The Photochemistry of Substituted Bicyclo[3.2.1]octan-6-ones. Chair–Chair Conformational Inversion of Biradical Intermediates

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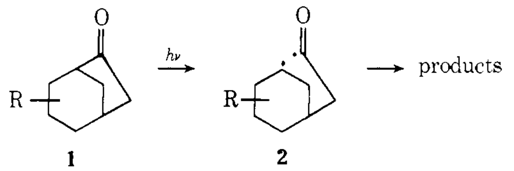
Abstract: The photochemical α-cleavage reaction of bicyclooctanones **5–16** has been studied in benzene containing $\sim$3.5% methanol at 30 ± 0.5 °C. In all cases but one the only volatile products formed are the expected aldehyde and ketene (trapped as its methyl ester). The results collected in Table I indicate that conformational relaxation of the six-membered ring of biradical **2a** competes successfully with disproportionation and that Scheme I must be considered in accounting for the products formed. Steric and temperature effects are also discussed; in one case (**12**) severe crowding leads to formation of the carbene-derived product **20** in addition to aldehyde and ketene. The preparation of bicyclooctanone **6** is described.

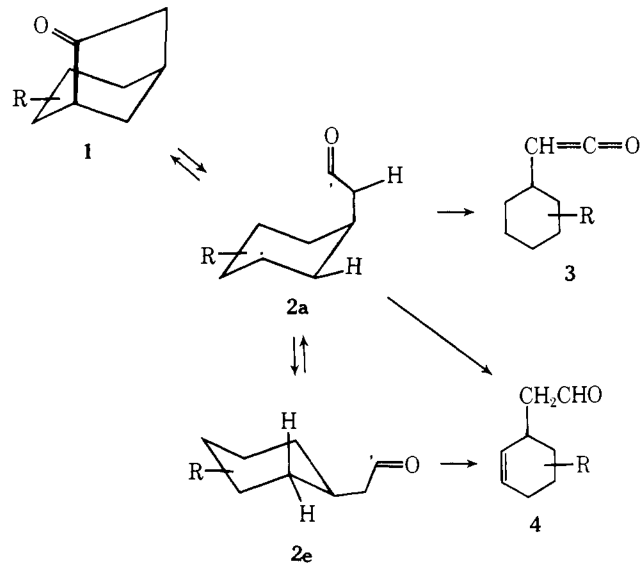
In recent years the chemistry of biradical species has received increasing careful study, and there is a growing fund of information on theoretical, mechanistic, and preparative aspects of the subject.[1] It remains difficult, nonetheless, to predict with assurance the behavior of biradicals for which multiple reaction pathways are available. These species are short-lived, and frequently they arise in thermolytic or photolytic processes of relatively high energy; yet for specific examples there are typically available only rough estimates of lifetime or energy content. In these circumstances it may prove impossible to evaluate without experiment the steric, conformational, and electronic factors which necessarily influence the fate of a given biradical intermediate. Such a situation underscores the value of experimental examination of these problems, and in this report we describe the effects of steric and conformational factors on the fate of the 1,5-biradicals (**2**) formed photochemically from bicyclo[3.2.1]octan-6-ones (**1**).[2]



The α-cleavage (Norrish type I) reaction of these bicyclic ketones appeared in advance to be particularly attractive for investigation in depth for several reasons: (1) Formation of the desired biradical intermediates in this photolytic process is now generally accepted,[3] and, indeed, in several instances radicals derived in this fashion from other types of ketones have been observed spectroscopically.[4] (2) Preparation of a variety of useful, specifically substituted bicyclo[3.2.1]octan-6-ones seemed feasible, although appropriate compounds were not already known. (3) Elucidation of the factors controlling the fate of this series of biradical intermediates should be particularly instructive, since they offer a system in which the conformational preference of a substituted cyclohexyl radical **2** may influence the course of reaction.

As shown in Scheme I,[5] α-cleavage of the bicyclooctanone **1** leads to biradical **2a** (axial acyl radical side chain), which may reclose to **1** or disproportionate to either ketene **3** or aldehyde **4**. Alternatively, **2a** could invert to **2e** (equatorial acyl radical side chain), from which the only disproportionation geometrically allowed leads to aldehyde **4**. Now the rates of the reclosure to **1** and of the disproportionations leading to **3** and **4** will be governed by the steric and electronic considerations delineated in a number of previous studies of the α-cleavage reaction;[6,7] their effects in the present situation will be made apparent below. In contrast to these factors, however, conformational relaxation of the biradical (**2a** ⇄ **2e**) can affect the course of reaction only if it competes successfully with disproportionation to **3** and **4**; that is, conformational relaxation can play a role only if **2** is sufficiently long-lived.[8] At present, the quantitative information available is inadequate to permit reliable prediction of the behavior of intermediate **2**, and it is this situation that makes the photochemistry of bicyclo[3.2.1]octan-6-ones particularly worthy of experimental examination.

Scheme I



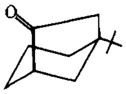
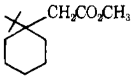
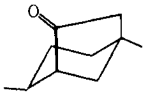
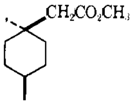
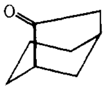
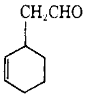
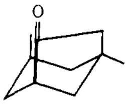
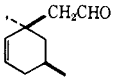
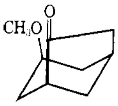
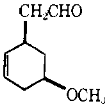
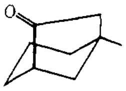
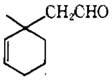
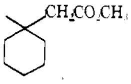
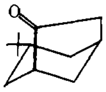
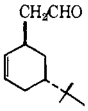
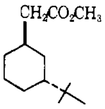
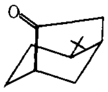
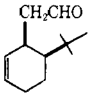
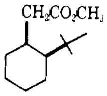
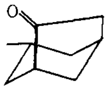
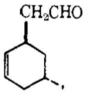
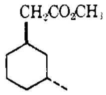
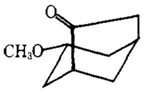
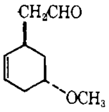
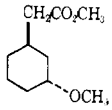
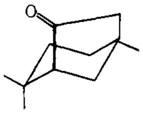
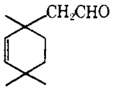
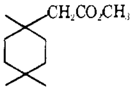
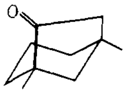
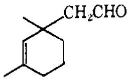
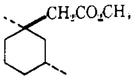
We have accordingly prepared and photolyzed a number of bicyclooctanones of known stereochemistry. Solutions of these ketones ($\sim$0.014 M) in benzene containing $\sim$3.5% methanol (v/v, $\sim$0.87 M) were irradiated through Pyrex (λ >2800 Å) at 30 ± 0.5 °C. Under these conditions ketene products are trapped as the related photochemically unreactive methyl esters. The results are presented in Table I. Products and unreacted starting ketone were isolated by preparative vapor phase chromatography (VPC). Yields are based on calibrated VPC measurements. Products for which structures are given were completely characterized and in a number of cases could be compared directly with authentic samples.[9] These results are analyzed in the paragraphs below, followed by discussion of studies at other temperatures and preparative experiments.

Confining attention for the moment to ketones **5–10**, we note that there is an excellent correlation between the expected conformational preference of the derived biradical **2** and the products formed. Ketones **5** and **6**, for which **2a** is the stable conformation of the intermediate, yield ketene and essentially no aldehyde. Although formation of aldehyde from **2a** is geometrically feasible, this path does not compete successfully in **5** and **6** with that leading to ketene, and we shall return below to consideration of this behavior. For ketones **7–9** the inverted conformer **2e** is clearly the more stable, and here the observed product is aldehyde with essentially no ketene. The monomethyl ketone **10** should yield a conformationally balanced intermediate with similar equilibrium concentrations of **2a** and **2e**, and in this case the observed product is a 0.86:1.0 mixture of aldehyde and ketene.[10] These results with **5–10** provide strong evidence that the conformational equilibrium of Scheme I (**2a** $\rightleftarrows$ **2e**) must be taken into consideration and that disproportionation of biradical intermediate **2** occurs from the stable cyclohexane chair conformer(s) in each instance.

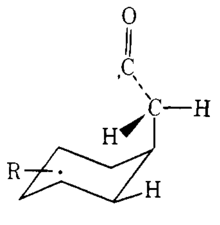
We turn now to consideration of the exclusive formation of ketene from **5** and **6**. Since earlier investigations have demonstrated an important role for even small steric effects in determining the course of α-cleavage reactions,[6,7] it seemed plausible to ascribe the specificity here to a sterically determined, preferential orientation of the acyl radical side chain. On this basis the formation solely of ketene from **2a** would reflect a lower energy for **17** or **18**, which can lead to ketene, than for **19**, which would lead to aldehyde. Such a possibility suggests that changing the steric environment of the acyl side chain could influence the behavior of conformer **2a**, and this we have investigated with ketones **11** and **12**. The three ketones **5**, **11**, and **12** all have an equatorial *tert*-butyl group which should anchor the biradical in conformer **2a**, but the steric interaction of this group with the acyl side chain will be different in each case. From examination of models it appears that in **11** the *tert*-butyl group is far enough removed to have no direct effect on side-chain rotation, but that in **12** significant nonbonded interactions between the two groups are present in virtually all orientations of the side chain, including **17–19**. This latter situation correlates well with the observed result that from **12**, production of any volatile product is very inefficient; clearly disproportionation to either aldehyde or ketene is particularly unfavorable in this case. Also **12** is the only ketone in the entire study to yield any carbene-derived product. In this case there was 8% of the enol ether **20**, which we believe arises from carbene **21**.[11] Formation of such carbenes on photolysis of saturated, cyclic ketones is known to be favored in a number of cases in which the alternative isomerizations to aldehyde and ketene are impossible or unusually slow.[12] Furthermore, the total recovery of volatile material from **12** is low (45%) in comparison with an average of 88% from the other bicyclooctanones. This suggests the availability of some process leading to nonvolatile photoproducts, which is operative with **12** but too slow to be significant when α-cleavage and disproportionation to **3** and **4** is favorable. Photolysis of **11** and **12** gives both aldehyde and ketene, and this fact supports the steric explanation suggested for the behavior of **5** and **6**. Geminal substitution at C(1) in **5** and **6** apparently disfavors **19** sufficiently through nonbonded interactions to cause the observed specific formation of ketene from conformer **2a**, but in the absence of such steric interaction (as in **11**), disproportionation to both products does occur from **2a**.[13]

These results permit us now to account for the product distribution from **13** and **14**, two ketones lacking substitution at C(1) which should therefore furnish both aldehyde and ketene from **2a**. Monomethyl ketone **13**, like its position isomer **10**, will disproportionate about equally from **2a** and **2e**. Conformer **2e** can give only aldehyde, while **2a** can give both products. The predicted result is formation of both ketene and aldehyde, with the latter in excess, and this is in qualitative agreement with observation. Methoxy ketone **14** differs from **13** for our purposes only in the proportion of reaction anticipated from **2a** and **2e**. For **14** the inverted conformer **2e** (≡**23**) is favored by ~0.8–0.9 kcal/mol,[14] so that most of the disproportionation will occur from **23** and give aldehyde. However, this conformational energy difference permits the presence of a small amount of **2a** (≡**22**) as well.[21] A minor amount of reaction

Table I. Products of Photolysis of Bicyclo[3.2.1]octan-6-ones

Bicyclooctanone	Aldehyde	Methyl ester (from ketene)
 **5**	<0.5%	 96%
 **6**	<1%	 96%
 **7**	 93%	<0.5%
 **8**	 96%	<1%
 **9**	 85%	<0.5%
 **10**	 44%	 51%
 **11**	 20%	 51%
 **12**[a]	 17%	 18%
 **13**	 68%	 6%
 **14**	 72%	 ~2.5%[b]
 **15**	 8%	 87%
 **16**	 46%	 43%

[a] See text for discussion of third product. [b] Determined only by identity of retention time with that of authentic ester.



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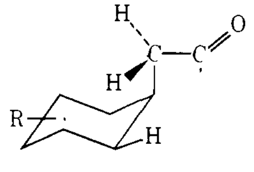

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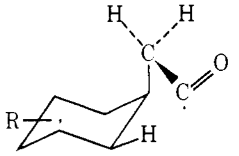

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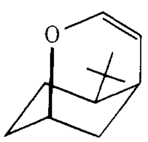

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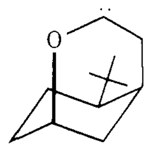

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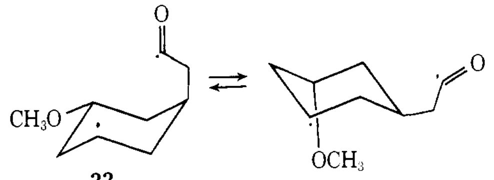
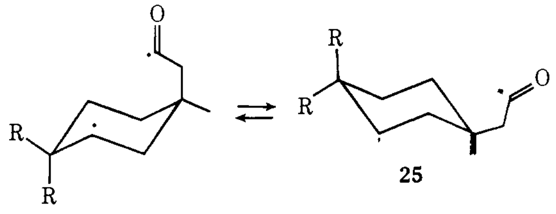


22 **23**

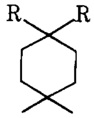
from **22** thus can be foreseen, and this should lead to both aldehyde and ketene. The prediction, in good accord with experiment, is a product mixture that is largely aldehyde with only a very small amount of ketene.

A particularly clear picture of the effect of chair-chair inversion on product distribution is available through comparison of the results with ketones **11**, **13**, **14**, and **7**. In this series the exo substituent at C(3) is progressively reduced in effective conformational size from *tert*-butyl, to methyl, methoxyl, and finally hydrogen. As we have seen, a substituent in this position will influence the course of reaction through its effect on the conformational equilibrium between **2a** and **2e**, with the initial conformer **2a** decreasing in stability as the size of the substituent at C(3) is reduced. The result should be increasing disproportionation from inverted conformer **2e** and therefore a progressive increase in aldehyde at the expense of ketene along the series **11**, **13**, **14**, **7**. This is in line with the experimental results. No doubt other, more subtle influences are also involved here, since the internal consistency of these data is quantitatively unsatisfactory. The qualitative agreement suggests, however, that the conformational effect under consideration principally determines the course of these reactions.

Our interpretation of the influence of substituents on the photochemical behavior of bicyclooctanones **5–14** has an interesting consequence. This is that, in principle, it should be possible to obviate the effect of cyclohexane chair-chair inversion on the distribution of photolytic products. For, if the rate of hydrogen transfer in **2a** were sufficiently increased, or alternatively if the rate of inversion of **2a** to **2e** were sufficiently decreased, all disproportionation necessarily would take place from **2a**, regardless of the position of the conformational equilibrium. This possibility leads to an attractive explanation for the behavior of the trimethylbicyclooctanone **15**, a ketone that differs from **10** only in the introduction of two methyl groups at C(4). This change does not alter the conformational equilibrium in the derived biradical, and the two chair forms **24a** and **25a** should be of comparable stability. Nor is it apparent in models that the distant geminal dimethyl substituents should exercise any direct steric effect on the rotational behavior of the acyl side chain of **24a** or **25a**. On the basis of the effects we have discussed in accounting for the photochemistry of **5–14**, ketone **10** and the derived species **24b** and **25b** should be good models for the behavior of **15**, **24a**, and **25a**. However, **15** gives mainly ketene, a result indicating that it reacts primarily from **24a**, while as we have seen above, **10** reacts about equally from each of the conformers **24b** and **25b**. A possible explanation of this anomaly is suggested by the fact that the barrier ($\Delta G^{\ddagger}$) to chair-chair inversion of 1,1-dimethylcyclohexane (**26b**) is ~1.1 kcal/mol lower than it is in 1,1,4,4-tetramethylcyclohexane (**26a**).[22] This suggests that introduction of the two additional methyl groups in **15** should reduce the rate of inversion of the derived biradical, since this is now a 1,1,4,4-tetralkylcyclohexyl species.[23] That is, inversion of **24a** to **25a** should be slower than inversion of **24b** to **25b**, and this reduced rate of inversion could permit increased disproportionation from **24a**. Since **24a** is expected to yield only ketene, such an effect would suffice to account for ketene as the major product from **15**.



24 **25**



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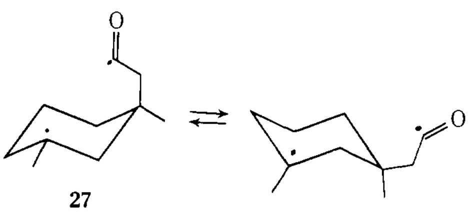
a, R = CH_3; **b**, R = H

This explanation for the observed differences between **10** and **15** made it attractive to investigate the effect of temperature on the photochemistry of these two ketones. If the dominant effect of increased temperature is on the rate of ring inversion rather than on the rates of hydrogen transfer (or any of the other steps involved), it should be possible by raising the temperature of photolysis to cause more inversion of **24a** to **25a** prior to disproportionation and therefore formation from **15** of more aldehyde and less ketene. If an increased rate of inversion were the only effect of temperature, there should be less corresponding change in aldehyde-ketene ratio from **10** insofar as **10** is already reacting about equally from both conformers **24b** and **25b**. Temperature effects on multi-step processes are necessarily complex, so that product yield data here can be only suggestive.[25] In any event the data given in Table II are in line with the above possibility. While the total yield of the two products from both **10** and **15** remains approximately constant from 0 to 80 °C, the ratio of aldehyde to ketene (as methyl ester) increases. The small temperature effect found with **10** may signal additional complexities, but the fact that the relative amount of aldehyde increases considerably faster with temperature for **15** than for **10** does suggest that increasing the rate of chair-chair inversion is significant for the photochemistry of **15**. These considerations concerning chair-chair inversion rates thus provide an attractive rationale for the various differences found between the photochemistry of **10** and that of **15**; appropriate tests of the assumptions made here will require detailed and quantitative investigations of the processes involved.

We direct attention now to two minor points. As noted above, the cyclohexyl radical center in **2** is expected to be effectively planar. Substitution at this center should not influence the conformational equilibrium between **2a** and **2e**, and thus **16** with its derived species **27** and **28** should behave like **10**, **24b**, and **25b**. Photolysis of **16** under the standard conditions leads to comparable amounts of aldehyde and ketene and thus bears



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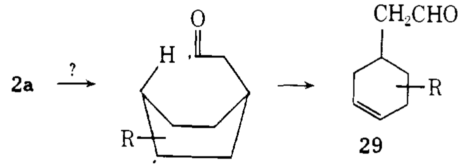


2b

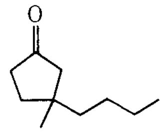
29

30, R = H

out this prediction.

In principle, **2a** could also invert to the boat conformer **2b**, which could lead to the substituted 3-cyclohexeneacetaldehyde **29**. None of the reactions summarized in Table I gave evidence for significant formation of this third product. In the case of ketone **7** the appropriate compound, **30**,[26] was on hand, and as little as 2.5% of it would have been detected.[27]

Preparative Experiments. We have previously given details of the synthesis of most of these bicyclooctanones and have also discussed their 220-MHz NMR spectra.[29] The parent compound **7** was prepared following one[30] of the several published procedures, and the preparation of **8** will be described in a future publication concerning this compound in another connection. The remaining substrate, dimethyl-substituted ketone **6**, was available by the following photochemical route. Treatment of 3-butyl-3-methylcyclopentanone (**31**)[31] with palladium (II) chloride and chloranil at 110 °C for 3 days in acetic acid-dioxane containing hydrochloric acid led to smooth oxidation and furnished the corresponding cyclopentenone **32**. We found this method,[32a] which is grounded in earlier observations of others,[32b] to be superior in both yield and convenience to the bromination-dehydrobromination procedure used earlier in similar situations.[29d,33] In analogy with earlier work,[29d] photoisomerization of **32** in benzene (λ >3400 Å) then led to hydrogen transfer and subsequent reaction of presumed biradical intermediate **33** to form three olefins **34–36** and a bicyclic ketone. Structures of the three unsaturated compounds were apparent from their spectroscopic properties, and hydrogenation of the trans olefin **34** led to **31**. Collapse of **33** could lead to two diastereomeric bicyclooctanones differing only in stereochemistry at C(4), as shown in **37**, but only a single isomer was obtained as a minor product from the irradiation. The structure and stereochemistry of this ketone are rigorously established as **6** by its photochemical transformation (Table I) into ester **38**, rather than the diastereomeric ester **39**. Authentic samples[13] of both **38** and **39** were on hand for comparison.



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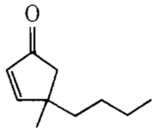

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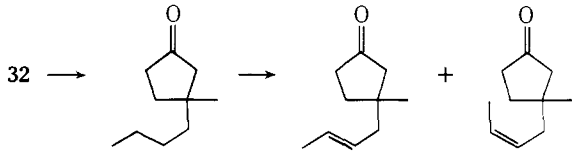

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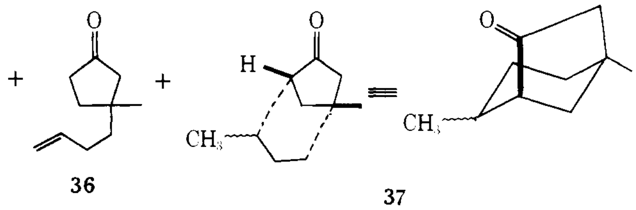

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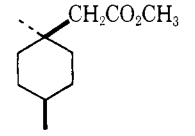
Table II. Effect of Temperature on Products from **10** and **15**

	Ratio of yields, aldehyde:methyl ester			
Ketone	0 °C	30 °C	55 °C	80 °C
10	0.67	0.86	1.0	1.2
15	0.051	0.091	0.24	0.38

The cis and trans isomers of 3-methoxycyclohexaneacetic acid methyl ester (**40a** and **41a**) were prepared to provide authentic comparison samples. The corresponding cyclohexanecarboxylic acids **40b** and **41b** were synthesized as previously described[34] and homologated using the Arndt-Eistert synthesis.[13] The cis acyl chloride **40c** was prepared at 0 °C and handled at room temperature or below to avoid intervention of the cyclic methoxonium ion,[34] but otherwise these transformations require no comment.



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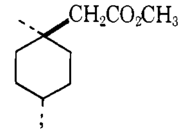

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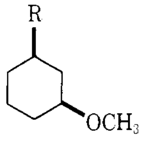

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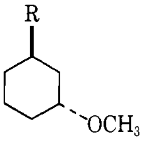
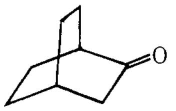


41

a, R = $CH_2CO_2CH_3$
b, R = COOH
c, R = COCl

These experiments demonstrate that conformational effects in the cyclohexane ring of biradical **2** play an important role in the photochemical α-cleavage reaction of bicyclo[3.2.1]-octan-6-ones (**1**). The lifetime and energy content of **2** appear to permit the application of ground-state conformational principles. Depending on the position of the conformational equilibrium between **2a** and **2b**, these effects may completely determine the course of disproportionation, or alternatively they may share control with the steric and electronic factors already recognized as significant determinants in this reaction. This conformational control is the result of a temperature dependent competition between rates of disproportionation and conformational change. The significance of such control in other photochemical reactions or other ring systems at a specific temperature, therefore, cannot be taken for granted.[35] Our results suggest, however, that such effects should be observable in other systems, particularly if the reaction can be examined over a sufficiently wide range of temperature.



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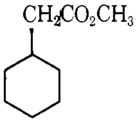

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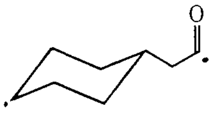

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Experimental Section

Materials and Equipment. All VPC was carried out using a Varian Aerograph Model A-90-P3 gas chromatograph with one of the following columns: A, 10 ft × 3/8 in., 30% DEGS; B, 48 ft × 1/4 in., 25% PDEAS; C, 25 ft × 1/4 in., 25% QF-1; D, 25 ft × 1/4 in., 25% DEGS; E, 50 ft × 1/4 in., 30% Carbowax 20M; F, 10 ft × 3/8 in., 25% Carbowax 1500. All columns were prepared using 45/60 Chromosorb W in aluminum tubing. Column oven temperatures are indicated and helium carrier gas flow rates varied between 90 and 135 ml/min. Ir spectra were obtained for CCl_4 solutions on a Perkin-Elmer Model 237B spectrophotometer. Most of the NMR spectra were obtained for CCl_4 solutions containing tetramethylsilane on a Varian HR-220 (220 MHz) spectrometer operating in continuous wave mode at a sweep width of 1000 Hz. A few spectra were recorded on this instrument operating in Fourier transform mode (FT) with a sweep width of 2500 Hz or on a Varian T-60A (60 MHz) spectrometer; the exceptions are noted. Mass spectra were obtained on a du Pont 21-492 double-focusing mass spectrometer with a resolution of 10^4, and the results were processed with an AEI DS-30 data system. Boiling points are uncorrected; all products were obtained as colorless oils.

General Procedure for Photolysis of Ketones 5–16. Unless otherwise indicated all preparative photochemical experiments were carried out on ~3.5% (v/v) methanolic benzene solutions of the ketone (1–2 mg/ml) contained in a toroidal Pyrex glass vessel (capacity ~70 ml) with a Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well containing a cylindrical Pyrex glass filter. The entire apparatus was immersed in a constant temperature bath adjusted to 30 ± 0.5 °C. The solutions were degassed by bubbling N_2 for 20–30 min and were maintained under a positive N_2 atmosphere during the irradiation. The photolyses were monitored by VPC, and preparative runs were terminated when either little starting material remained or extensive destruction of a photoproduct by secondary photolysis was observed. Most of the solvent was removed by careful distillation through a Vigreux column, and the products were isolated by preparative VPC. Yields were determined by calibrated VPC at low conversion and are based on converted starting material. In the case of analytical experiments in which the temperature was varied, the concentration of methanol was increased to 4% and that of the ketone to 4 mg/ml.

Photolysis of 1-*tert*-Butylbicyclo[3.2.1]octan-6-one (5). Irradiation of **5** was monitored by VPC on column A (185 °C) and afforded as the sole product 1-*tert*-butylcyclohexaneacetic acid methyl ester (96%): ir 2960 (s), 2895 (m), 1737 (s), 1427 (m), 1390 (w), 1367 (m), 1225 (m), 1180 (s), 1153 (s), 1140 (s), 1120 (s), 1012 (w), 867 (w) cm^{-1}; NMR δ 3.56 (s, 3 H), 2.34 (s, 2 H), 1.77–1.00 (br m, 10 H), 0.85 (s, 9 H).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.40; H, 11.42.

Photolysis of 1,*endo*-4-Dimethylbicyclo[3.2.1]octan-6-one (6). Photolysis of **6** in the manner described above was followed by VPC analysis on column C (178 °C) and gave as the only product 1,*c*-4-dimethyl-*r*-1-cyclohexaneacetic acid methyl ester (96%). This product had VPC retention time and ir spectrum identical with those of authentic ester **38**[13] and readily distinguishable from those of the authentic diastereomeric ester **39**.[13]

Photolysis of Bicyclo[3.2.1]octan-6-one (7). Irradiation of ketone **7** was followed by VPC on column A (145 °C). The sole product was collected and identified as 2-cyclohexene-1-acetaldehyde (93%): ir 3055 (w), 2960 (m), 2895 (w), 2870 (w), 2742 (w), 1728 (s), 1442 (w), 702 (w) cm^{-1}; NMR δ 9.70 (dd, J = ~0.5, 1 Hz, 1 H), 5.66 (m, 1 H), 5.47 (dd, J = 10, 2 Hz, 1 H), 2.65 (br m, 1 H), 2.35 (m, 2 H), 2.05–1.15 (m, 6 H); mass spectrum *m/e* 124.0814 (M^+, calcd for $C_8H_{12}O$, 124.0888); 2,4-dinitrophenylhydrazone mp 98.5–99 °C (lit. mp 99.5–100.5 °C[36]).

An upper limit of 0.5% for ester formed in this reaction was set using an authentic sample of cyclohexaneacetic acid methyl ester.

Photolysis of 1,*endo*-3-Dimethylbicyclo[3.2.1]octan-6-one (8). Photolysis of **8** was monitored by analysis on column C (178 °C) and yielded exclusively 1,*c*-5-dimethylcyclohex-2-ene-*r*-1-acetaldehyde (96%) identified on the basis of the transformations described below and the following data; ir 3012 (m), 2955 (s), 2907 (s), 2865 (m), 2840 (m), 2735 (w), 1725 (s), 1450 (m), 980 (w), 867 (w), 710 (m) cm^{-1}; NMR δ 9.66 (t, J = 3 Hz, 1 H), 5.64 (ddd, J = 10, 6, 2 Hz, 1 H), 5.48 (br d, J = 10 Hz, 1 H), 2.25 (dd, J = 15, 3 Hz, 1 H), 2.15 (dd, J = 15, 3 Hz, 1 H), 2.11–1.12 (br m, 5 H), 1.10 (s, 3 H), 0.96 (d, J = 6.5 Hz, 3 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.79; H, 10.69.

The structure assigned to this product was substantiated by transforming the unsaturated aldehyde to one of the two possible 1,3-dimethylcyclohexaneacetic acid methyl esters by hydrogenation in MeOH with 5% Pd/C catalysis to the saturated aldehyde, Jones oxidation, and esterification with diazomethane. This ester had an identical ir spectrum and VPC retention time with previously described 1,*c*-3-dimethyl-*r*-1-cyclohexaneacetic acid methyl ester.[29c]

Photolysis of *endo*-3-Methoxybicyclo[3.2.1]octan-6-one (9). Irradiation of **9** by the general procedure was monitored by VPC analysis on column A (165 °C) which indicated the formation of one compound; this was collected and identified as *cis*-5-methoxycyclohex-2-ene-1-acetaldehyde (85%): ir 3055 (m), 3010 (m), 2950 (s), 2845 (m), 2740 (m), 1729 (s), 1445 (m), 1370 (m), 1177 (m), 1100 (s), 972 (m), 710 (w) cm^{-1}; NMR δ 9.70 (t, J = ~1 Hz, 1 H), 5.57 (m, 1 H), 5.38 (m, 1 H), 3.37 (m, 1 H), 3.28 (s, 3 H), 2.77 (br s, 1 H), 2.48–2.27 (m, 3 H), 2.11 (m, 1 H), 1.87 (m, 1 H), 1.11 (ddd, J = 12, 11, 10.5 Hz, 1 H); mass spectrum *m/e* 154.0939 (M^+, calcd for $C_9H_{14}O_2$, 154.0993).

An upper limit of 0.5% yield of the ester formed in this reaction was set by means of standard solutions of authentic *cis*-3-methoxycyclohexaneacetic acid methyl ester (**40a**).

Photolysis of 1-Methylbicyclo[3.2.1]octan-6-one (10). Irradiation of **10** following the general procedure afforded two products as indicated by VPC analysis on column C. The first eluted photoproduct was identified as 1-methyl-2-cyclohexene-1-acetaldehyde[37] (44%); ir 2998 (m), 2925 (s), 2850 (m), 2835 (m), 2710 (m), 1723 (s), 1455 (m), 1370 (w), 720 (w) cm^{-1}; NMR 9.94 (t, J = 3 Hz, 1 H), 5.75 (ddd, J = 10, 3.5, 3.5 Hz, 1 H), 5.62 (br d, J = 10 Hz, 1 H), 2.29 (dd, J = 15, 3 Hz, 1 H), 2.22 (dd, J = 15, 3 Hz, 1 H), 1.97 (m, 2 H), 1.72–1.45 (m, 4 H), 1.11 (s, 3 H); mass spectrum *m/e* 138.1055 (M^+, calcd for $C_9H_{14}O$, 138.1045). The second photoproduct was identified as 1-methylcyclohexaneacetic acid methyl ester (51%) by comparison of its ir spectrum with that of an authentic sample.[13]

Photolysis of *exo*-3-*tert*-Butylbicyclo[3.2.1]octan-6-one (11). According to the general procedure, irradiation of **11** was followed by VPC analysis on column D (178 °C); the formation of two components was observed. The first, major component proved to be a mixture of ester and aldehyde dimethyl acetal. The ester was purified by basic hydrolysis, extraction of neutral material, acidification, and reesterification with diazomethane; this material was identified as *trans*-3-*tert*-butylcyclohexaneacetic acid methyl ester (51%) by comparison of its ir spectrum and VPC retention time with those of an authentic sample.[13]

The minor photoproduct was identified as *trans*-5-*tert*-butylcyclohex-2-ene-1-acetaldehyde (20%): ir 3050 (w), 2990 (s), 2895 (m), 2735 (w), 1728 (s), 1472 (w), 1365 (m), 690 (w) cm^{-1}; NMR (FT) δ 9.70 (s, 1 H), 5.67 (dd, J = 10, 5 Hz, 1 H), 5.56 (br d, J = 10 Hz, 1 H), 2.77 (br s, 1 H), 2.40 (m, 2 H), 2.08–1.11 (m, 5 H), 0.86 (s, 9 H); mass spectrum *m/e* 180.1508 (M^+, calcd for $C_{12}H_{20}O$, 180.1514).

Photolysis of *exo*-2-*tert*-Butylbicyclo[3.2.1]octan-6-one (12). Photolysis of **12** according to the general method proved to be impractical since 90 h were required for ~75% destruction of starting material. In another run only 50% conversion was achieved after 110 h. Convenient reaction times of ~25 h could be obtained without the Pyrex filter. VPC analysis on column D (170 °C) indicated the formation of three products; the first component was *endo*-6-*tert*-butyl-2-oxabicyclo[3.3.1]non-3-ene (**20**) (8%): ir 3055 (w), 2940 (s), 2865 (m), 1635 (s), 1368 (m), 1235 (s), 1090 (m), 1070 (m), 1030 (m), 972 (w), 890 (w) cm^{-1}; NMR (60 MHz) δ 6.37 (d, J = 6 Hz, 1 H), 4.52 (dd, J = 6, 6 Hz, 1 H), 4.18 (br s, 1 H), 2.44 (br s, 1 H), 2.18–1.00 (br m, 7 H), 0.87 (s, 9 H), mass spectrum *m/e* 180.1512 (M^+, calcd for $C_{12}H_{20}O$, 180.1514).

The second component was *cis*-2-*tert*-butylcyclohexaneacetic acid methyl ester (18%) which was partially contaminated with the dimethyl acetal of the aldehyde. Purification was achieved in the same manner as for the ester derived from **11**: ir 2920 (s), 2850 (m), 1740 (s), 1450 (m), 1430 (m), 1363 (m), 1283 (m), 1157 (s) cm^{-1}; NMR δ 3.59 (s, 3 H), 2.48–2.32 (m, 3 H), 1.87–1.07 (br m, 9 H), 0.91 (s, 9 H).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.42; H, 11.49.

The third component was identified as *cis*-6-*tert*-butylcyclohex-2-ene-1-acetaldehyde (17%): ir 3010 (w), 2950 (s), 2860 (m), 2705 (w), 1727 (s), 1467 (w), 1362 (m), 702 (w) cm^{-1}; NMR (FT) δ 9.75 (t, J = ~1 Hz, 1 H), 5.71 (m, 1 H), 5.59 (br, d, J = 10 Hz, 1 M), 2.92–1.29 (m, 8 H), 0.95 (s, 9 H); mass spectrum m/e 180.1512 (M^+ calcd for $C_{12}H_{20}O$, 180.1514).

Photolysis of *exo*-3-Methylbicyclo[3.2.1]octan-6-one (13). Photolysis of **13** was monitored by VPC analysis on column C (137 °C). The major photoproduct was *trans*-5-methylcyclohex-2-ene-1-acetaldehyde (68%): ir 3005 (w), 2945 (m), 2900 (s), 2812 (w), 2705 (w), 1726 (s), 1450 (w), 705 (w) cm^{-1}; NMR (60 MHz) δ 9.75 (t, J = 1.5 Hz, 1 H), 5.76–5.28 (m, 2 H), 2.73 (br s, 1 H), 2.47–1.18 (m, 7 H), 0.95 (d, J = 6 Hz, 3 H); mass spectrum 138.1045 (M^+, calcd for $C_9H_{14}O$, 138.1044).

The second component was *trans*-3-methylcyclohexaneacetic acid methyl ester (6%), which was identified by comparison of its NMR spectrum and VPC retention time with those of an authentic sample.[13]

Photolysis of *exo*-3-Methoxybicyclo[3.2.1]octan-6-one (14). Irradiation of **14** under the standard conditions yielded two photoproducts observed by VPC analysis on column E (170 °C). The first component, having a retention time identical with that of independently synthesized *trans*-3-methoxycyclohexaneacetic acid methyl ester, could not be isolated due to its low yield (2.5%). The second component was identified as *trans*-5-methoxycyclohex-2-ene-1-acetaldehyde (72%): ir 3060 (m), 2955 (s), 2850 (s), 2740 (m), 1727 (s), 1355 (w), 1107 (s), 1090 (s), 700 (w) cm^{-1}; NMR δ 9.70 (t, J = 2 Hz, 1 H), 5.48 (m, 2 H), 3.45 (m, 1 H), 3.27 (s, 3 H), 2.84 (m, 1 H), 2.42 (ddd, J = 16, 7, 2 Hz, 1 H), 2.32 (ddd, J = 16, 8, 2 Hz, 1 H), 2.27–1.79 (br m, 3 H), 1.43 (ddd, J = 14, 8, 3 Hz, 1 H); mass spectrum m/e 154.0991 (M^+, calcd for $C_9H_{14}O_2$, 154.0993).

Photolysis of 1,4,4-Trimethylbicyclo[3.2.1]octan-6-one (15). Irradiation of **15** was monitored by VPC analysis on column D (152 °C). The first component was identified as 1,4,4-trimethylcyclohex-2-ene-1-acetaldehyde (8%): ir 2995 (w), 2950 (s), 2920 (s), 2855 (m), 2805 (w), 2715 (w), 1726 (s), 1462 (m), 1367 (w), 1357 (w) cm^{-1}; NMR (60 MHz) δ 9.70 (t, J = 3 Hz, 1 H), 5.25 (s, 2 H), 2.23 (d, J = 3 Hz, 2 H), 1.70–1.23 (m, 4 H), 1.08 (s, 3 H), 0.97 (s, 6 H); mass spectrum m/e 166.1356 (M^+, calcd for $C_{11}H_{18}O$, 166.1357). The major photoproduct has been identified previously as 1,4,4-trimethylcyclohexaneacetic acid methyl ester (87%).[29d]

Photolysis of 1,5-Dimethylbicyclo[3.2.1]octan-6-one (16). The photolysis of **16** according to the standard conditions was followed by VPC analysis on column C. The first component (43%) was identified as 1,*t*-3-dimethyl-*r*-1-cyclohexaneacetic acid methyl ester; the second component was 1,3-dimethylcyclohex-2-eneacetaldehyde (46%). (Photolysis of **16** under different conditions has been described,[29c] but analysis of the aldehyde was not reported.)

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.75; H, 10.55.

Preparation of 4-Butyl-4-methylcyclopentenone (32). Palladium chloride (1.30 g, 7.33 mmol) was dissolved in concentrated HCl (1.0 ml) with warming. To this was added acetic acid (7.5 ml), dioxane (3.75 ml), chloranil (1.84 g), and 3-butyl-3-methylcyclopentanone[31] (1.16 g, 7.5 mmol), and the mixture was heated at 110 °C for 3 days. The reaction mixture was cooled, added to water (100 ml), and extracted (3×) with ether. The combined ethereal extracts were washed with 5% NaOH and brine and were dried over $MgSO_4$. After removal of ether in vacuo, the residue (1.442 g) was distilled bulb-to-bulb (145 °C; 20 mm) to give 1.009 g of a colorless distillate. Analytical VPC on column A (162 °C) indicated only trace amounts of saturated ketone, the product, and a compound with longer retention time. Preparative VPC gave 410 mg of **32**: ir 2955 (s), 2938 (s), 2875 (m), 1721 (s), 1585 (w), 1460 (w), 1405 (w), 1370 (w), 1355 (w), 1065 (w), 1012 (w) cm^{-1}; NMR δ 7.38 (d, J = 6 Hz, 1 H), 6.02 (d, J = 6 Hz, 1 H), 2.18 (d, J = 18 Hz, 1 H), 1.98 (d, J = 18 Hz, 1 H), 1.59–1.09 (br m, 6 H), 1.20 (s, 3 H), 0.90 (t, J = 7 Hz, 3 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.88; H, 10.45.

Photolysis of 4-Butyl-4-methylcyclopentenone (32). A solution of **32** (230 mg) in benzene (250 ml) was degassed and irradiated through a uranium glass filter (Corning No. 3320) until the enone carbonyl absorption was no longer visible by ir spectroscopy. The solvent was removed by distillation, and the residue was analyzed by VPC on column A (145 °C), which indicated a three component mixture. These were isolated and identified as the following: 1,*endo*-4-dimethylbicyclo[3.2.1]octan-6-one (**6**) (5%): ir 2955 (s), 2930 (s), 2875 (m), 1742 (s), 1450 (m), 1390 (w), 1373 (m), 1227 (w), 1157 (w), 1098 (w), 1075 (w), 1057 (w), 1008 (w), 968 (w) cm^{-1}; NMR δ 2.09 (br s, 1 H), 1.93 (dd, J = 18, 4 Hz, 1 H), 1.81 (d, J = 18 Hz, 1 H), 1.85–1.42 (br m, 7 H), 1.14 (s, 3 H), 0.93 (d, J = 7 Hz, 3 H); mass spectrum m/e 152.1199 (M^+, calcd for $C_{10}H_{16}O$, 152.1200).

3-(*trans*-2-Buten-1-yl)-3-methylcyclopentanone (**34**) (32%): ir 3027 (w), 2955 (s), 1748 (s), 1448 (m), 1400 (m), 1373 (m), 1155 (m), 957 (m) cm^{-1}; NMR δ 5.58–5.38 (m, 2 H), 2.27–1.63 (m, 11 H), 1.04 (s, 3 H); mass spectrum m/e 152.1200 (M^+, calcd for $C_{10}H_{16}O$, 152.1200).

Hydrogenation of this material with 5% Pd/C catalyst in methanol at atmospheric pressure afforded **31** which was identified by comparison of its ir spectrum and VPC retention time with those of an authentic sample.[31]

3-(*cis*-2-Buten-1-yl)-3-methylcyclopentanone (**35**) (14.5%): ir 3025 (m), 2955 (s), 2940 (s), 2875 (m), 1747 (s), 1450 (m), 1400 (m), 1374 (w), 1150 (m), 680 (w) cm^{-1}; NMR δ 5.72–5.40 (br m, 2 H), 2.25–1.45 (m, 8 H), 1.62 (br d, J = 7 Hz, 3 H), 1.07 (s, 3 H); mass spectrum m/e 152.1209 (M^+, calcd for $C_{10}H_{16}O$, 152.1200).

Detected in this third component was the presence of 3-(3-buten-1-yl)-3-methylcyclopentanone (**36**) (1%), identified on the basis of ir bands at 1637 and 895 cm^{-1} and NMR signals at δ 5.93–5.72 (m, 1 H) and 5.12–4.94 (m, 2 H).

Photolysis of Bicyclo[2.2.2]octan-2-one (42). VPC analysis on column A of the photolysate produced from overnight (~15 h) irradiation of **42** indicated the presence of three components. The first component (4%) was not collected and was presumed to be cyclohexaneacetic acid methyl ester on the basis of identical retention times with an authentic sample (established by coinjection with the crude photolysate). The second component was identified as 3-cyclohexeneacetaldehyde (41%): ir 3055 (m), 2955 (s), 2870 (m), 2740 (m), 1731 (s), 1430 (m), 632 (w) cm^{-1}; NMR δ 9.70 (t, J = 2 Hz, 1 H), 5.76–5.49 (m, 2 H), 2.33 (m, 2 H), 2.27–1.97 (m, 4 H), 1.82–1.66 (m, 2 H), 1.39–1.22 (m, 2 H), 0.88 (br t, J = 7 Hz, 1 H); mass spectrum m/e 124.0911 (M^+, calcd for $C_8H_{12}O$, 124.0887). The DNP of this material had mp 124.5–126 °C (lit. mp 125–126 °C[26]). Spectral evidence suggested that the third component was a secondary product, 7-hydroxybicyclo[4.2.0]oct-4-ene (8%): ir 3670 (m), 3600–3150 (br, s), 3050 (m), 2998 (m), 2955 (s), 2867 (m), 1637 (w), 1430 (m), 1085 (s), 1020 (m), 900 (m), 680 (m) cm^{-1}; NMR δ 5.76 (m, 2 H), 3.92 (dd, J = 6.5, 6.5 Hz, 1 H), 3.36 (br s, 1 H), 2.54 (m, 1 H), 2.44–1.30 (br m, 7 H) (additional minor resonances throughout the spectrum suggested that this component is a mixture of epimers); mass spectrum m/e 124.0900 (M^+, calcd for $C_8H_{12}O$, 124.0887).

Preparation of *cis*- and *trans*-3-Methoxycyclohexaneacetic Acid Methyl Esters. To a benzene solution (10 ml) of a mixture of *cis*- and *trans*-3-methoxycyclohexanecarboxylic acids[34] (2.237 g, 14.1 mmol), cooled to 0 °C and protected from moisture, was added oxalyl chloride (6 ml). The ice bath was removed, and the reaction was allowed to warm to room temperature over a period of 0.75 h. Ir analysis indicated little remaining acid, and the solvent and excess reagent were removed in vacuo at 20 °C. Without further purification, the acid chloride was homologated according to previously described procedures.[13] Bulb-to-bulb distillation of the Wolff rearrangement product afforded 2.322 g (88%) of a colorless oil. VPC analysis on column B (170 °C) indicated two components in the ratio of ~1:10; these were collected and identified as the following:

trans-3-Methoxycyclohexaneacetic acid methyl ester: ir 2962 (s), 2845 (w), 1745 (s), 1430 (m), 1187 (m), 1150 (m), 1077 (s) cm^{-1}; NMR δ 3.58 (s, 3 H), 3.39 (m, 1 H), 3.21 (s, 3 H), 2.18–0.82 (br m, 11 H).

Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.40; H, 9.78.

cis-3-Methoxycyclohexaneacetic acid methyl ester: ir 2960 (s), 2890 (m), 2848 (w), 1742 (s), 1442 (m), 1428 (m), 1155 (s), 1087 (s) cm^{-1}; NMR δ 3.60 (s, 3 H), 3.24 (s, 3 H), 3.03 (m, 1 H), 2.16 (d, J = 7 Hz, 2 H), 2.00 (br s, 1 H), 1.86–0.75 (br m, 8 H).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.56; H, 9.55.

Because of the unfavorable ratio of products, it was more convenient to prepare the trans isomer from pure *trans*-3-methoxycyclohexanecarboxylic acid obtained as described by Noyce[34] and using the same Arndt–Eistert procedure.[13]

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References and Notes

(1) Recent pertinent reviews include P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971); L. Salem and C. Rowland, *Angew. Chem.*, **84**, 86 (1972) and *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); R. G. Bergman in "Free Radicals", J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 5; R. Kh. Freidlina and A. B. Terent'ev, *Usp. Khim.*, **43**, 294 (1974) and *Russ. Chem. Rev.* (*Engl. Transl.*) **43**, 129 (1974); W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975).

(2) A portion of this investigation has been reported in preliminary form: W. C. Agosta and S. Wolff, *J. Am. Chem. Soc.*, **97**, 456 (1975).

(3) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970); N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Acc. Chem. Res.*, **5**, 92 (1972).

(4) G. L. Closs and C. E. Doubleday, *J. Am. Chem. Soc.*, **94**, 9248 (1972); **95**, 2735 (1973); R. Kaptein, R. Freeman, and H. D. W. Hill, *Chem. Phys. Lett.*, **26**, 104 (1974); B. Blank, A. Henne, and H. Fischer, *Helv. Chim. Acta*, **57**, 920 (1974), and references cited therein; W. B. Moniz and C. F. Poranski, Jr., *J. Am. Chem. Soc.*, **97**, 3258 (1975).

(5) Two generally accepted conclusions are incorporated here. These are that cyclohexyl radical behaves conformationally like cyclohexane or cyclohexanone and that the radical center itself is effectively planar or nearly so. These points are discussed by F. R. Jensen, L. H. Gale, and J. E. Rodgers, *J. Am. Chem. Soc.*, **90**, 5793 (1968), and references cited therein; A. Rassat, *Pure Appl. Chem.*, **25**, 623 (1971); L. Kaplan in "Free Radicals", J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 18; W. C. Danen, T. J. Tipton, and D. G. Saunders, *J. Am. Chem. Soc.*, **93**, 5186 (1971).

(6) G. Quinkert, A. Moschel, and G. Buhr, *Chem. Ber.*, **98**, 2742 (1965); P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968); P. J. Wagner and R. W. Spoerke, *J. Am. Chem. Soc.*, **91**, 4437 (1969); W. C. Agosta and W. L. Schreiber, *ibid.*, **93**, 3947 (1971); J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop, and J. D. Coyle, *ibid.*, **93**, 7213 (1971); J. D. Coyle, *J. Chem. Soc. B*, 1736 (1971); A. G. Fallis, *Can. J. Chem.*, **53**, 1657 (1975).

(7) N. C. Yang and R. H.-K. Chen, *J. Am. Chem. Soc.*, **93**, 530 (1971).

(8) In their interesting analysis of the photochemistry of certain 1-hydrindanones and 1-decalones, Yang and Chen (ref 7) made the explicit assumption that "most photochemical processes are faster than ring inversion in cyclohexane". No other specific consideration of this problem has come to our attention, and the present study involves inversion of substituted cyclohexyl radicals rather than substituted cyclohexanes.

(9) Full details and spectroscopic data are recorded in the Experimental Section.

(10) It is plausible that the rates of disproportionation from **2a** and **2e** be similar, but there is no expectation that they are identical.

(11) For examples of formation of enol ethers from oxycarbenes, see W. C. Agosta and D. K. Herron, *J. Am. Chem. Soc.*, **90**, 7025 (1968), and A. M. Foster and W. C. Agosta, *ibid.*, **94**, 5777 (1972).

(12) A thorough review of this point and other aspects of the ring expansion of cyclic ketones through such carbenes is given by P. Yates and R. O. Loutfy, *Acc. Chem. Res.*, **8**, 209 (1975); see also P. Yates and J. C. L. Tam, *Chem. Commun.*, 737 (1975).

(13) A parallel example of geminal substitution at C(1) controlling the behavior of a two-carbon side chain is seen in the thermal decomposition of the cyclohexyl diazo ketones used to prepare several of the bicyclooctanones under discussion here. For details, see W. C. Agosta and S. Wolff, *J. Org. Chem.*, **40**, 1027 (1975). Our results with **5**, **11**, and **12** do not eliminate the possibility that a stereoelectronic effect may also be operative here, and indeed we have recently obtained evidence implicating such an effect in the disproportionation of biradical **2**: W. C. Agosta and S. Wolff, *J. Am. Chem. Soc.*, in press.

(14) In calculating this energy difference we take the accepted[15,16] $-\Delta G^\circ_x$ (*A* value) for methoxyl (0.5 kcal/mol) and assume that $-\Delta G^\circ_x$ for the acyl side chain is equivalent to that of methyl or ethyl (1.7 or 1.8 kcal/mol, respectively[16,17]). These values overestimate the interactions in both **22** and **23**, where one 1,3-diaxial interaction is lacking because of the radical center. The situation resembles that leading to the 3-alkylketone effect[18] or that influencing the conformational behavior of 5-alkyl-1,3-dioxanes,[19] and a reduction in magnitude of each $-\Delta G^\circ_x$ by approximately one-third is required.[20] This gives then as the estimated energy difference $\sim(2/3)\cdot(1.75 - 0.5)$ or ~ 0.85 kcal/mol.

(15) E. L. Eliel and E. C. Gilbert, *J. Am. Chem. Soc.*, **91**, 5487 (1969).

(16) F. R. Jensen and C. H. Bushweller, *Adv. Alicyclic Chem.*, **3**, 139 (1971).

(17) J. A. Hirsch in "Topics in Stereochemistry", Vol. 1, N. L. Allinger and E. L. Eliel, Ed., New York, N.Y., 1967, p 199.

(18) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Wiley, New York, N.Y., 1965, Chapter 2, and references cited therein.

(19) E. L. Eliel and M. C. Knoeber, *J. Am. Chem. Soc.*, **90**, 3444 (1968).

(20) J. B. Hendrickson, *J. Am. Chem. Soc.*, **84**, 3355 (1962); E. L. Eliel, *Acc. Chem. Res.*, **3**, 1 (1970).

(21) At 30 °C a $-\Delta G^\circ$ of 0.85 kcal/mol yields an equilibrium constant of **4**.1.

(22) $\Delta G^\ddagger$ for inversion of **26a** and **26b** are reported to be $\sim$11.7 and 10.6 kcal/mol by NMR measurements: H. Friebolin, H. G. Schmid, S. Kabuss, and W. Faisst, *Org. Magn. Reson.*, **1**, 147 (1969). [See also in this regard R. W. Murray and M. L. Kaplan, *Tetrahedron*, **23**, 1575 (1967).] Only 1,1,4,4-tetrasubstitution was found to cause a substantial increase over the barrier of cyclohexane itself (10.5 kcal/mol). At 30 °C **26b** inverts about five times as fast as **26a**.

(23) It seems reasonable that substituent effects on inversion of cyclohexyl radicals should be qualitatively similar to those observed in cyclohexanes, but we are unaware of any direct information on this point. Caution is encouraged by the fact that the reported barrier for chair–chair inversion of cyclohexyl radical ($\sim$5 kcal/mol in solid cyclohexane[24]) is so much lower than the inversion barrier of cyclohexane itself (see ref *22*).

(24) N. Ya. Buben, Yu. N. Molin, A. I. Pristupa, and V. N. Shamshev, *Dokl. Akad. Nauk SSSR*, **152**, 352 (1963); S. Ogawa and R. W. Fessenden, *J. Chem. Phys.*, **41**, 994 (1964).

(25) Temperature effects on the photochemistry of cyclopentanones and cyclohexanones are discussed by J. D. Coyle, *J. Chem. Soc., Perkin Trans. 2*, 683 (1972).

(26) M. Schwartz, A. Besold, and E. R. Nelson, *J. Org. Chem.*, **30**, 2425 (1965).

(27) It is clear that quantitative data will be necessary for a thorough understanding of the results in Tables I and II. In the absence of such detailed information concerning rates and energetics we can offer only brief speculation about one additional matter. The well-known reasoning embodied in the Curtin–Hammett principle[28] requires that, in certain reacting systems consisting of two interconverting conformers, each of which leads to a different product, the distribution of these products depend only on the difference in the transition-state energies associated with the products and not on the relative populations of the ground-state conformational isomers undergoing reaction. By virtue of assumptions made in its derivation, application of this principle is quite specifically limited to systems in which the barrier to conformational interconversion is negligible relative to the activation energies of the processes leading to products. The results in Table I indicate an important role for conformational effects in these disproportionations, and thus it is experimentally established that the Curtin–Hammett principle does not apply here. The simplest plausible explanation for this fact is that the precondition for application of the principle is not met; that is, it seems likely that the barrier between **2a** and **2e** is sufficiently similar in magnitude to the activation energies for disproportionation that this inversion barrier may not be neglected.

(28) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, pp 149–156, and references cited therein.

(29) (a) **5**, **10–13**: ref 13; (b) NMR spectra and **9**, **14**: W. C. Agosta and S. Wolff, *J. Org. Chem.*, **40**, 1665 (1975); (c) **16**: S. Wolff and W. C. Agosta, *ibid.*, **38**, 1694 (1973); (d) **15**: S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Am. Chem. Soc.*, **94**, 7797 (1972), wherein the photolysis of **15** is originally described under other conditions.

(30) K. B. Wiberg and B. A. Hess, Jr., *J. Org. Chem.*, **31**, 2250 (1960).

(31) W. C. Agosta and S. Wolff, *J. Org. Chem.*, **40**, 1699 (1975).

(32) (a) S. Wolff and W. C. Agosta, *Synthesis*, 240 (1976); (b) R. J. Theissen, *J. Org. Chem.*, **36**, 752 (1971); B. Bierling, K. Kirschke, H. Oberender, and M. Schulz, *J. Prakt. Chem.*, **314**, 170 (1972).

(33) E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965); W. C. Agosta and A. B. Smith, III, *J. Am. Chem. Soc.*, **93**, 5513 (1971).

(34) D. S. Noyce and H. I. Weingarten, *J. Am. Chem. Soc.*, **79**, 3093 (1957).

(35) For example, under our conditions bicyclo[2.2.2]octanone (**42**) yields as the volatile primary products aldehyde **30** and ester **43**. Neither of these can arise from the stable chair conformation **44** of the biradical. [For other recent studies of the photochemistry of **42**, see W. B. Hammond and T. S. Yeung, *Tetrahedron Lett.*, 1173 (1975), and references therein.]

(36) D. L. Garin, *J. Org. Chem.*, **34**, 2355 (1969).

(37) A. W. Burgstahler and I. C. Nordin, *J. Am. Chem. Soc.*, **83**, 198 (1961).