclic ketones.

We now wish to report our results of an extensive study of the mechanisms of photochemical reactions of a series of cyclopentanones and cyclohexanones, with particular emphasis on cases for which a competition between type I and type II processes is possible.

### Results

**Products.** The irradiation of a series (Charts I and II) of cyclohexanones (1-13) and cyclopentanones (14-21) with approximately 300-nm light results in the formation of products which are expected from photoisomerization reactions (eq 3 and 4) and intra- or intermolecular hydrogen abstraction. In benzene or cyclohexane solutions, the major isomeric product detected or isolated is the enal; enal structure proofs are generally based on ir, nmr, and mass spectral data, the ir showing the presence of an aldehyde (1720 and 2700  $\text{cm}^{-1}$ ) and double bond (910 and 990  $\text{cm}^{-1}$ ), and for enals from 2-alkylcycloalkanones a disubstituted double bond (975  $\text{cm}^{-1}$ ). In all cases, except 1, 6, 7, 14, and 19, the enal products appeared as two overlapping peaks on vpc suggesting the presence of the cis and trans isomers of the aldehyde. The enal isomers from 2-ethylcyclohexanone (3) were separated by preparative vpc. The *trans*-aldehyde (A,  $n = 1$ ; R =

(9) C. C. Badock, M. J. Perona, G. O. Pritchard, and B. Rickborn, *J. Amer. Chem. Soc.*, **91**, 453 (1969).

(10) R. Srinivasan, *Advan. Photochem.*, **1**, 84 (1963).

(11) P. J. Wagner and R. W. Spoerke, *J. Amer. Chem. Soc.*, **91**, 4437 (1969).

(12) G. Quinkert, *Angew. Chem., Int. Ed. Engl.*, **4**, 211 (1965).

(13) P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968).

(14) J. A. Barltrop and J. D. Coyle, *Chem. Commun.*, 1081 (1969).

(15) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

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

(17) J. K. Crandall and R. J. Seidewald, *J. Org. Chem.*, **35**, 697 (1970).

(18) A. Sonoda, I. Moritani, J. Miki, and T. Tsuji, *Tetrahedron Lett.*, 3187 (1969).

(19) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1521 (1938).

(20) R. Srinivasan and S. E. Cremer, *J. Phys. Chem.*, **69**, 3145 (1965).

(21) N. J. Turro and D. S. Weiss, *J. Amer. Chem. Soc.*, **90**, 2185 (1968).

(22) J. A. Barltrop and J. D. Coyle, *Chem. Commun.*, 390 (1970).

(23) N. J. Turro, D. S. Weiss, and J. C. Dalton, *Mol. Photochem.*, **2**, 91 (1970).

(24) K. Dawes, J. C. Dalton, and N. J. Turro, *ibid.*, **3**, 71 (1971).

Chart I. Cyclohexanones Investigated in This Study

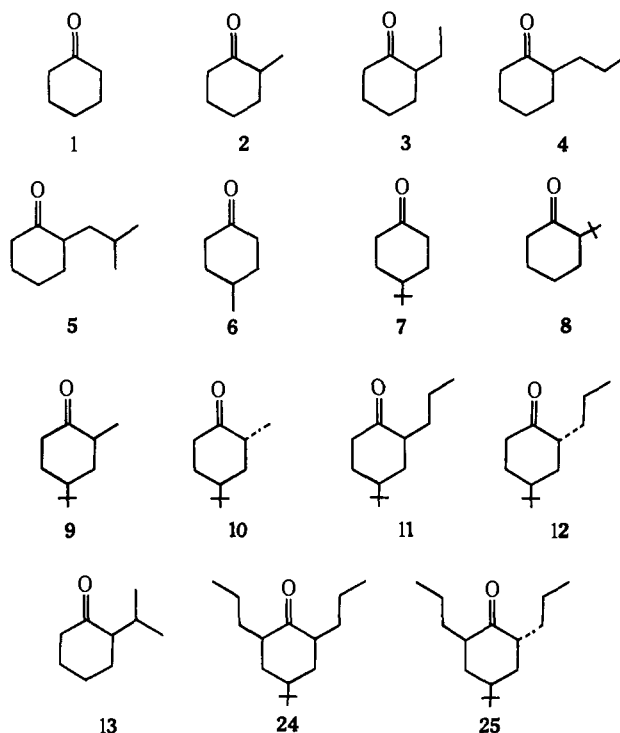
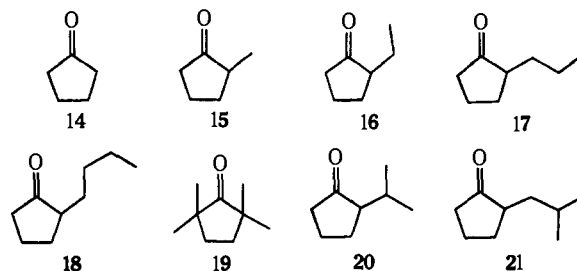


Chart II. Cyclopentanones Investigated in This Study



$\text{C}_2\text{H}_5$ ) was found to be the major isomer, in agreement with the results of Rickborn<sup>9</sup> who studied the photolysis of 2-methylcyclohexanone (2). The *trans* isomer (A,  $n = 0$ ; R =  $\text{C}_3\text{H}_7$ ) was also the major product from 2-*n*-propylcyclopentanone (17).

The 2-alkyl cyclic ketones (3, 4, 5, 8, 11, 13, 16-18, 20, and 21) gave products which were shown to be the corresponding unsubstituted cyclic ketone by comparison with authentic samples. These products arise from type II photoelimination. Some of the relative yields of the type II products are given in Table I.

Table I. Percentage of Type II Photoelimination Product<sup>a</sup>

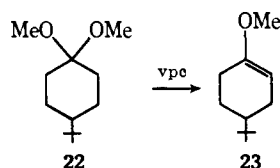
Ketone	% yield	Ketone	% yield
3	<1	16	<1
4	65	17	<1
13	14	20	<1
5	77	21	20
8	49		

<sup>a</sup> Methanol as solvent, per cent yield of type II product relative to other products formed.

In methanol solutions, in addition to the enal, another product was isolated, for which the spectral data were consistent with a saturated ester. This product presumably resulted from attack of methanol on an

initially formed ketene. Only small amounts of esters were formed on the photolysis of the cyclopentanones in methanol, in agreement with a recent report.<sup>25</sup> On the other hand, photolysis of cyclohexanones in methanol generally results in much larger relative amounts of ester. The 4-*tert*-butylcyclohexanones (7, 9–12) gave little or no aldehyde product on irradiation in methanol, saturated esters being the major products.

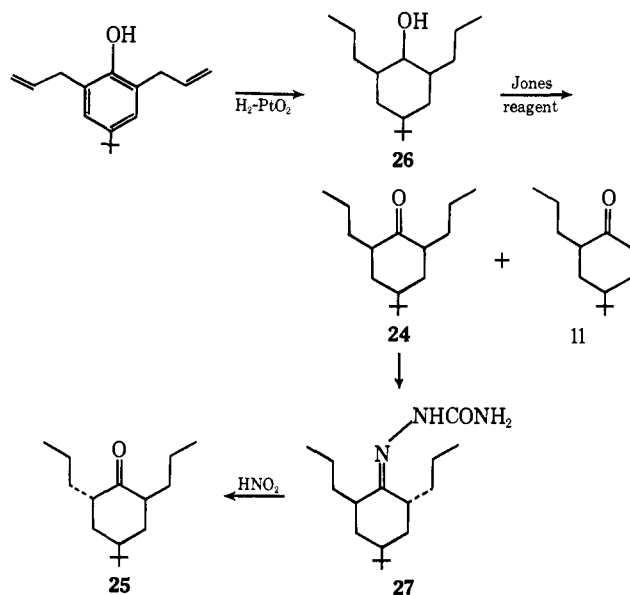
All irradiations in methanol were either performed (a) in glassware which had been previously base washed, or (b) in the presence of solid sodium bicarbonate. If such precautions were not taken, then products such as ketals were formed. For example, the irradiation of 4-*tert*-butylcyclohexanone (7) in methanol in untreated glassware gave the dimethyl ketal (22). Attempts to isolate the ketal by vpc gave 1-methoxy-4-*tert*-butylcyclohexene (23).<sup>26</sup>



The irradiation of 4-*tert*-butylcyclohexanone (7) in cyclohexane resulted in no isomeric products. The only products isolated were *cis*- and *trans*-4-*tert*-butylcyclohexanols, *i.e.*, products of intermolecular photo-reduction.

As part of a qualitative study of the stereoelectronic requirement<sup>21</sup> for  $\gamma$ -hydrogen abstraction the epimers of 2,6-di-*n*-propyl-4-*tert*-butylcyclohexanone, 24 and 25, were synthesized by the route shown in Scheme II.

Scheme II



Jones oxidation of the cyclohexanol (26) resulted in an approximately 1:1 mixture of the di- and mono-*n*-propylcyclohexanones 24 and 11, respectively. Ketone 11 may result from thermal elimination of propene during work-up. Conia<sup>27</sup> has recently studied thermal reactions of some cyclic ketones. Conversion of the

(25) C. C. Badcock, B. Rickborn, and G. O. Pritchard, *Chem. Ind. (London)*, 1053 (1970).

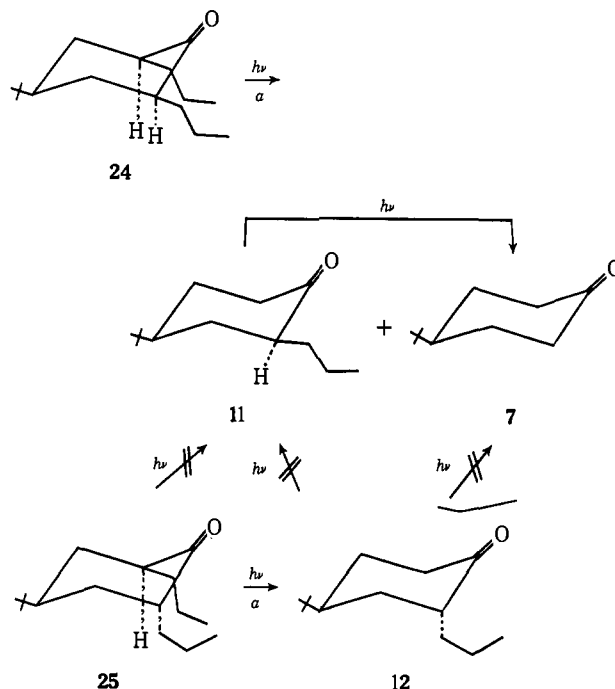
(26) For similar examples, see ref 13.

(27) P. Beslin, R. Block, G. Moinet, and J. M. Conia, *Bull. Soc. Chim. Fr.*, 508 (1969), and references therein.

*cis* epimer 24 to the *trans* epimer 25 was achieved using the method of Johnson<sup>28</sup> *via* the semicarbazone (27).

Irradiation of each epimer was conducted in neat piperylene (Scheme III). The epimer ratio and

Scheme III



<sup>a</sup> The irradiation was carried out in piperylene as solvent.

products were analyzed by analytical vpc. The *cis* epimer 24 gave *cis*-2-*n*-propyl-4-*tert*-butylcyclohexanone (11), which underwent further photolysis to 4-*tert*-butylcyclohexanone (7); the *trans* epimer 25 gave only *trans*-2-*n*-propyl-4-*tert*-butylcyclohexanone (12). Under the conditions of photolysis no *cis*-*trans* or *trans*-*cis* epimerization was observed.

**Quantum Yields.** The results of our quantum yield determinations are given in Tables II–IV. The quan-

**Table II.** Quantum Yields and Quenching Data for Monoalkylcyclohexanones<sup>a</sup>

Ketone	$\phi_{11}^b$	$\phi_A^c$	$k_q\tau^d$	$\tau^{-1} \times 10^8$ sec <sup>-1</sup> <sup>e</sup>
1		0.09	450	0.11
2		0.31	20	2.5
		0.31 <sup>f</sup>	50 <sup>f</sup>	1.3 <sup>g</sup>
3	0.016	0.21	25	2.0
	0.021 <sup>f</sup>	0.24 <sup>f</sup>	59 <sup>f</sup>	1.3 <sup>g</sup>
4	0.025	0.047	6.5	7.7
	0.036 <sup>f</sup>	0.039 <sup>f</sup>	10 <sup>f</sup>	6.6 <sup>g</sup>
	0.04 <sup>f</sup>	0.03 <sup>f</sup>	7.0 <sup>f</sup>	9.4 <sup>g</sup>
5		0.07 <sup>f</sup>	>100 <sup>f</sup>	<0.66 <sup>g</sup>
6		0.07 <sup>f</sup>	>100 <sup>f</sup>	<0.66 <sup>g</sup>
7		0.0 <sup>f,h</sup>	>100 <sup>f</sup>	<0.66 <sup>g</sup>

<sup>a</sup> Benzene as solvent. <sup>b</sup> Quantum yield for cyclohexanone formation. <sup>c</sup> Quantum yield for enal formation. <sup>d</sup> Stern–Volmer 1,3-pentadiene quenching of enal formation. <sup>e</sup> Assuming a value of  $k_q = 5 \times 10^9 M^{-1} \text{sec}^{-1}$  for benzene. <sup>f</sup> Cyclohexane as solvent. <sup>g</sup> Assuming  $k_q = 6.6 \times 10^9 M^{-1} \text{sec}^{-1}$  for cyclohexane. <sup>h</sup> Value for the formation of 4-*tert*-butylcyclohexanol, 0.06.

tum yields were determined by irradiating degassed benzene, cyclohexane, acetonitrile, methanol, or *tert*-butyl alcohol solutions of the ketones through Pyrex

(28) F. Johnson and L. G. Duquette, *Chem. Commun.*, 1448 (1969).

**Table III.** Quantum Yields and Quenching Data for a Series of Cyclopentanones<sup>a</sup>

Ketone	$\phi_{II}^b$	$\phi_A^c$	$k_q\tau^d$	$\tau^{-1} \times 10^9$ sec <sup>-1</sup> <sup>e</sup>
<b>14</b>		0.11		
<b>15</b>		0.26	1.4	3.6
<b>16</b>			1.4	3.6
<b>17</b>	0.014	0.38	1.6	3.1
<b>18</b>	0.004	0.27		
	0.012 <sup>f</sup>	0.45 <sup>f</sup>	2.5 <sup>f</sup>	2.6 <sup>g</sup>
<b>19</b>		0.61	<0.1	>50

<sup>a</sup> Benzene as solvent unless otherwise stated. <sup>b</sup> Quantum yield for cyclopentanone formation. <sup>c</sup> Quantum yield for enal formation. <sup>d</sup> Stern-Volmer 1,3-pentadiene quenching of enal formation. <sup>e</sup> Assuming a value of  $k_q = 5 \times 10^9 M^{-1} \text{sec}^{-1}$  for benzene. <sup>f</sup> Cyclohexane as solvent. <sup>g</sup> Assuming a value of  $k_q = 6.6 \times 10^9 M^{-1} \text{sec}^{-1}$  for cyclohexane.

**Table IV.** Quantum Yields for Type II and Aldehyde Formation in Various Solvents

Ketone	Solvent	$\phi_{II}$	$\phi_A$
<b>4</b>	Cyclohexane	0.036	0.039
	Acetonitrile	0.005	0.050
	<i>tert</i> -Butyl alcohol	0.036	0.051
<b>11</b>	Methanol	0.036	
	Cyclohexane	0.05	
	Acetonitrile	<0.001 (0.03) <sup>a</sup>	
	<i>tert</i> -Butyl alcohol	0.10 <sup>b</sup>	
<b>12</b>	Cyclohexane	0.005	

<sup>a</sup> Unknown product assuming the same response factor as 4-*tert*-butylcyclohexanone. <sup>b</sup> Type II product plus unknown product assuming both have the same response factor.

glass and 1 cm of a filter solution of potassium chromate which served to isolate the 313-nm line. Several different photochemical systems were used as actinometers: (a) the photoisomerization of neat cyclopentanone to 4-pentenal which was assumed to have a quantum yield of 0.37,<sup>29</sup> (b) the type II photoreaction of 2-hexanone in cyclohexane ( $\phi = 0.25$ ),<sup>30</sup> (c) uranyl oxalate,<sup>31,32</sup> and (d) benzophenone-benzhydrol.<sup>33</sup> Using the uranyl oxalate actinometer we observed that the potassium chromate filter solution transmitted significant amounts of light of wavelength greater than 400 nm, a region in which the actinometer absorbed light and was photolyzed. Since the ketones employed do not have appreciable absorption beyond the 313-nm region, the light intensity actually reaching the samples was less than that calculated from the actinometer. A correction factor of 1.54 was determined by running the uranyl oxalate actinometer simultaneously with a benzophenone-benzhydrol actinometer which was used to adjust the quantum yields. Irradiations were run to less than 5% conversion and the reaction mixtures were analyzed by vpc. A pronounced effect on the quantum yield of type II reaction ( $\phi_{II}$ ) for 2-*n*-propylcyclohexanone (**4**) and *cis*-2-*n*-propyl-4-*tert*-butylcyclohexanone (**11**) was observed in going from

(29) P. Dunoin and C. N. Trumbore, *J. Amer. Chem. Soc.*, **87**, 4211 (1965).

(30) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(31) G. S. Forbes and W. G. Leighton, *ibid.*, **52**, 3192 (1930).

(32) C. R. Masson, V. Boeckelheide, and W. A. Noyes, Jr., *Tech. Org. Chem.*, **2**, 275 (1956).

(33) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).

cyclohexane to acetonitrile (Table IV). In acetonitrile, type II reaction is almost absent, although an unidentified product was formed. The maximum error limits are believed to be about  $\pm 20\%$  for the reported quantum yield data.

**Quenching Studies.** Quenching studies were conducted using piperylene as quencher and irradiating the ketones at 313 nm in several solvents containing varying amounts of piperylene. Relative quantum yields of aldehyde, ester, or type II products were determined by vpc. Stern-Volmer treatment (plot of  $\phi_0/\phi$  vs. [quencher]) of the quenching data for  $\alpha$ -cleavage products (enal and ester) gave, in general, linear plots of slope  $k_q\tau$ , where  $k_q$  is the rate constant for quenching of the ketone triplet by piperylene and  $\tau$  is the triplet lifetime in the absence of quencher. Assumption of  $k_q$  values allows calculation of  $\tau^{-1}$  values (Tables V and VI).

**Table V.** Quenching Data for a Series of Cyclohexanones in Methanol

Ketone	$k_q\tau$ (ald)	$k_q\tau$ (ester)	$k_q\tau$ (type II) <sup>b</sup>	$\tau^{-1} \times 10^8$ sec <sup>-1</sup> <sup>a</sup>
<b>1</b>	264	266		0.2
<b>2</b>	10	9.8		5.0
<b>4</b>	5.8	5.9	6.7	8.6
<b>5</b>	10.5	11	13	4.5
<b>8</b>	9.3	10.2	10.6	5.0
<b>9</b>		20.5		2.5
<b>10</b>		20.3		2.5
<b>11</b>		12	12.2	4.2
<b>12</b>		20.7		2.5

<sup>a</sup> Assuming a value of  $k_q = 5 \times 10^9 M^{-1} \text{sec}^{-1}$  for 1,3-pentadiene in methanol. <sup>b</sup> Calculated after subtracting out singlet reaction (see text).

**Table VI.** Quenching Data for a Series of Cyclopentanones in Methanol

Ketone	$k_q\tau$ (ald)	$k_q\tau$ (type II) <sup>b</sup>	$\tau^{-1} \times 10^9$ sec <sup>-1</sup> <sup>a</sup>
<b>14</b>	20		0.25
<b>15</b>	1.7		3.0
<b>17</b>	1.2		4.2
<b>21</b>	0.93	0.89	5.3

<sup>a</sup> Assuming a value of  $k_q = 5 \times 10^9 M^{-1} \text{sec}^{-1}$  for 1,3-pentadiene. <sup>b</sup> Calculated after subtracting out the singlet reaction (see text).

However, the quenching plots for the type II reaction products were nonlinear and solvent dependent. In benzene for 2-*n*-propylcyclohexanone (**4**), *ca.* 20% of the type II reaction could be quenched, whereas in methanol *ca.* 50% of the type II reaction was quenched. In other cases the type II reaction could only be quenched to the extent of *ca.* 10% in benzene; *i.e.*, more type II reaction was quenchable in methanol than in benzene. Figure 1 shows the plots for quenching of the type II reaction for 2-*n*-propylcyclohexanone (**4**) in methanol, and it can be seen that above a concentration of 0.4 *M* piperylene, there is little or no further quenching. We therefore assume this portion of the curve reflects only singlet reaction and hence from the plot,  $\phi_0/\phi_s = 1.37$ , *i.e.*, the relative quantum yield due to singlet reaction. We can now calculate the percentage of singlet reaction, since

$$\% \text{ reaction from singlet state} = ((\phi_0/\phi)/(\phi_0/\phi_s)) \times 100$$

By subtracting out the amount of singlet reaction at the lower concentrations we can further calculate  $\phi_0^T/\phi^T$ , *i.e.*, the relative quantum yields for type II from the triplet state. A plot of  $\phi_0^T/\phi^T$  vs. [quencher] gave in general a linear plot whose slope was the same (within experimental error) as that for quenching of enal or ester. The values of  $k_q\tau$  (type II) in Tables V and VI were calculated using the method described above.

**Singlet Lifetimes.** Table VII has the values obtained from the measurement of the singlet lifetimes using the

**Table VII.** Singlet Lifetimes and Relative Fluorescence Quantum Yields<sup>a</sup>

Ketone	$\phi_f^{\text{rel}}$	$\tau_s$	Ketone	$\phi_f^{\text{rel}}$	$\tau_s$
<b>1</b>	1.0	2.5 (2.7) <sup>b</sup>	<b>11</b>	0.24	1.2 <sup>c</sup>
<b>2</b>	1.12	3.0	<b>12</b>	0.85	2.7 <sup>c</sup>
<b>3</b>	0.63	1.7 <sup>d</sup>	<b>14</b>	1.0	1.9
<b>4</b>	0.27	0.72 <sup>d</sup>	<b>15</b>	1.6	2.7
<b>7</b>		2.9	<b>17</b>	0.86	2.8
<b>9</b>	0.62	3.0 <sup>c</sup>	<b>19</b>	11.2	8.7
<b>10</b>	1.00	4.2 <sup>c</sup>			

<sup>a</sup> Measured by the single photon counting technique,<sup>34</sup> cyclohexane solvent. **1–4** are relative to **1**, **9–12** are relative to **10**, and **14–19** are relative to **14**, *i.e.*, the  $\phi_f$  values.  $\tau_s$  is in nanoseconds. <sup>b</sup> Acetonitrile as solvent. <sup>c</sup> See ref 24. <sup>d</sup> Using similar method as given in ref 24.

single photon counting technique.<sup>34</sup> The quantum yields of fluorescence ( $\phi_f^{\text{rel}}$ ) for the cyclohexanone and cyclopentanone series are relative to cyclohexanone (**1**) and cyclopentanone (**14**), respectively. The  $\tau_s$  values for the 4-*tert*-butyl-substituted cyclohexanones (**9–12**) are based on the relative fluorescence quantum yields and on the assumption that  $\tau_s$  for 2-methyl-4-*tert*-butylcyclohexanone (**9**) is the same as that for 2-methylcyclohexanone (**2**); it should be pointed out that these calculated values are considered to be order of magnitude estimates.<sup>24</sup>

## Discussion

Analysis of our results is best achieved by considering the mechanism in Scheme IV for the photolysis of cycloalkanones, where K is the ketone, <sup>1</sup>B<sub>II</sub> and <sup>3</sup>B<sub>II</sub> are the singlet and triplet biradicals formed from <sup>1</sup>K and <sup>3</sup>K, respectively, by intermolecular hydrogen abstraction. <sup>1</sup>B<sub>I</sub> and <sup>3</sup>B<sub>I</sub> are the singlet and triplet biradicals resulting from  $\alpha$  cleavage of <sup>1</sup>K and <sup>3</sup>K, respectively. The rate constants for the various processes are also shown, *e.g.*,  $k_{II}^S$  is the rate constant for  $\gamma$ -hydrogen abstraction and  $k_{-II}^S$  is the rate constant for back transfer from the singlet biradical <sup>1</sup>B<sub>II</sub> to regenerate the ketones; the other rate constants follow the same notation. Stern-Volmer treatment of the triplet state gives rise to the usual expression 5, where  $\tau$  is the triplet lifetime of the ketone.

$$\phi_0/\phi = 1 + k_q\tau[Q] \quad (5)$$

$$\tau = \frac{1}{k_{II}^T + k_I^T + k_d} \quad (6)$$

**Type I Reaction.** The quenching studies on the cyclohexanones (**1–12**) indicate that in all cases the  $\alpha$ -

(34) For a description of this technique, see J. B. Birks and J. H. Munroe, *Progr. React. Kinet.*, **4**, 215 (1967); W. R. Ware in "Creation and Detection of the Excited States," A. A. Lamola, Ed., Vol. 1, Part A, Marcel Dekker, New York, N. Y., 1971, p 213.

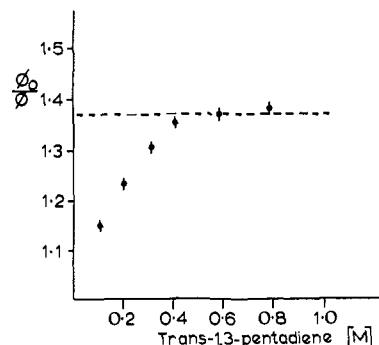
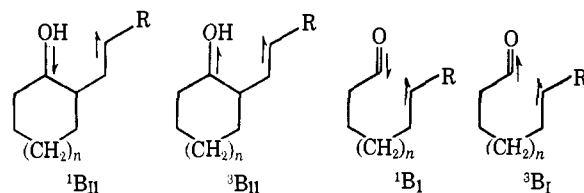
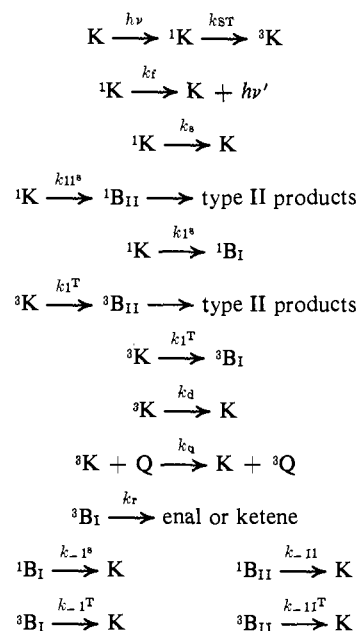


Figure 1. Quenching of type II reaction of 2-*n*-propylcyclohexanone (**4**) in methanol.

cleavage products are only arising from the triplet state, since *these products (enal and ester) can be completely quenched with piperylene*. These observations are in agreement with the results of Wagner<sup>11</sup> who studied a series of substituted cyclohexanones. The

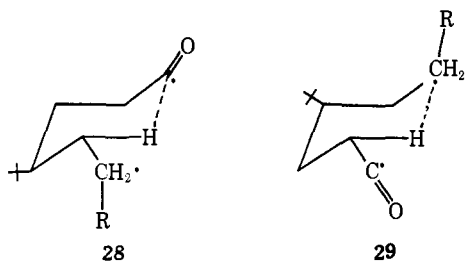
## Scheme IV



quantum yield for aldehyde formation ( $\phi_A$ ) increases (relative to cyclohexanone) with 2-alkyl substitution, as do the rate constants for  $\alpha$  cleavage. This result is consistent with the proposition that  $\alpha$  cleavage occurs through a transition state which resembles a biradical such as <sup>3</sup>B<sub>I</sub> (Scheme IV), since substitution on the  $\alpha$ -carbon is then able to stabilize the biradical. The fact that both *cis* and *trans* isomers of the unsaturated aldehyde are formed is also consistent with the postulated biradical, but is in contrast to the results of Srinivasan<sup>10</sup> who postulated that  $\alpha$ -cleavage products arise *via* a concerted mechanism. Evidence<sup>14</sup> of a biradical resulting from  $\alpha$  cleavage is available by the observation

that the triplet-state photorearrangement of *cis*- or *trans*-2,3-dimethylcyclohexanone to aldehydes and ketenes leads to the same *cis*-*trans* ratio of enals. Our results and those of other workers<sup>9,11,14,35,36</sup> provide rather convincing evidence in favor of a biradical intermediate, although there remains the possibility that in special cases there may be concerted pathways involving different conformations of the excited cyclohexanones.

The quantum yields for aldehyde formation (Tables II and III) decrease with 4 substitution on the ring. In fact, ketones with a large group (*tert*-butyl) in the 4 position of the ring of cyclohexanone gave little or no enal on irradiation in methanol or benzene; however, in methanol some ester was still isolated. These results can be rationalized by consideration of the transition-



state **28** for enal formation. The presence of the large bulky group in the 4 position could lead to large nonbonded interactions in the transition state for enal formation and hence result in an increase in the activation energy for hydrogen transfer. The transition state **29** for hydrogen transfer leading to ketene is not affected to the same extent since the *tert*-butyl group is now not involved in gauche interactions in the transition state. These types of arguments explain the difference<sup>37</sup> in the enal-ester ratio resulting from the irradiation of a series of cyclohexanones and cyclopentanones in methanol. The introduction of a *tert*-butyl group in the 4 position also seems to decrease the rate of  $\alpha$  cleavage of 2-alkylcyclohexanones, cf. **2** relative to **9** in Table V. This may be explained as resulting from the nonbonded interaction of the large *tert*-butyl group which causes a destabilization of the biradical (and its preceding transition state) formed from  $\alpha$  cleavage.

The fact that 4-*tert*-butylcyclohexanone (**7**), on irradiation in cyclohexane, gives rise to photoreduction products is not surprising since one would predict that the rate of  $\alpha$  cleavage of **7** would be slower than that of cyclohexanone **1**. In addition, we have seen that the introduction of a 4-*tert*-butyl group decreases the efficiency of enal formation from the biradical. Hence, in the presence of cyclohexane, in which 12 secondary hydrogens are available, photoreduction is able to compete with  $\alpha$  cleavage. The irradiation of cyclohexanone in ether or cyclohexane has been shown<sup>38</sup> to give rise to products which result from hydrogen abstraction, thus demonstrating that intermolecular hydrogen abstraction is able to compete with  $\alpha$  cleav-

age. However, cyclohexanones with  $\alpha$  substituents do not give rise to photoreduction products, presumably because the  $\alpha$ -cleavage process is too fast for intermolecular hydrogen abstraction to compete, unless a hydrogen donor much more reactive than cyclohexane or ether is available.

The 2-alkylcyclopentanones (**15**-**19**) behave in a similar manner to the cyclohexanones, but in all cases the rate of  $\alpha$  cleavage is an order of magnitude greater than for the corresponding cyclohexanones. This difference is presumably due to a greater relief of strain in the five-membered ketone, relative to the six-membered ketone, when the ring is opened.

With only one exception, the  $\alpha$ -cleavage products from cyclopentanones were quenched by piperylene, although total quenching was not achieved. The formation of enal from 2,2,5,5-tetramethylcyclopentanone (**19**) was not measurably quenched. This product apparently arises from a singlet or a very short-lived triplet excited state. The reactivity of the  $S_1$  and  $T_1$  states toward  $\alpha$  cleavage for a series of cyclic ketones has been compared.<sup>28,39</sup> If any triplets of **19** are formed then the rate constant for  $\alpha$  cleavage from the triplet state of ketone **19** must be greater than  $5 \times 10^{10} \text{ sec}^{-1}$ . However,  $1/\tau_s$  ( $1.1 \times 10^8 \text{ sec}^{-1}$ ), the inverse of the measured fluorescence lifetime, must be the upper limit of the rate constant for  $\alpha$  cleavage from the excited singlet state. Hence, there are at least two orders of magnitude difference in the reactivity of the triplet and singlet states toward  $\alpha$  cleavage in ketone **19**. The relatively long singlet lifetime (8.7 nsec) of **19** may be indicative of little or no  $\alpha$  cleavage from the singlet state. For cyclopentanones **14** and **15** which have much shorter lived excited singlets  $\alpha$  cleavage occurs mainly from the triplet state, since  $\alpha$  cleavage is quenchable (>90%) by 1,3-dienes.

The striking difference in the reactivities of the singlet and triplet states toward  $\alpha$  cleavage merits comment. Acyclic ketones have triplet states which are also much more reactive than the singlet states in giving  $\alpha$ -cleavage reaction, the rate constants again differing by *ca.* two orders of magnitude.<sup>40</sup> Figure 2, which represents a diatomic approximation to potential energy surfaces of the CO-R bond for alkyl ketones, suggests a source of the reactivity difference. This type of diagram has been put forward to explain some results of  $\alpha$  cleavage from hexafluoroacetone.<sup>41</sup> Excitation from the ground state to the upper vibrational levels of the excited singlet state occurs initially and is followed by rapid internal conversion to the lowest vibrational level of  $S_1$ . During rapid exchange of vibrational energy among the various modes sufficient energy will then from time to time accumulate in the CO-C mode to energize it above the lower limit of the shaded area. From this region a transition to the repulsive curve can occur. In solution, collisions will reduce the total vibrational energy of the molecule, and thus reduce the probability that sufficient energy can accumulate in the CO-C mode in the excited singlet state to permit transition to the repulsive curve. However,  $\alpha$  cleavage from the triplet

(35) B. Rickborn, R. L. Alumbaugh, and G. O. Pritchard, *Chem. Ind. (London)*, 1951 (1964).

(36) A. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

(37) J. D. Coyle, *J. Chem. Soc. B*, 1736 (1971).

(38) (a) J. P. Morizur, B. Furth, and K. J. Kossanyi, *Bull. Soc. Chim. Fr.*, 1959 (1970); (b) M. Barnard and N. C. Yang, *Proc. Chem. Soc.*, 302 (1958).

(39) J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2564 (1970).

(40) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 6974 (1970).

(41) R. K. Boyd, G. B. Carter, and K. O. Kutsche, *Can. J. Chem.*, **46**, 175 (1968).

state may occur over the reduced energy barrier  $E_T$  in Figure 2. Therefore, Figure 2 represents a method of explaining why  $\alpha$  cleavage occurs mainly from the triplet state in solution. Cundall<sup>42</sup> has carried out a study of the gas-phase photolysis of acetone and the effects of varying temperature; at 48° there is negligible  $\alpha$  cleavage from the singlet state, whereas at 100° some  $\alpha$  cleavage from the singlet was observed. From Figure 2 we can see that at higher temperatures the upper vibrational levels of the singlet excited state are more readily populated and hence the probability of  $\alpha$  cleavage from the  $S_1$  state is increased. Cundall's results<sup>42</sup> also showed that the rate constant for  $\alpha$  cleavage from acetone from the triplet state is much greater than from the singlet state.

We should note that the above discussion is aimed at understanding the reactivity difference between the  $S_1$  and  $T_1$  states of alkanones, and does not suggest that  $S_1$  is totally inert to  $\alpha$  cleavage. Indeed,  $\alpha$  cleavage does appear to occur for some singlet states,<sup>40,43,44</sup> but, in the known cases, always with reduced reactivity relative to  $T_1$ .

**Type II Reactions.** Our results (Scheme III) with the *cis*- and *trans*-2-*n*-propyl-4-*tert*-butylcyclohexanones (**11** and **12**)<sup>21,24</sup> and the *cis*- and *trans*-2,6-di-*n*-propyl-4-*tert*-butylcyclohexanones (**24** and **25**)<sup>24</sup> demonstrate a stereoelectronic requirement for  $\gamma$ -hydrogen abstraction, since only the  $\gamma$ -hydrogen which is in the plane of the carbonyl (*i.e.*, the position of the localized half-vacant  $n$  orbital of the  $n-\pi^*$  state) is abstracted. From the singlet and triplet lifetimes of the ketones **11** and **12** we can infer that this requirement holds for both the  $S_1$  and  $T_1$  states of the cyclic ketones.<sup>24</sup> Since no observed  $\gamma$ -hydrogen abstraction occurs in the cases of the axial *n*-propyl groups, *i.e.*, **12** and **25**, then it is unlikely that conversion to the boat form (from which the stereoelectronic requirement for  $\gamma$ -hydrogen abstraction is met) is an important factor.

To a fair approximation,<sup>45</sup> 2-alkylcyclohexanones exist predominantly in the most thermodynamically stable conformation, which is the chair form with the 2-alkyl group in the equatorial position. In this conformation the  $\gamma$ -hydrogen has easy access to the plane of the carbonyl group and can readily meet the stereoelectronic requirement for  $\gamma$ -hydrogen abstraction.

We find that the solvent does not appear to greatly effect the type II reaction except when the solvent is acetonitrile. In benzene or methanol the quantum yield for type II reaction is nearly the same for ketone **4**. The ratio of singlet to triplet reaction is greater in the nonpolar than in the polar solvent, *e.g.*, for **4** in benzene 80% singlet, whereas in methanol *ca.* 50% singlet, although the effect is small, as it is in the acyclic ketone systems.<sup>46,47</sup> In both solvents the percentage of the type II product from ketone **4** which is derived from the singlet state is greater than for the comparable acyclic ketone, *i.e.*, one with a secondary hydrogen atom in the  $\gamma$  position. In contrast, therefore, to the ring-

(42) R. B. Cundall and A. S. Davies, *Proc. Roy. Soc., Ser. A*, **290**, 563 (1966).

(43) N. C. Yang and E. D. Feit, *J. Amer. Chem. Soc.*, **90**, 504 (1968).

(44) (a) N. C. Yang and R. H.-K. Chen, *ibid.*, **93**, 530 (1971); (b) K. Dawes, N. J. Turro, and J. M. Conia, *Tetrahedron Lett.*, in press.

(45) E. I. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience-Wiley, New York, N. Y., 1965.

(46) P. J. Wagner, *Tetrahedron Lett.*, 1753 (1967); 5385 (1968).

(47) J. A. Barltrop and J. D. Coyle, *ibid.*, 3235 (1968).

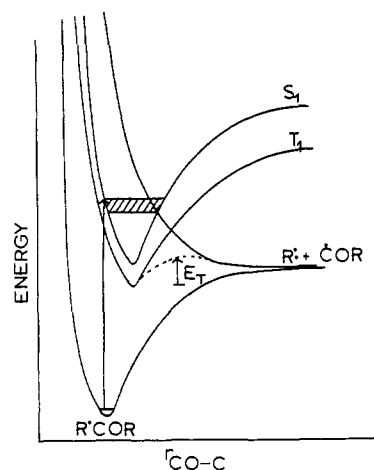


Figure 2. Diatomic approximation to potential energy surfaces for an alkyl ketone. The diagram is schematic and not to scale.

opening reactions (type I) which occur largely from the triplet state, the  $\beta$ -cleavage reactions occur from both the singlet and triplet states of the ketones. Stern-Volmer treatment of the data for the triplet type II reaction indicates that this process arises from the same triplet state as does  $\alpha$  cleavage, since the slopes are the same (within experimental error) for quenching either  $\alpha$  cleavage or type II from  $T_1$ . In acetonitrile, hardly any type II photoelimination is observed, and unidentified products were isolated.

The quantum yields of fluorescence (Table VII) of  $\alpha$ -substituted cyclohexanones relative to cyclohexanone ( $\phi_f^{rel}$ ) decrease in the order 2-methylcyclohexanone (**2**) (1.12), 2-ethylcyclohexanone (**3**) (0.63), 2-*n*-propylcyclohexanone (**4**) (0.27). If the quantum yield of intersystem crossing for 2-methylcyclohexanone is assumed to be 1.0, then, using the measured value for  $\tau_s$  of 3.0 nsec, the rate of intersystem crossing can be estimated to be around  $3.3 \times 10^8 \text{ sec}^{-1}$ . If it is further assumed that the rate constant of intersystem crossing is the same for all the 2-alkylcyclohexanones, then the measured relative quantum yields of fluorescence imply that the reactivity of the  $S_1$  state ( $k_r^s$ ) toward the intramolecular  $\gamma$ -hydrogen abstraction process for a primary hydrogen in 2-ethylcyclohexanone is  $\sim 2 \times 10^8 \text{ sec}^{-1}$ , whereas  $k_r^s$  for a secondary  $\gamma$ -hydrogen in 2-*n*-propylcyclohexanone (**4**) is around  $1 \times 10^9 \text{ sec}^{-1}$ . These values are very close to those obtained for singlet reactivity toward  $\gamma$ -hydrogen abstraction for a primary ( $1.8 \times 10^8 \text{ sec}^{-1}$ ) and a secondary ( $9.9 \times 10^8 \text{ sec}^{-1}$ )  $\gamma$ -hydrogen of acyclic ketones, measured from spectroscopic data<sup>48</sup> or photochemical data.<sup>49a</sup>

Since the rate of  $\alpha$  cleavage in the triplet state of the substituted cyclopentanones ( $k_{IT}^T \sim 4 \times 10^9 \text{ sec}^{-1}$ ) and the rate from  $T_1$  of intramolecular abstraction of a tertiary  $\gamma$ -hydrogen ( $k_{IT}^T \sim 0.6-6 \times 10^9 \text{ sec}^{-1}$ ) are similar<sup>7</sup> then these processes should be able to compete in appropriately substituted molecules. This is reflected by the percentage of type II product in the cyclopentanone series (Table I), where the ketones with primary and secondary  $\gamma$ -hydrogens give very little

(48) J. C. Dalton and N. J. Turro, *J. Amer. Chem. Soc.*, **93**, 3569 (1971).

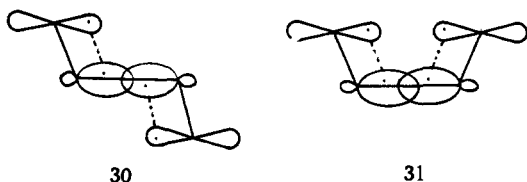
(49) (a) N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, **91**, 7551 (1969); (b) C. H. Bibart, M. G. Rockley, and F. S. Wettack, *ibid.*, **91**, 2802 (1969).

type II products (<1%) but the cyclopentanone with a tertiary  $\gamma$ -hydrogen, *i.e.*, 2-isobutylcyclopentanone (**21**), gives a relatively high yield (20%) of cyclopentanone. Srinivasan<sup>20</sup> has reported that 2-*n*-propylcyclopentanone (**17**), when irradiated neat, gives a fair yield of type II product. Our rate constants are also consistent with this proposal, since the sum of the rate constants for the triplet processes of 2-methyl, 2-ethyl, and 2-*n*-propylcyclopentanones is in the range  $3\text{--}4 \times 10^9 \text{ sec}^{-1}$ , whereas for 2-isobutylcyclopentanone the rate constant sum increases to  $5\text{--}6 \times 10^9 \text{ sec}^{-1}$ . If we assume the difference in lifetimes arises solely because of competitive hydrogen abstraction, then a value of  $1\text{--}2 \times 10^9 \text{ sec}^{-1}$  can be estimated for the triplet rate constant for hydrogen abstraction in 2-isobutylcyclopentanone.

Since in the cyclohexanone series the rates of  $\alpha$  cleavage from the triplet states are much slower ( $k_{\text{I}}^{\text{T}} \sim 4 \times 10^8 \text{ sec}^{-1}$ ) than the cyclopentanones, one would predict that in the triplet state<sup>7</sup> intramolecular hydrogen abstraction of a secondary ( $k_{\text{II}}^{\text{T}} \sim 1\text{--}10 \times 10^8 \text{ sec}^{-1}$ ) or tertiary ( $k_{\text{II}}^{\text{T}} \sim 0.6\text{--}6 \times 10^9 \text{ sec}^{-1}$ )  $\gamma$ -hydrogen should be able to compete efficiently with type I cleavage, but abstraction of a primary hydrogen should not. The yields (Table I) of type II products are consistent with this prediction, in that 2-*n*-propyl- and 2-isobutylcyclohexanone give type II yields of 65 and 77%, respectively, whereas 2-ethylcyclohexanone (**3**) gives very little type II (<1%). There is a report that 2-isopropylcyclohexanone undergoes type II reaction with a yield of 9.5%,<sup>38a</sup> in the same study 2-isopropylcyclopentanone gave no type II products. The rate constants for unimolecular  $\text{T}_1$  decay also reflect our prediction, in that they increase from a value of  $1\text{--}2 \times 10^8 \text{ sec}^{-1}$  for 2-methylcyclohexanone (**2**) and 2-ethylcyclohexanone (**3**) to  $7 \times 10^8 \text{ sec}^{-1}$  for 2-*n*-propylcyclohexanone (**4**) and to  $9 \times 10^8 \text{ sec}^{-1}$  for 2-isobutylcyclohexanone (**5**), in cyclohexane or benzene. In methanol the same trend is noted although the value for 2-isobutylcyclohexanone is surprisingly low ( $4.5 \times 10^8 \text{ sec}^{-1}$ ).

The rate constants for intramolecular hydrogen abstraction by the singlet and triplet states seem to indicate that the singlet is at least as reactive as the triplet, if not more reactive. This is in agreement with comparable data obtained in the case of acyclic ketones.<sup>49</sup>

Yang<sup>50</sup> in his excellent study of the photolysis of the optically active ketone (*S*)-(+)-5-methyl-2-heptanone has shown that photoracemization occurs from the triplet state, suggesting the existence of a triplet biradical sufficiently long lived to allow racemization at the  $\gamma$ -carbon. The results with acyclic ketones<sup>49</sup> also show that the triplet is efficient (relative to the singlet state) in giving type II products. We feel that the most probable transition state for  $\beta$  cleavage in the 1,4 biradicals is one which allows maximum development of the double bond character of the olefin and the enol as the  $\beta$  bond cleaves. Transition states such as **30** and **31** meet this requirement, *i.e.*, the carbon 2p

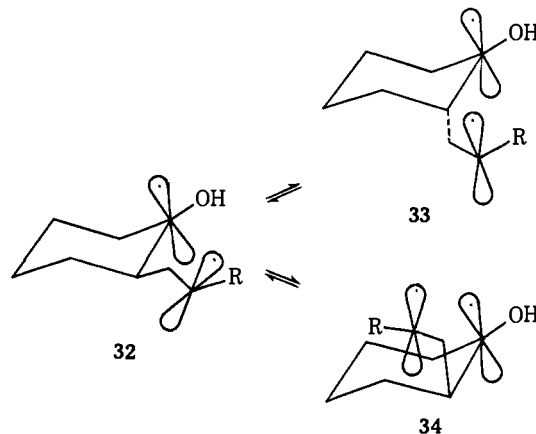


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(50) N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, **91**, 7550 (1969).

orbitals at the radical centers and the  $\beta$  bond are parallel. The 1,4 biradicals generated from the 2-alkylcyclohexanones undergo  $\beta$  cleavage with less efficiency than the acyclic cases and one possible explanation for the difference is that after initial hydrogen abstraction a transition state such as **32** is formed. In order to attain transition states for  $\beta$  cleavage such as **30** and **31**, either the high-energy conformation **33** or the twisted chair form **34** must be formed. The fact that formation



of these transition states is endothermic may be the reason for the inefficiency of type II from the triplet state, since the conformation **32** is well set up for back transfer of the hydrogen. 1,4-Biradicals from acyclic alkyl ketones can explore more conformations since the 1,2 bond is not rigid, and hence the required transition state is more readily attained and, therefore, the efficiency of  $\beta$  cleavage from the triplet is greater for acyclic ketones. Similar types of arguments may explain the lack of any appreciable amounts of cyclization products, *i.e.*, cyclobutanols, from the cyclic ketones. However, there are some reports<sup>38a,51</sup> of cyclobutanol formation from cyclic ketones.

In methanol the efficiency of  $\beta$  cleavage from the triplet for 2-*n*-propylcyclohexanone (**4**) is enhanced (type II *ca.* 50%  $\text{T}_1$  in methanol, but only 20% in benzene). One can explain this by intermolecular hydrogen bonding of the 1,4-hydroxy biradical **32**, making the biradical sufficiently long lived to allow a greater probability of attaining the required transition states for  $\beta$  cleavage, **33** and **34**. The hydrogen-bonding rationalization has been used previously to explain enhanced triplet reaction in going to polar solvents for acyclic ketones.<sup>46,47</sup>

The type II reaction from the singlet excited state is also inefficient in the case of 2-*n*-propylcyclohexanone (**4**). A singlet biradical as intermediate could explain this inefficiency by the fact that back transfer of the hydrogen to give the original ketone is occurring. The singlet biradical generated from the  $\text{S}_1$  state may be higher in energy than the biradicals generated from the  $\text{T}_1$  state (followed by spin inversion), and transition states such as **33** and **34** may not be required for  $\beta$  cleavage.<sup>52</sup> The results of Yang<sup>50</sup> with the optically active ketone showed that the total quantum yield of observed events from  $\text{T}_1$  (type II, cyclobutanol and

(51) E. J. Corey, R. B. Mitri, and H. Uda, *ibid.*, **86**, 488 (1964); I. Fleming, A. V. Kemp-Jones, and E. J. Thomas, *Chem. Commun.*, 1158 (1971).

(52) For a similar viewpoint, see L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971).



racemization) is only 0.14. Since  $\phi_{ST}$  was determined to have a comparable value (0.11) and the quantum yield for reaction from  $S_1$  is 0.07, then the remaining quantum yield of 0.79 must represent nonradiative decay from  $S_1$ . This  $S_1$  decay appears to lead to no racemization and is not affected by changes in solvent, which implies that if it does occur through the formation of a singlet biradical and subsequent back transfer of the hydrogen, then the biradical must be extremely short lived. Stephenson, *et al.*,<sup>53</sup> have also presented evidence which is consistent with the intermediacy of a singlet biradical in the type II photoreaction.

Another possibility is that type II from the  $S_1$  state occurs *via* a concerted pathway, and the efficiency of  $\beta$  cleavage is 1.0. Yang<sup>54</sup> has suggested that deactivation of the  $S_1$  state may involve internal conversion of the excited singlet state to the upper vibrational levels of the  $\gamma$  C-H stretching mode of the ground state.

In summary, the results show that there is no major difference in the reactivities of the singlet and triplet states of alkanones toward type II photoelimination. The triplet state reaction probably involves a discrete 1,4-biradical intermediate, whereas the singlet state reaction is possibly proceeding *via* either a concerted or a biradical mechanism.<sup>50</sup> Unfortunately, one can only speculate on the mechanism involved from the singlet state and there is no direct evidence in favor of either a concerted or biradical mechanism.

## Experimental Section

**Preparation of Ketones.** Cyclopentanone, cyclohexanone, 2-methylcyclohexanone, 4-methylcyclohexanone, 2-*n*-propylcyclohexanone, and 4-*tert*-butylcyclohexanone were obtained from commercial sources. 2-Methyl-, 2-*n*-propyl-, and 2-isobutylcyclopentanone and 2-ethyl- and 2-isobutylcyclohexanone were made from the cycloalkanone or the ethyl cycloalkanone-2-carboxylate by standard procedures. *cis*-2-*n*-Propyl-4-*tert*-butylcyclohexanone and *cis*-2-methyl-4-*tert*-butylcyclohexanone were prepared by hydrogenation of the phenols followed by Jones oxidation of the resulting alcohol. The trans isomers were prepared *via* the pyrrolidine enamine using the conditions of Caine.<sup>55</sup> 2,2,5,5-Tetramethylcyclopentanone was prepared by Dr. R. M. Southam by exhaustive methylation of cyclopentanone with dimethyl sulfate and sodium amylate. We thank Professor G. Stork for a gift of 2-*n*-butylcyclopentanone.

**Preparation of *cis*-2,6-Di-*n*-propyl-4-*tert*-butylcyclohexanone (24).** 2,6-Di-allyl-4-*tert*-butylphenol was prepared from 4-*tert*-butylphenol according to the published procedure.<sup>56</sup> It had: nmr (CCl<sub>4</sub>)  $\tau$  8.73 (s, 9 H), 6.68 (m, 4 H), 5.24 (s, 1 H, -OH), 3.66–5.13 (m, 6 H, allylic), 3.11 (s, 2 H, aromatic); ir  $\nu_{\max}^{\text{CCl}_4}$  3520, 1650, 1497, 1220, 995, 915 cm<sup>-1</sup>.

A solution of 2,6-diallyl-4-*tert*-butylphenol (17.6 g) in glacial acetic acid (170 ml) with 1 g of Adam's catalyst was hydrogenated in a Parr apparatus with an initial pressure of 50 psi. After 12 hr the theoretical amount of hydrogen had been taken up. The catalyst was filtered off and chloroform (200 ml) was added, followed by water (200 ml); the acetic acid was then decomposed by the addition of solid sodium bicarbonate. Separation of the layers and removal of the chloroform gave a residue which was distilled to give 2,6-di-*n*-propyl-4-*tert*-butylcyclohexanol (mixture of isomers) (15.0 g; 83%); bp 90–98° (0.8 mm); ir  $\nu_{\max}^{\text{CCl}_4}$  3600, 1100 cm<sup>-1</sup>. The nmr showed the presence of some 2,6-di-*n*-propyl-4-*tert*-butylphenol; this was not removed and the crude alcohol was used for the next step of the synthesis.

To a solution of the alcohol (12.9 g) obtained above, in acetone (100 ml), was added dropwise Jones reagent (8 *N*) until the orange-

brown color persisted. The mixture was poured into water (200 ml), the solution was extracted with ether (three 50-ml portions), and the combined ether extracts were washed with saturated sodium bicarbonate solution and water, and dried (MgSO<sub>4</sub>). Removal of the solvent and distillation of the residue gave two fractions, 2-*n*-propyl-4-*tert*-butylcyclohexanone (5.84 g), bp 86° (0.85 mm), identical with authentic sample, and *cis*-2,6-di-*n*-propyl-4-*tert*-butylcyclohexanone (24) (5.31 g), bp 87–89° (0.85 mm). A pure sample of 24 was obtained by preparative vpc on a 10 ft  $\times$  1/4 in. XF1150 column at 180°. It had: nmr (CCl<sub>4</sub>)  $\tau$  7.7–9.15 (m, with a singlet at  $\tau$  9.08); ir  $\nu_{\max}^{\text{CCl}_4}$  1708 cm<sup>-1</sup>; mass spectrum (75 eV) *m/e* (relative intensity) 238 (M<sup>+</sup>, vw), 196 (100), 181 (87), 154 (41), 139 (37), 112 (48), 83 (48), 57 (66), 55 (48).

**Preparation of *trans*-2,6-Di-*n*-propyl-4-*tert*-butylcyclohexanone (25).** This ketone was prepared using the method of Johnson<sup>28</sup> by formation of the semicarbazone of *trans*-2,6-di-*n*-propyl-4-*tert*-butylcyclohexanone using a solution of semicarbazide acetate and the *cis*-ketone 24 in methanol. The semicarbazone was formed in 37% yield, and it had mp 139.5–140°; nmr (CDCl<sub>3</sub>)  $\tau$  1.9 (broad, 1 H), 4.31 (broad, 2 H), 7.78–9.21 (m, 30 H, with a singlet at  $\tau$  9.12).

*Anal.* Calcd for C<sub>17</sub>H<sub>33</sub>N<sub>3</sub>O: C, 69.15; H, 11.18; N, 14.24. Found: C, 69.36; H, 11.10; N, 14.12.

The semicarbazone was decomposed with nitrous acid in acetic acid giving *trans*-2,6-di-*n*-propyl-4-*tert*-butylcyclohexanone (25). Preparative vpc (12 ft  $\times$  1/4 in. 20% XF1150 on Chromosorb W; column temperature 166°) gave pure 25. It had: nmr (CCl<sub>4</sub>)  $\tau$  7.52–9.19 (m, with a singlet at  $\tau$  9.09); ir  $\nu_{\max}^{\text{CCl}_4}$  1710 cm<sup>-1</sup>; mass spectrum (75 eV) *m/e* (relative intensity) 238 (M<sup>+</sup>, 5), 223 (7), 196 (100), 181 (80), 167 (16), 154 (48), 139 (39), 112 (59), 57 (57), 55 (66).

Reaction of the ketone 25 with sodium methoxide in methanol gave the ketone 24 as the major isomer, as shown by analytical vpc. All the ketones were purified by preparative vpc and were distilled before use.

**Identification of Photoproducts.** Solutions of the various ketones, usually 0.1 *M*, were irradiated at 313 nm, and the products were isolated by preparative vpc. The following is a description of a typical procedure.

A solution of 2-isobutylcyclohexanone (5) in cyclohexane was irradiated at 313 nm; preparative vpc (6 ft  $\times$  1/4 in. 20% XF1150 on Chromosorb P at 100°) of the reaction mixture gave cyclohexanone, identical with an authentic sample, and a mixture of *cis*- and *trans*-8-methylnonanal, which had the following spectral properties: nmr (CCl<sub>4</sub>)  $\tau$  9.19 (d, 6 H, *gem*-dimethyl), 7.58–8.7 (m, 9 H, methylenes), 4.50 (m, 2 H, -CH=CH-), 0.10 (2 t, CHO protons from different isomers); ir  $\nu_{\max}^{\text{CCl}_4}$  2700, 1725, 1370, 960 cm<sup>-1</sup>; mass spectrum (75 eV) *m/e* (relative intensity) 154 (M<sup>+</sup>, 0.9), 136 (7.5), 121 (18), 110 (31), 98 (29), 95 (34), 81 (22), 69 (26), 68 (36), 67 (51), 41 (100).

**Quantum Yields.** Solutions of the ketones with internal standard in purified solvents were degassed and sealed in 10-mm o.d. Pyrex tubes. The tubes were then photolyzed on a merry-go-round apparatus using a Hanovia 450-W medium-pressure mercury lamp and a potassium chromate filter to isolate the 313-nm wavelength. Photolyses were carried to 5% or less conversion, and the solutions were analyzed by vpc. Actinometers were photolyzed simultaneously. Either a benzophenone-benzhydrol,<sup>33</sup> or uranyl oxalate,<sup>31,32</sup> or the photoisomerization of neat cyclopentanone to 4-pentenol,<sup>29</sup> or the type II reaction of 2-hexanone<sup>30</sup> actinometers was used. Each quantum yield was the average of three or more analyses.

**Quenching Studies.** Samples were prepared as for the quantum yield determinations except that varying amounts of piperylene were added to the solutions. Four or more concentrations of piperylene, in addition to blanks containing no piperylene, were used for each Stern-Volmer plot. The solutions were analyzed by vpc.

**Spectra.** Relative fluorescence quantum yields were determined using an Aminco-Bowman spectrofluorimeter. Uv spectra were recorded on a Cary 14 and mass spectra on a Hitachi-Perkin-Elmer RMU-6D.

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