

alkylation with dimethyl sulfate, analogous to previously reported syntheses⁵¹ and was fully characterized by spectral properties (uv, ir, and nmr). These compounds were stored over P₄O₁₀ *in vacuo*. The lanthanide-shift reagent used in this study was europium(III) tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione, which was stored over P₄O₁₀ *in vacuo*. Tetramethylsilane was used as an internal reference for all measurements. The solvent employed for all samples was molecular-sieve dried CCl₄.

The runs were performed in the following manner. The concen-

(51) R. Adams and A. W. Schrecker, *J. Amer. Chem. Soc.*, **71**, 1186 (1949); J. E. Eldridge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

tration of the substrate was kept constant and only the lanthanide shift reagent concentration varied. The initial sample was prepared in a clean, oven-dried nmr tube by first putting in 0.3 g of Eu(fod)₃ and the appropriate amount of substrate, so that after the addition of CCl₄ and TMS, the concentration of the substrate was at the desired value. Since the correctness of the substrate concentration is crucial, a solution approximately 0.5 M in substrate was added to the tube (its exact amount determined gravimetrically) rather than the pure substrate. Successive samples were then prepared by adding aliquots of a substrate stock solution (usually 0.15 M in CCl₄ with 4% TMS) of the same concentration of substrate as in the initial sample.

The Photochemistry of 3-Alkylidenecyclohexanones. The Role of Olefin Geometrical Isomerization in the Triplet-State Reactivity of β,γ -Unsaturated Ketones¹

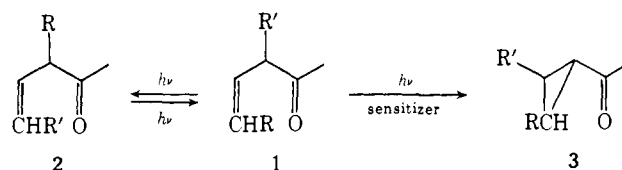
Kenneth G. Hancock* and Ronald O. Grider

Contribution from the Department of Chemistry, University of California at Davis, Davis, California 95616. Received July 31, 1973

Abstract: The photochemical reactions of 3-methylene-2,2,5,5-tetramethylcyclohexanone (**4**), 3-ethylidene-2,2,5,5-tetramethylcyclohexanone (**5**), and their photoproducts have been investigated. Direct irradiation of **4** produces a singlet-state 50:50 photoequilibrium of **4** and 3,3-dimethyl-5-isopropylidenecyclohexanone (**9**). Direct irradiation of (*Z*)-3-ethylidene-2,2,5,5-tetramethylcyclohexanone (**5-(Z)**) produces a 68:32 singlet-state photoequilibrium of (*E*)-3-ethylidene-2,2,5,5-tetramethylcyclohexanone (**5-(E)**) and 3-isopropylidene-2,5,5-trimethylcyclohexanone (**14**). Quantum yields were 0.13, 0.18, 0.20, and 0.30 for reactions **4** → **9**, **9** → **4**, **5** → **14**, and **14** → **5**, respectively. No direct singlet-state isomerization of **5-(Z)** to **5-(E)** was observed. The stereospecificity of the **14** → **5-(E)** isomerization is discussed in terms of intimate diradical and/or concerted mechanisms for the 1,3-acyl shifts. The triplet state of **4** is unreactive although it was shown to accept triplet energy from acetophenone. Photosensitization of **5-(Z)** causes isomerization to a triplet-state 1:4 photoequilibrium of **5-(Z)** and **5-(E)**, with a zero-conversion quantum yield of 0.53. The $\pi-\pi^*$ configuration of the triplet state was demonstrated by phosphorescence. The contrast between the triplet reactivity of **5** and isostructural units in steroids is discussed in terms of the relative energetics of cis-trans isomerization *vs.* the 1,2-acyl shift.

A particularly intricate structure-reactivity relationship apparently characterizes the photochemistry of β,γ -unsaturated ketones.^{4,5} From the welter of diverse reactions that have been reported, the dominant pattern to emerge has been that of a general reaction dichotomy separating singlet-state and triplet-state processes. In this generalization singlet excited states of β,γ -unsaturated ketones most typically undergo a reversible photochemical 1,3-acyl shift to isomeric β,γ -unsaturated ketones (**1** ⇌ **2**). In contrast, triplet excited states generated by photosensitization typically rearrange *via* a 1,2-acyl shift to cyclopropyl ketones (**1** → **3**, the oxa-di- π -methane rearrangement).^{6,7}

There are for both singlets and triplets, however, a



number of photoreactions which are more or less competitive with the 1,3- and 1,2-acyl shifts, depending on subtle structural features of the β,γ -unsaturated ketones in ways which are currently more enigmatic.^{4,5} For example, although mechanistic details of these processes are only now emerging, both decarbonylation^{8,9} and γ -hydrogen abstraction^{5,10,11} are competitors to the singlet-state 1,3-acyl shift. Triplet-state β,γ -unsat-

(1) Portions of this work have appeared in preliminary communications.^{2,3}

(2) K. G. Hancock and R. O. Grider, *Tetrahedron Lett.*, 4281 (1971).

(3) K. G. Hancock and R. O. Grider, *Tetrahedron Lett.*, 1367 (1972).

(4) In the absence of a detailed review, a recent compendium of references to the varied photochemical reactions of β,γ -unsaturated ketones is given by K. N. Houk, D. J. Northington, and R. E. Duke, Jr., *J. Amer. Chem. Soc.*, **94**, 6233 (1972).

(5) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 9252 (1972).

(6) W. G. Dauben, M. S. Kellogg, J. I. Seeman, and W. A. Spitzer, *J. Amer. Chem. Soc.*, **92**, 1786 (1970).

(7) (a) R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 3957 (1971); R. S. Givens and W. F. Oettle, *ibid.*, **93**, 3963 (1971).

(8) (a) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966); (b) D. I. Schuster, F.-T. Lee, A. Padwa, and P. G. Gassman, *ibid.*, **30**, 2262 (1965); (c) N. C. Yang and D. M. Thap, *Tetrahedron Lett.*, 3671 (1966).

(9) Note, however, that P. S. Engel and H. Ziffer [*Tetrahedron Lett.*, 5181 (1969)] report quenching of decarbonylation in bicyclo[4.3.0]-non-1(6)-en-8-one by piperylene.

(10) J. C. Dalton and H.-F. Chan, *J. Amer. Chem. Soc.*, **95**, 4085 (1973).

(11) Other examples include: (a) ref 8c; (b) E. F. Kiefer and D. A. Carlson, *Tetrahedron Lett.*, 1617 (1967); (c) T. Matsui, A. Komatsu, and T. Moroe, *Bull. Chem. Soc. Jap.*, **40**, 2204 (1967); (d) R. C. Cookson, J. Hudec, G. E. Usher, and A. Szabo, *Tetrahedron*, **24**, 4353 (1968); (e) R. C. Cookson and N. R. Rogers, *J. Chem. Soc., Chem. Commun.*, 809 (1972).

urated ketones have been implicated not only in the oxa-di- π -methane rearrangement, but also in cycloadditions¹² and photoreductions.^{9,12a} Cis-trans photoisomerization about the olefinic portion of β,γ -unsaturated ketones has also been reported occasionally,¹³ but the mechanistic relevance of olefin torsion to the general structure-reactivity profile has not been elucidated previously. This paper describes the photochemistry of several 3-alkylidenecyclohexanones, a group of β,γ -unsaturated ketones whose reactions shed some light on the roles of the C=C bond and geometrical isomerization in guiding triplet-state reactivity.

At the outset of our work, the existence of the singlet-triplet 1,3- vs. 1,2-acyl shift dichotomy was apparent, but the structural features of reactants which governed their behavior were less than obvious. Acyclic, monocyclic, and bicyclic β,γ -unsaturated ketones underwent both 1,3- and/or 1,2-acyl shifts under a variety of experimental circumstances, unlike the analogous 1,4-dienes whose singlet-triplet reactivity differences had been linked to the cyclic or acyclic character of the reactant.¹⁴ *A priori*, the photochemistry of β,γ -unsaturated ketones would be expected to differ somewhat from that of 1,4-dienes, but the geometric factors which are responsible for the reaction partitioning in di- π -methanes might have been expected to manifest themselves in a similar manner in the photochemical transformations of β,γ -unsaturated ketones.

One structural feature which did seem common to most β,γ -unsaturated ketones for which oxa-di- π -methane rearrangements had been reported was structural rigidity about the olefinic portion of the β,γ -unsaturated ketone chromophore.^{6,15} Accordingly, we chose a set of β,γ -unsaturated ketones incorporating the olefinic portion of the chromophore as an exocyclic double bond, both to complement previous studies of cyclic and acyclic systems and to probe the structure-reactivity relationship of 3-en-1-ones with a different, superficially intermediate, olefin geometry. The 3-alkylidenecyclohexanones were attractive as (a) being relatively readily available; (b) exhibiting a well-defined and rather rigid carbonyl-olefin orientation different from most previously scrutinized systems; and (c) potentially allowing an analysis of the effect of olefinic geometry on β,γ -unsaturated ketone reactivity, particularly when viewed as the simplest models for an isostructural unit in certain steroids.

Results

Synthesis of 3-Alkylidenecyclohexanones. Both to facilitate comparison to previously studied steroids¹⁶

(12) (a) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966); (b) A. Shani, *Tetrahedron Lett.*, 569 (1972); (c) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 4357 (1972).

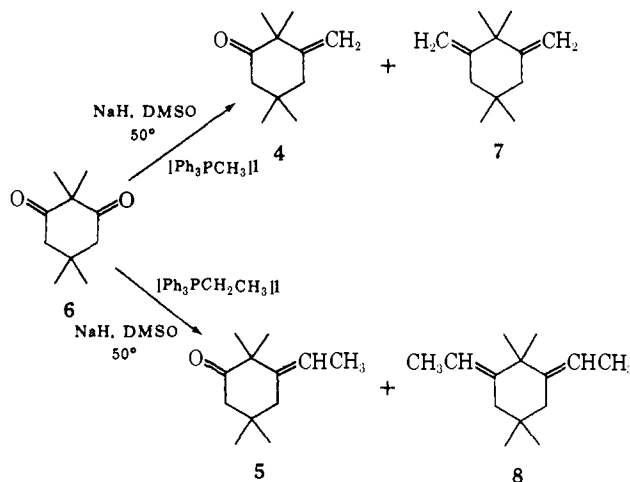
(13) (a) H. Morrison, *Tetrahedron Lett.*, 3653 (1964); (b) D. O. Cowan and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 1153 (1971); (c) K. Takeda, I. Horibe, and H. Minato, *Chem. Commun.*, 87 (1971).

(14) (a) J. S. Swenton, A. R. Crumrine, and T. J. Walker, *J. Amer. Chem. Soc.*, **92**, 1406 (1970); (b) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 1407, 1409 (1970); (c) H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970); (d) H. E. Zimmerman and A. A. Baum, *ibid.*, **93**, 3646 (1971), and references therein.

(15) The one exception (ref 6) is presumably the reflection of conjugation of the olefin unit with a phenyl group.

(16) (a) N. Furutachi, Y. Nakadaira, and K. Nakanishi, *J. Amer. Chem. Soc.*, **91**, 1028 (1969); (b) N. Furutachi, J. Hayashi, H. Sato, and K. Nakanishi, *Tetrahedron Lett.*, 1061 (1972); (c) J. R. Williams and H. Ziffer, *Chem. Commun.*, 469 (1967); (d) *Tetrahedron*, **24**, 6725 (1968); (e) K. Kojima, K. Sakai and K. Tanabe, *Tetrahedron Lett.*,

and to minimize the possibility of isomerizations to α,β -unsaturated systems, α,α -dimethylation was employed. Thus, 3-methylene-2,2,5,5-tetramethylcyclohexanone (**4**) was chosen as the simplest readily preparable model. Later, 3-ethylidene-2,2,5,5-tetramethylcyclohexanone (**5**) was prepared to allow assessment of olefin torsion effects. Both could be readily synthesized from 2,2,5,5-tetramethylcyclohexane-1,3-dione (**6**), which in turn was made from commercial dimedone by the method of Halsall and Thomas.¹⁷



Synthesis of **4** was accomplished by reaction of **6** at 50° in DMSO under nitrogen with the Wittig reagent from methyltriphenylphosphonium iodide¹⁸ and dimethylsodium.¹⁹ The use of dimethylsodium proved synthetically superior to the use of phenyllithium. Yields of *ca.* 50% of **4** were achieved using an ylide/diketone ratio of 1.4:1.0,²⁰ but the reaction inherently also produced 1,3-dimethylene-2,2,5,5-tetramethylcyclohexane (**7**)²¹ as a side product which was separated from **4** by preparative gas chromatography. Similarly, reaction of **6** with ethylenetriphenylphosphorane gave *ca.* 55% yields of ethylidene ketone **5**, with 1,3-diethylidene-2,2,5,5-tetramethylcyclohexane (**8**, isomer mixture) as the major by-product. Analysis of ethylidene ketone **5** by 100-MHz nmr spectroscopy showed it to be a mixture of *syn* (**5-Z**) and *anti* (**5-E**) isomers in an 85:15 ratio. Although the *Z* and *E* isomer mixture could not be resolved, even on a 500 ft \times 0.03 in. SF96 capillary glpc column,²² unequivocal structural assignment was possible by 100-MHz nmr. The chemical shifts (*cf.* Figure 1)²³ and coupling constants (*cf.* Experimental Section) are wholly compatible with known deshielding

1925 (1969); (f) S. Domb, G. Buzzato, J. A. Saboz, and K. Schaffner, *Helv. Chim. Acta*, **52**, 2436 (1969); (g) S. Domb and K. Schaffner, *ibid.*, **53**, 677 (1970); (h) K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Lett.*, 3399 (1969); (i) H. Sato, N. Furutachi, and K. Nakanishi, *J. Amer. Chem. Soc.*, **94**, 2150 (1972); (j) H. Sato, K. Nakanishi, J. Hayashi, and Y. Nakadaira, *Tetrahedron*, **29**, 275 (1973).

(17) T. G. Halsall and D. B. Thomas, *J. Chem. Soc.*, 2438 (1956).

(18) G. Wittig and U. Schoellkopf, *Org. Syn.*, **40**, 66 (1960).

(19) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(20) This is the optimum reagent ratio for maximizing the yield of **4**.

(21) The photochemistry of 1,3-dimethylene-2,2,5,5-tetramethylcyclohexane (**7**) has been the subject of a separate investigation: K. G. Hancock and R. O. Grider, unpublished observations.

(22) The expert technical advice of Professor R. E. Kepner in attempted glpc separations is gratefully acknowledged.

(23) Assignments for the acyclic methylenes in **4**, **5-Z**, and **5-E** were verified by D-for-H exchange at the α carbon (C-6), using sodium methoxide in MeOD, followed by quenching with D₂O and extraction into carbon tetrachloride (for nmr) or benzene (for photolysis); *cf.* Experimental Section.

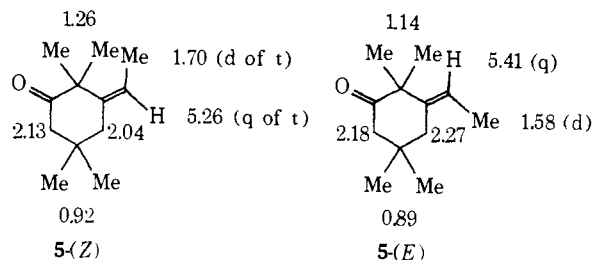
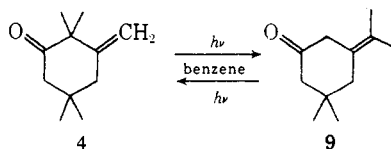


Figure 1. Nmr chemical shifts for 5-(Z) and 5-(E) relative to $(\text{CH}_3)_4\text{Si}$ on the δ scale (CCl_4 solvent).

effects of proximal methyls,^{3,24} more pronounced allylic coupling in cisoid arrangements,²⁵ and stronger homoallylic coupling in transoid configurations.²⁶ Infrared, uv, and mass spectra, and elemental analysis (*cf.* Experimental Section) were also in accord with the structures assigned as 4, 5-(Z), and 5-(E).

Direct Irradiations. In a typical preparative experiment, *ca.* 5% solutions of methylene ketone 4 in deoxygenated²⁷ benzene (alternatively, dioxane) were irradiated with a corex-filtered^{28,29} mercury arc lamp. Periodic nmr and glpc examinations of the photolysis mixture showed the formation of a single photoproduct, which leveled off at a photostationary value of 50%, with 50% of 4 remaining unreacted. Extended irradiation had no effect, and the photolysate remained clear and colorless.

Early glpc separation attempts on several columns at temperatures above 90° gave two overlapping product peaks in addition to starting material 4. The ratio of the two products was temperature dependent with higher temperatures favoring thermal decomposition of the primary photoproduct to another compound of slightly longer retention time. However, by glpc at 65° (1.5 ft \times 0.375 in. butanediol succinate) or below, the thermal reaction was completely suppressed, and isolation of the photoproduct was facile.



On the basis of ozonolysis to dimedone and acetone, the photoproduct was identified as 3,3-dimethyl-5-isopropylidene-cyclohexanone (9), a structure also compati-

(24) J. C. Nouls, G. Van Binst, and R. H. Martin, *Tetrahedron Lett.*, 4065 (1967).

(25) See, for example, R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967.

(26) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 316 ff.

(27) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948). However, elimination of nitrogen purging was without effect on the photolysis results.

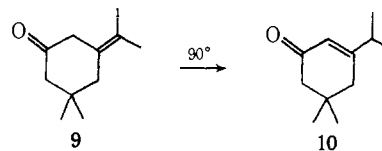
(28) Although Pyrex filtering was also occasionally employed, with a resulting increase required in irradiation time, the corex filter was particularly advantageous due to the near coincidence at 260–265 nm of the onset of the absorption spectrum of corex and the $\pi-\pi^*$ band of the 3-alkylidene-cyclohexanones.

(29) The opacity of the corex filter below 260 nm was verified in view of recent reports to the contrary.³⁰ With different irradiation times, use of RUL-3000 Å lamps (Southern New England Ultraviolet Co.) gave comparable results.

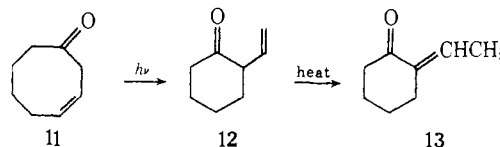
(30) H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **95**, 3246 (1973), quoting H. Morrison's unpublished observations.

ble with the ir, nmr, uv, and mass spectra (*cf.* Experimental Section).^{2,31,32}

At temperatures below 70°, 9 was thermally stable; however, isomerization was rapid (complete for 100 mg in 3 hr at 90°) at higher temperatures. The isomerization product was identified by its spectral properties (*cf.* Experimental Section)³⁴ as 5,5-dimethyl-3-isopropylcyclohex-2-en-1-one (10).



Such thermal isomerization of a β,γ -unsaturated ketone is well preceded. Crandall, *et al.*, encountered a similar situation in isolating 2-vinylcyclohexanone (12) from direct irradiation of cyclooct-3-en-1-one (11).³⁵ Separation of 12 from a reaction mixture by glpc resulted in isomerization to a mixture of the syn and anti isomers of 2-ethylidenecyclohexanone (13).



The photoisomerization of 4 to 9 was shown to be readily reversible. Irradiation of 5% solutions of 9 in benzene under the same conditions used in photolysis of 4 produced 4 as the sole product. A photostationary state of 50:50 4:9 was again reached upon continued irradiations. In addition, a small, steadily increasing amount of 10 was observed after prolonged irradiation due to thermal reorganization of 9.

Direct irradiations of 5 (as the 85:15 Z:E isomer mixture) were also carried out in deoxygenated²⁷ benzene solutions, with periodic monitoring by nmr and glpc. As with 4, photolysis of 5 gave a single photoproduct whose concentration eventually reached a photostationary value of 32% (68% 5), and which was not affected by prolonged irradiation. Separation of the photoproduct was effected by preparative glpc (3 ft \times 0.25 in. butanediol succinate) at 65°; no thermal isomerization of either 5 or the photoproduct was noted in handling or separation.

The spectra of the photoproduct (ir, nmr, uv, and mass spectra; *cf.* Experimental Section) together with ozonolysis to acetone and 2,5,5-trimethyl-1,3-cyclohex-

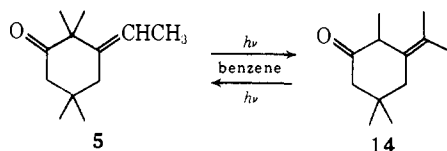
(31) Assignment of the δ 2.13 and 2.28 nmr resonances to the acyclic and allylic methylenes, respectively (*cf.* Experimental Section), was corroborated by irradiation of 4-6,6-*d*₂,²³ which gave 9 in which the δ 2.13 resonance was missing. These values are in correction of the reversed assignment made by us earlier² on reasonable chemical expectations,^{25,26} but without the benefit of isotopic labeling.

(32) Interestingly, unambiguous distinction between acyclic (C-6) and allylic (C-4)³³ methylene protons in the 3-alkylidene-cyclohexanone nmr spectra was not possible by chemical shift data alone,^{25,26,31} since shifts for these protons were susceptible to subtle structural changes. Although base-catalyzed D-for-H exchange was quite unequivocal, assignment of resonances in the absence of isotopic labeling can also be made on the basis of peak widths at half-height. Resonances for the allylic (C-4)³³ protons were invariably broader by *ca.* 50% because of homoallylic coupling.

(33) The numbering system used here is that of 4, 5, and 14 in which the carbonyl is C-1; for simplicity in this digression the carbonyl carbon of 9 is also taken as C-1.

(34) N. F. Firrell and P. W. Hickmott, *J. Chem. Soc. C*, 716 (1970).

(35) J. K. Crandall, J. P. Arrington, and J. Hen, *J. Amer. Chem. Soc.*, **89**, 6208 (1967).



anedione¹⁷ conclusively identified it as 3-isopropylidene-2,5,5-trimethylcyclohexanone (**14**).

As is usual with β,γ -unsaturated ketones, the 5-to-14 photoisomerization was found to be reversible. Irradiation of a 10% solution of **14** in benzene with a corex-filtered 450-W mercury lamp showed, by periodic nmr and glpc examination, a steady increase in the concentration of **5** until, after *ca.* 45 hr,³⁶ a photostationary state of 68:32 **5**:**14** was reached. Extended irradiation caused no change in the net ratio of **5**/**14**. However, the ethylidene ketone **5** formed in photolysis of **14** was almost exclusively the *E* isomer **5-(E)**, as determined by integration of methyl resonances in the nmr spectrum. Similarly, when a 15:85 *E*:*Z* isomer mixture of **5** was irradiated, production of **14** was accompanied by a gradual change in the ratio of the geometric isomers **5-(E)** and **5-(Z)** in recovered **5**. From the initial 15:85 *E*:*Z* ratio, the relative proportions changed to *ca.* 50:50 **5-(E)**:**5-(Z)** near the time when the **5**/**14** photoisomer ratio stabilized, and eventually to $\geq 99:1$ *E*:*Z* ratio upon very long irradiation (*cf.* Figure 2).

Photosensitized Irradiations. Although the weight of chemical precedent^{4,7} strongly implied that the direct irradiation $4 \rightleftharpoons 9$ and $5 \rightleftharpoons 14$ interconversions were singlet-state photoreactions, photosensitization experiments were carried out both to ascertain the multiplicity of the direct photolysis rearrangements and to probe any separate and distinct triplet-state photochemistry.

However, irradiation of benzene solutions of **4** containing sufficient added sensitizer (xanthone, acetophenone, benzophenone) to absorb *ca.* 99% of incident light caused no detectable photoreaction, even after irradiation periods 25 times longer than those required for the direct irradiation conversion of **4** to a stationary state mixture of **4** and **9**. In view of the apparent inertness of **4** to photosensitized reaction, it was necessary to determine whether the cause was a genuinely unreactive triplet state or merely an instance of ineffectual energy transfer.

First, it was observed that, relative to a control sample, methylene ketone **4** did not appreciably (<5%) quench the photoreduction of benzophenone with benzhydrol in benzene at 300 nm,³⁷⁻³⁹ thus demonstrating that indeed benzophenone ($E_T = 287$ kJ/mol⁴⁰) was incapable of effective triplet photosensitization of **4**. On the other hand, the photoreduction of acetophenone ($E_T = 308$ kJ/mol^{40,41}) in isopropyl alcohol showed a dramatic (94%) quenching, relative to a control sample,

(36) The protracted irradiation periods required here are reflections of greatly reduced efficiency in light capture during microscale (nmr tube) irradiations.

(37) J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Amer. Chem. Soc.*, **81**, 1068 (1959).

(38) (a) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961); (b) G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2795 (1961).

(39) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **85**, 528 (1963).

(40) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(41) V. L. Ermolaev, *Usp. Fiz. Nauk*, **80**, 3 (1963).

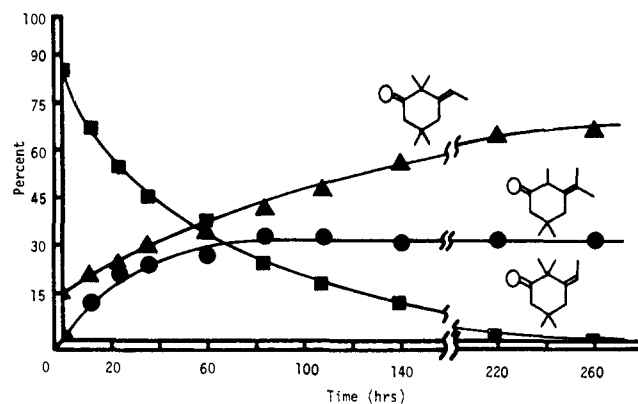
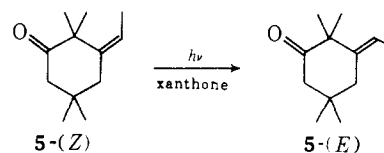


Figure 2. Comparison of approaches to photochemical stationary-state ratios from 15:85 **5-(E)**:**5-(Z)** to the **5**-**14** mixture of 1,3-shift isomers and the **5-(E)**-**5-(Z)** mixture of geometrical isomers. Compounds **5-(E)**, **5-(Z)**, and **14** are represented by \blacktriangle , \blacksquare , and \bullet , respectively.

by addition of **4** (0.05 *M*), demonstrating that energy transfer from acetophenone to **4** was very efficient. Additionally, the phosphorescence of acetophenone in ethanol glass at 77°K was quenched by added **4**. A linear Stern-Volmer relationship between Φ_0/Φ_Q for phosphorescence and the concentration of **4** was noted with a $k_q\tau$ value of $6.4 M^{-1}$. Energy transfer to **4** from acetophenone, but not benzophenone, brackets the energy of **4**'s unreactive triplet between 287 and 308 kJ/mol. Independent determination of the triplet energy of **4** was provided by its phosphorescence spectrum in ethanol glass at 77°K, which had a 0-0 band at 405 nm, corresponding to 295 kJ/mol.^{42,43}

Similar quenching of acetophenone photoreduction and phosphorescence by **5** (isomer mixture) was observed. The $k_q\tau$ value from the linear Stern-Volmer plot of Φ_0/Φ_Q vs. concentration of **5** was $65 M^{-1}$, indicative of efficient energy transfer from acetophenone to **5**. Unlike methylene ketone **4**, however, the ethylidene ketone **5** was not inert when photosensitized.

When a solution of **5** (15:85 *E*:*Z*) in benzene containing sufficient xanthone to absorb >98% of incident light was irradiated at 350 nm, nmr analysis indicated that cis-trans isomerization was occurring. The concentration of anti isomer **5-(E)** steadily increased at the expense of **5-(Z)** to an approximately stationary value of 78% **5-(E)** and 22% **5-(Z)**.



That geometrical isomerization was the sole triplet-sensitized reaction of **5** was confirmed by ozonolysis of the photolysate (after removal of volatiles from xanthone by distillation) and hydrogen peroxide work-up to yield only 2,2,5,5-tetramethylcyclohexane-1,3-dione (**6**)¹⁷

(42) K. G. Hancock and R. O. Grider, *J. Chem. Soc., Chem. Commun.*, 580 (1972).

(43) Although the phosphorescence spectra observed for **4** and **5** are believed authentic, the nonobservation of phosphorescence in three β,γ -unsaturated ketones studied by Engel and Schexnayder⁹ presents a disquieting contrast. Although the structures and reactivity of **4** and **5** differ considerably from the behavior reported by Engel and Schexnayder, the differing emissive properties are being examined in detail.

and acetic acid, the former in stoichiometric isolated amounts.

In addition to xanthone ($E_T = 310$ kJ/mol^{40,41}), acetophenone, benzophenone, thioxanthone ($E_T = 274$ kJ/mol⁴⁰), anthraquinone ($E_T = 261$ kJ/mol^{40,41}), and phenanthrene ($E_T = 259$ kJ/mol^{40,41,44}) all effected net isomerization of **5**-(Z) to **5**-(E). The efficiency of sensitization (as reflected by conversion times), however, decreased with decreasing triplet energy of the sensitizer. Michler's ketone ($E_T = 255$ kJ/mol^{40,45}), 2-acetonaphthone ($E_T = 248$ kJ/mol⁴⁰), and 1-acetonaphthone ($E_T = 236$ kJ/mol^{40,45}) failed to sensitize the isomerization of **5**-(Z) to **5**-(E). In an attempt to determine the spectroscopic triplet energy, phosphorescence spectra of the 15:85 **5**-(E):**5**-(Z) isomer mixture were recorded in ethanol and isopentane glasses. From the rather diffuse spectra, 0-0 band estimates of 418 nm (ethanol) and 412 nm (isopentane) were made, corresponding to triplet energies of 286 and 290 kJ/mol, respectively.

Quantum Yields. Quantum efficiencies for the $4 \rightleftharpoons 9$ and $5 \rightleftharpoons 14$ rearrangements and for the **5**-(Z) \rightarrow **5**-(E) isomerization are recorded in Table I. Potassium fer-

Table I. Quantum Yields for Photoproduct Appearance^a

Photo-reaction	Φ_{direct}^b	$\Phi_{\text{sensitized}}^c$	Φ_{quenched}^d
4 \rightarrow 9	0.13 ^{e,f}	0.00	0.13 ^e
9 \rightarrow 4	0.18 ^e	0.00	0.18 ^e
5 \rightarrow 14	0.20; ^{g,h} 0.40 ⁱ	0.00	0.20 ^g
14 \rightarrow 5	0.30 ^g	0.00	0.30 ^g
5 -(Z) \rightarrow 5 -(E)	0.04; ^j 0.00 ^k	0.26; ^j 0.53 ^k	

^a Quantum yields for reactant disappearance were within 5% of product appearance quantum yields. ^b In benzene at 35° and 300–320 nm. ^c In benzene with 0.19 M xanthone at 35°, 350 nm. ^d In benzene with 2.6 M piperylene at 35°, 300–320 nm. ^e Apparent quantum yield at 11% conversion by glpc. ^f Reference 2. ^g Apparent quantum yield at 16% conversion by glpc. ^h Reference 3. ⁱ By extrapolation of nmr–glpc determinations to zero conversion, $\pm 15\%$ estimated uncertainty. ^j Apparent quantum yield at 25% conversion by nmr. ^k By extrapolation of yields determined by nmr to zero conversion.

rioxalate actinometry was employed,⁴⁶ and was checked by uranyl oxalate actinometry.⁴⁷

The quantum yields for the $4 \rightleftharpoons 9$ and $5 \rightleftharpoons 14$ 1,3-shift interconversions by direct irradiation fall in a relatively narrow range of 0.13–0.30 mol/einstein at 11–16% conversions. Such quantum efficiencies are indicative of synthetically useful processes. Extrapolation from a series of determinations for direct irradiation of **5** to zero conversion gave a somewhat higher value, 0.40. The quantum efficiencies in direct irradiations were undiminished by addition of 2.6 M piperylene; under photosensitization by 0.19 M xanthone, quantum yields for the $4 \rightleftharpoons 9$ and $5 \rightleftharpoons 14$ rearrangements were zero.

Under direct irradiation, conversion of **5** to **14** was accompanied by an increase in the **5**-(E):**5**-(Z) isomer ratio, for which an apparent quantum yield of 0.04 was determined at 25% conversion. A plot of quantum yield vs. per cent conversion for the direct irradiation conversion of **5**-(Z) to **5**-(E) had a maximum Φ of ca.

(44) D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

(45) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).

(46) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(47) W. G. Leighton and G. S. Forbes, *J. Amer. Chem. Soc.*, **52**, 3139 (1930).

0.06 at ca. 35% **5**-(E), and extrapolated to $\Phi = 0$ at both high and zero mole fractions of **5**-(E).

In contrast, irradiation of benzene solutions of **5**-(Z) (containing 15% **5**-(E)), with 0.19 M xanthone absorbing $\geq 98\%$ of incident 350-nm light, caused efficient photosensitized isomerization of **5**-(Z) to **5**-(E). A quantum efficiency of 0.26 at 25% conversion was determined. Extrapolation from a series of quantum yield measurements at different **5**-(Z):**5**-(E) ratios gave a zero-conversion quantum yield of 0.53 mol/einstein. Near the photostationary **5**-(Z):**5**-(E) ratio of 22:78 observed under xanthone photosensitization conditions, the quantum yield is zero.

Discussion

Singlet-State Photochemistry. The direct-irradiation photochemical interconversions of **4** and **9** and of **5** and **14** fit the established pattern of β,γ -unsaturated ketones whose singlet excited states rearrange to isomeric β,γ -unsaturated ketones via reversible 1,3-acyl shifts.^{4,7} Singlet-state intermediacy in the $4 \rightleftharpoons 9$ and $5 \rightleftharpoons 14$ rearrangements was established by the insensitivity of the direct irradiation quantum yields to addition of piperylene (up to 2.6 M) and by the nonoccurrence of any 1,3-acyl shifts under photosensitization conditions.

Experimental values for the photostationary ratios under direct 300-nm irradiation were 50:50 for **4**:**9** and 68:32 for **5**:**14**. For both rearrangement pairs, photoequilibrium ratios predicted by eq 1 were within 2% of

$$[A]_{\lambda}/[B]_{\lambda} = \Phi_{B \rightarrow A, \lambda} \epsilon_{B, \lambda} / \Phi_{A \rightarrow B, \lambda} \epsilon_{A, \lambda} \quad (1)$$

the observed values, despite approximations implicit in the use of that equation here.⁴⁸ Close similarities of quantum yields (Table I) and uv absorption spectra (Table II) for the five ketones **4**, **5**-(E), **5**-(Z), **9**, and **14**

Table II. Exalted $n-\pi^*$ Absorptivities in 3-Alkylidenecyclohexanones

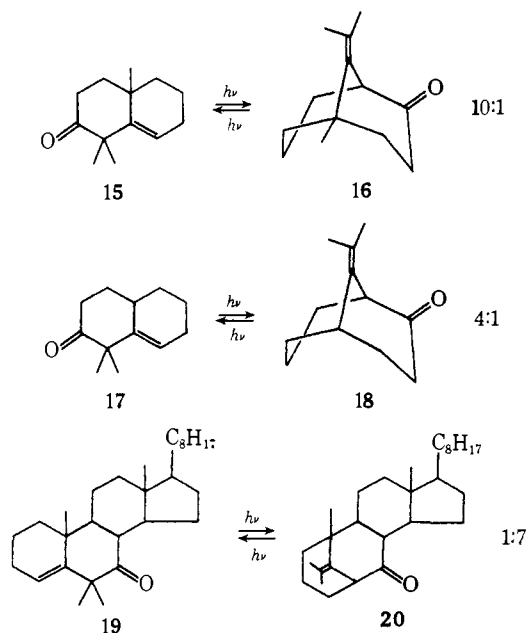
	Compound				
	4	5 -(E)	5 -(Z)	9	14
$\epsilon_{\lambda_{\text{max}}} (\text{C}_6\text{H}_{12})$	72	104	54	118	113
$\lambda_{\text{max}}, \text{nm}$	298	298	298	298	299

were to be expected considering their structural similarity. Although the 3-alkylidenecyclohexanone structural unit is present in several β,γ -unsaturated ketones studied previously,^{16,49} constraint of the olefinic moiety into another ring clearly affects the photochemistry.

Thus, 1,1,4a-trimethyl-1,3,4,4a,5,6,7-heptahydronaphthalen-2-one (**15**) and 9-isopropylidene-5-methylbicyclo[3.3.1]nonan-2-one (**16**) have been reported to give a ca. 10:1 photoequilibrium ratio (Vycor optics).^{16i,49} Similarly, ketones **17** and **18** give a ca. 4:1 photostationary state favoring the nonbridged ketone **17**,^{16i,49} but steroidal ketone **19** is the minor isomer (ca. 1:7) at photoequilibrium with **20**.¹⁶ⁱ Clearly, the ketonic pairs **15**–**16**, **17**–**18**, and **19**–**20** have lopsided photoequilibria that presumably reflect different $n-\pi^*$ absorp-

(48) Equation 1 is strictly true only under monochromatic irradiation conditions, but is a good approximation whenever the light bandwidth is narrow and when species A and B have qualitatively similar absorption spectra (i.e., no crossings). Both of these conditions are satisfied for the $4 \rightleftharpoons 9$ and $5 \rightleftharpoons 14$ interconversions.

(49) L. A. Paquette and G. V. Meehan, *J. Org. Chem.*, **34**, 450 (1969).



tivities and 1,3-shift quantum yields of bridged and non-bridged ketones, whereas the similar geometries of **4**, **5**, **9**, and **14** result in similar spectra and reactivity, and in more equitable photostationary states.

The stereoelectronic origins of enhanced $n-\pi^*$ absorptivity in β,γ -unsaturated ketones have been discussed^{4,16i,50} in terms of mixing of the carbonyl and olefin portions of the chromophore. Intensification is greatest when the carbonyl-alkene dihedral angle closes to near 90° , and is minimal when that angle of local planes is near 180° . A correlation between $n-\pi^*$ absorptivity enhancement, proclivity toward α cleavage, and the occurrence of the 1,3-acyl shift has been suggested.⁵¹ The predominance of **20** over **19** at photoequilibrium has been contrasted with the minor amounts of analogs **16** and **18** present in photostationary mixtures and explained in terms of the boat conformation forced upon **20** by the steroid geometry.¹⁶ⁱ The boat conformation spreads the olefin-carbonyl angle and reduces the $n-\pi^*$ absorptivity. Although quantum yields were not reported for ketones **15**–**20**, if it can be assumed that **19** and **20** are comparably quantum efficient, then the conformation-determined absorptivity governs the ketone distribution.

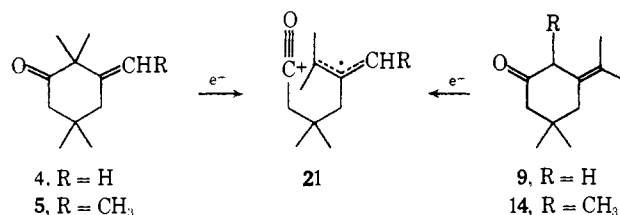
Dihedral angles of *ca.* 130° between the carbonyl and alkene local planes can be estimated for **4**, **5-(E)**, **9**, and **14** from molecular models, and are compatible with the high observed efficiencies of 1,3-acyl migration.⁵¹ The diminished $n-\pi^*$ exaltation of **5-(Z)** (Table II) is most likely the result of a ground-state conformational change to relieve repulsion of ethylidene and C-2 methyls, and which results in a spreading of the carbonyl-olefin angle (a distortion of a chair conformation toward a boat), a conformational change maximized in **20**.¹⁶ⁱ Clearly, however, the quantum yield for the 1,3-shift of **5-(Z)** is not reduced relative to similar

(50) (a) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); (b) H. Labhart and G. Wagniere, *Helv. Chim. Acta*, 42, 2219 (1959); (c) A. Moscovitz, K. Mislav, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, 84, 1945 (1962); (d) J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, p 165; (e) D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. B*, 215 (1967).

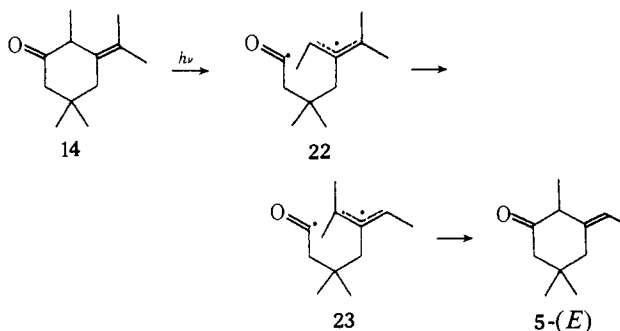
(51) J. R. Williams and G. M. Sarkisian, *Chem. Commun.*, 1564 (1971).

ketones. Thus, the partitioning of an excited singlet between α cleavage and intersystem crossing, while undoubtedly strongly influenced by geometry, is probably not always a predictable function of the carbonyl-olefin dihedral angle.

Parenthetically, it is worth noting that the different $n-\pi^*$ absorptions of ketone pairs such as **15** and **16**, involving differing amounts of ring strain, were paralleled by different behavior in the mass spectrometer.⁴⁹ In contrast, the mass spectrum of **9** was virtually identical with that of **4**, and the spectra of **5** and **14** were also indistinguishable. The obvious explanation is that α cleavage, giving rise to a single radical ion **21** from either **4** or **9** (or **5** or **14**), dominates the electron impact induced fragmentation in another indication of the effect of olefin geometry on the reactivity of 3-alkyldienecyclohexanones.



Finally, the high stereoselectivity of the **14** \rightarrow **5-(E)** 1,3-shift is to be noted; this observation is in accord with those of Nakanishi, *et al.*, on the stereospecific interconversions of methyl-deuterated **15** and **16**.¹⁶ⁱ Two equally viable explanations for the high stereoselectivity are possible. The first involves the intermediacy of intimate diradical **22** and rotamer **23**,

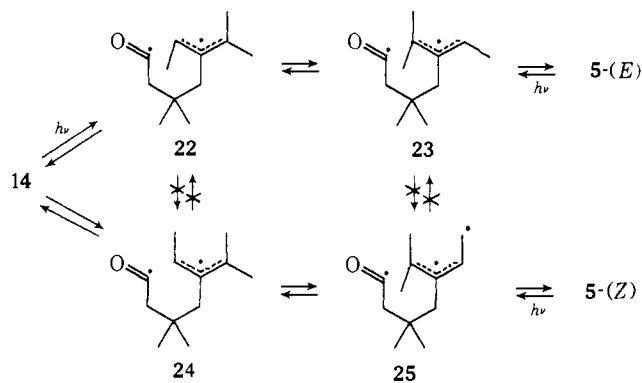


formed by Norrish type I cleavage, followed by C_3-C_4 bond rotation. The absence of **5-(Z)** in photolysates from **14** is reasonable, assuming no *cis-trans* isomerization within the allylic radical moiety.⁵² In fact, no singlet-state isomerization of **5-(Z)** to **5-(E)** (the thermodynamically favored direction) was detectable, despite one report of singlet *cis-trans* photoisomerization in the literature.⁵³ In the present case, extrapolation of quantum yields to zero conversion left little doubt that the only singlet-state route effecting net conversion of **5-(Z)** to **5-(E)** was two consecutive 1,3-acyl shifts; *i.e.*, **5-(Z)** \rightarrow **14** \rightarrow **5-(E)**. Thus, the stereochemical integrity of diradicals such as **22**, **23**, **24**, and **25** appears to be preserved.

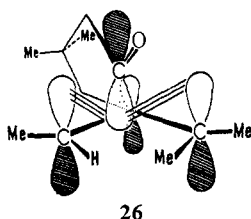
The alternative explanation is a concerted, suprafacial 1,3-sigmatropic shift of the acyl group ($\sigma_2 + \pi_2$), an orbital symmetry-allowed excited-state re-

(52) Configurational stability of *cis-* and *trans-*butenyl radicals in solution at 40° has been established.⁵³

(53) C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, 83, 3877 (1961).

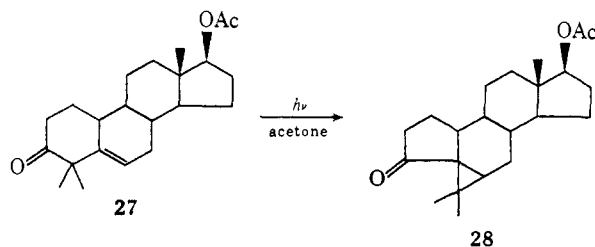


organization.⁵⁴ The only evidence which might favor a concerted rearrangement through a transition state such as **26** rather than the diradical mechanism is the absence of potential diradical byproducts. Thus, no aldehyde or decarbonylation products were noted despite their occurrence elsewhere,^{6,8,16,35} particularly in structurally similar systems.¹⁶¹



In either view of the 1,3-shift, both the high stereoselectivity (**14** → **5-(E)** only) and the order of quantum yields (**14** → **5** more efficient than **5** → **14**; **9** → **4** more efficient than **4** → **9**) suggest that acyl migration across the molecular face less encumbered with methyl groups is preferred.

The Role of the Triplet State. The typical triplet-state reactivity of steroidal ketones and other previously studied systems containing the 3-alkylidenecyclohexanone unit¹⁶ has been photosensitized conversion to cyclopropyl ketones, the oxa-di- π -methane reaction.^{6,7} A case in point is the acetone-sensitized rearrangement of 17 β -acetoxy-4,4-dimethyl-19-norandrost-5-en-3-one (**27**) to the cyclopropyl ketone derivative **28**.^{16e} In con-



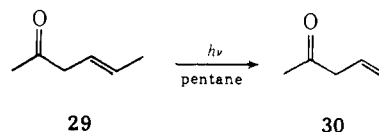
trast, methylene ketone **4** was totally inert under triplet photosensitization, even when it was demonstrated that triplet energy transfer to **4** did occur. Thus, **4** quenched the photoreduction of acetophenone (and the phosphorescence at 77°K), but showed no observable reaction.

The apparent inertness of **4**, of course, is understandable in light of the triplet-state reactivity of ethylidene ketone **5**. Xanthone sensitization of **5-(Z)** solutions resulted exclusively in *cis-trans* photoisomerization about the exocyclic olefin bond, producing **5-(E)**. The

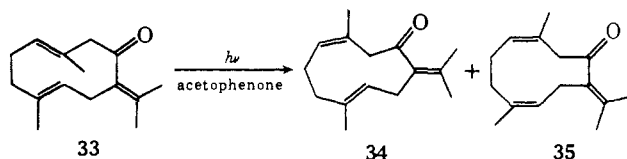
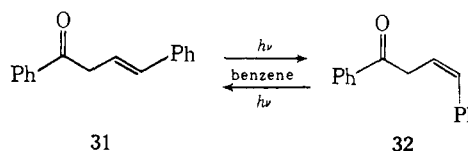
(54) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

steady-state ratio of **5-(E)**:**5-(Z)** under photosensitization was *ca.* 4:1, in contrast to the *ca.* 100:1 ratio eventually produced by direct irradiation through the intermediacy of **14**. In sensitized irradiations total depletion of **5-(Z)** was never observed, nor was any conversion to **14** or to cyclopropyl ketones.

Prior to our communication,³ geometrical photoisomerization in β,γ -unsaturated ketones had been noted only rarely,¹³ and the multiplicity of the ketonic species involved had not been unequivocally ascertained.⁵⁵ Morrison had reported *trans-cis* isomerization of pent-4-en-2-one (**29** → **30**) upon direct irradiation,^{13a} but drew no mechanistic conclusions.



Cowan and Baum observed similar isomerization of *trans*-1,4-diphenylbut-3-en-1-one (**31**), determined the quantum yield to be 0.53, and advanced a scheme of mixed $n-\pi^*$ and $\pi-\pi^*$ triplets to account for the non-Stern-Volmer quenching encountered.^{13b} Minato, *et al.*, noted sensitized *trans-cis* photoisomerization of germacrone (**33**) to two isomers **34** and **35**.^{13c,56} Clearly, these isolated and varied results shed little light on the role of geometrical photoisomerization in the overall reactivity scheme of β,γ -unsaturated ketones.



The finding that sensitized, triplet-state *cis-trans* isomerization between **5-(Z)** and **5-(E)** occurs demonstrates that virtually isosteric ketones such as steroid **27** and ethylidene ketone **5** differ in their triplet-state photochemical reactivity largely because of the presence (in **27**) or lack (in **5**) of a steric constraint to geometric isomerization. When no such restraint is present, the olefinic moiety is capable of acting as a "free rotor," undergoing geometrical isomerization. The "free rotor" effect is thus a mechanism for energy dissipation from the excited triplet state, and is analogous to that encountered in di- π -methane reactions.¹⁴ When free rotation is impaired (as in **27**), the cyclopropyl ketone producing 1,2-acyl shift may be an alternate triplet reaction pathway. In the case of **5**, at least, the 0.53 quantum yield for sensitized geometrical isomerization indicates the "free-rotor" olefinic torsion is a very effective energy dissipation mechanism.⁵⁷ Quantum yields for oxa-di- π -methane reactions are generally smaller.⁵ An interesting and still open point concerns the degree

(55) More recently Engel and Schexnayder⁵ have also reported triplet-state isomerization of geometrical isomers.

(56) As a β,γ -unsaturated ketone which is also α,β -unsaturated, germacrone is of less certain pertinence to the present work.

(57) Note that the analogous isomerization in **31** also proceeded with a very high quantum efficiency.^{13b}

of constraint that must be applied to the alkene portion of a β,γ -unsaturated ketone in order for the 1,2-acyl shift to supplant geometrical isomerization.

Of considerable mechanistic interest is the difference in the triplet-state energy of **5** as measured by triplet sensitization and phosphorescence techniques. Although the spectroscopic triplet energy of **5** was shown to be *ca.* 290 kJ/mol in isopentane at 77°K, sensitizers with E_T 's as low as 260 kJ/mol (anthraquinone, phenanthrene) were capable of effecting **5**-(*Z*):**5**-(*E*) isomerization in solution at 25°.

Both the 6-nm red shift of the phosphorescence of **5** in ethanol relative to isopentane and the 156-msec mean lifetime suggest the triplet state of **5** has essentially a $\pi-\pi^*$ configuration. The recent theoretical model developed by Houk, *et al.*,⁴ is in accord with this assignment. It is thought^{58,59} that twisting the $\pi-\pi^*$ triplet state of an olefin 90° results in substantial stabilization, giving a "non-Franck-Condon" triplet *ca.* 20–40 kJ/mol below the spectroscopic state. It thus seems plausible that sensitization of **5**, at least with sensitizers of E_T less than 290 kJ/mol, may be causing nonvertical excitation to a twisted $\pi-\pi^*$ state,⁶⁰ whose E_T could be as low as 260 kJ/mol, 30 kJ/mol below the spectroscopic triplet state. The twisted triplet could be the "free-rotor" entity in sensitized isomerizations.⁶¹ By inference, similar triplet-energy dissipation mechanisms are operating invisibly for the ketones **4**, **9**, and **14** whose triplets show no visible reaction.

That the phosphorescent state of **5** at 77°K and the isomerizing triplet of **5** at room temperature are virtually the same species seems likely. Xanthone-sensitized irradiations of **5**-(*Z*) at 77°K caused no visible *cis*-*trans* isomerization; however, continued irradiation at 25° caused isomerization to proceed with normal efficiency.

Summary

In short, the singlet-state behavior of the 3-alkyldenedecyclohexanones studied fits the established pattern of stereoselective 1,3-acyl shifts. The triplet-state behavior of these systems, however, depends on the geometry of the β,γ -double bond. Where geometrical isomerization is not sterically prevented, that course appears to be the triplet-state reaction of choice, and high quantum efficiencies are noted. When steric constraint (as in steroids) precludes geometrical isomerization at reasonable energetic costs, the 1,2-acyl shift (a reaction of lower quantum efficiency) is observed.

Experimental Section

Spectra were recorded as follows: nmr on Varian A60A and/or Jeolco MH-100 instruments *vs.* internal tetramethylsilane; infrared on a Beckman IR-8 spectrophotometer; ultraviolet on a Cary 15 spectrometer; mass spectra on CEC 21-104 and Varian M-66

(58) R. S. Mulliken and C. C. J. Roothan, *Chem. Rev.*, **41**, 219 (1947).

(59) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

(60) "Nonvertical excitation" may be more properly thought of as vertical excitation from a twisted ground state to the twisted excited state.

(61) The alternative mechanistic possibility for *cis*-*trans* isomerization *via* reversible formation of a biradical intermediate from an $n-\pi^*$ ketone sensitizer and the olefin seems unlikely considering (a) the efficacy of sensitization by phenanthrene, and (b) the inability of ketone sensitizers of low triplet energies to effect isomerization.

instruments; emission on a Perkin-Elmer MPF-2A spectrophotometer. Gas chromatographic separations were performed on either Varian A90P or Hewlett-Packard 776 machines. Melting points were observed on a Mel-Temp hot block and are uncorrected. Microanalyses were done by Chemalytics, Inc., Tempe, Ariz.

3-Methylene-2,2,5,5-tetramethylcyclohexanone and 1,3-Dimethylene-2,2,5,5-tetramethylcyclohexane. To 50 ml of dimethyl sulfoxide (Mallinckrodt, dried over calcium hydride) was added 7.3 g (0.30 mol) of dry sodium hydride, prepared by washing 12.8 g of a 57% mineral oil dispersion (Ventron) with dry pentane under nitrogen.¹⁹ The mixture was heated at 80° under nitrogen until hydrogen evolution ceased (*ca.* 0.5 hr), then cooled in ice. To the green solution was added 123 g (0.304 mol) of methyltriphenylphosphonium iodide¹⁸ in 100 ml of warm dimethyl sulfoxide. The solution was stirred at 25° for 0.5 hr. To the reddish solution was then added 30.0 g (0.178 mol) of 2,2,5,5-tetramethylcyclohexane-1,3-dione¹⁷ in 50 ml of dimethyl sulfoxide. The solution was stirred 24 hr at 50°, then poured into 800 ml of water and allowed to stand 2 hr. Precipitated triphenylphosphine oxide was separated by filtration. Both solid and filtrate were washed with four 150-ml portions of ether. The combined ether extracts were washed consecutively with water (3 × 150 ml), 10% aqueous sodium hydroxide (2 × 150 ml), and water (2 × 150 ml), dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was distilled at reduced pressure through a short-path apparatus until unreacted 2,2,5,5-tetramethylcyclohexane-1,3-dione began to solidify in the condenser. The distillate was chromatographed at 140° through a 6 ft × 0.75 in. UC-W98 (10% on Chromosorb P) column, giving two major fractions of 3.3- and 4.5-min retention times.

The first fraction was distilled, bp 95° (43 mm), to give 11.0 g (38%) of clear, colorless 1,3-dimethylene-2,2,5,5-tetramethylcyclohexane: ir (CCl₄) 3100, 1630, 1460, 1435, 1380, 1360, and 890 cm⁻¹; nmr (CCl₄) δ 0.83 (s, 6 H, 5,5-dimethyl), 1.20 (s, 6 H, 2,2-dimethyl), 2.10 (s, 4 H, C=CCH₂), 4.57 (broad s, 2 H_a, vinyl H anti to 2,2-dimethyls), and 4.72 (d, 2 H_b, $J_{ab} = 2$ Hz, vinyl H syn to 2,2-dimethyls); uv (C₆H₁₂) end absorption to solvent cut-off, ϵ 7800 at 205 nm; major mass spectral peaks at *m/e* 164 (P), 149, 121, 107, 93, 41, and 15.

Anal. Calcd for C₁₂H₂₀: C, 87.73; H, 12.27. Found: C, 87.63; H, 11.99.

Distillation of the second fraction, bp 110° (43 mm), yielded 13.8 g (46%) of clear, colorless 3-methylene-2,2,5,5-tetramethylcyclohexanone: mp 24–25°; ir (CCl₄) 3100, 1710, 1635, 1460, 1380, 1370, and 900 cm⁻¹; nmr (CCl₄) δ 0.92 (s, 6 H, 5,5-dimethyl), 1.22 (s, 6 H, 2,2-dimethyl), 2.28 (s, $\Delta\nu = 2.0$ Hz, 2 H, CH₂CO), 2.37 (s, $\Delta\nu = 2.7$ Hz, 2 H_a, CH₂C=C), 4.77 (overlapping doublet of triplets, 1 H_b, $J_{bc} = 1.0$ Hz, $J_{ab} = 1.0$ Hz, vinyl H anti to 2,2-dimethyls), and 4.88 (d, 1 H_c, $J_{bc} = 1.0$ Hz, vinyl H syn to 2,2-dimethyls); uv (C₆H₁₂) absorption with vibrational fine structure at 316 nm (ϵ 27), 307 (59), 298 (72), and 289 (64); major mass spectral peaks (rel intensities) at *m/e* 167 (3.4), 166 (28, P), 151 (5), 123 (5), 110 (10), 109 (7), 95 (5), 91 (3), 84 (4), 83 (74), 82 (100), 81 (10), 79 (4), 77 (5), 69 (4), 68 (11), 67 (43), 66 (3), 65 (5), 63 (2), 57 (3), 56 (6), 55 (19), 54 (8), 53 (20), 52 (4), 51 (8), 50 (2), 43 (7), 42 (7), 41 (37), 40 (7), 39 (27), 29 (13), 28 (5), 27 (21), 15 (8).

Anal. Calcd for C₁₁H₁₈O: C, 79.46; H, 10.91. Found: C, 79.52; H, 10.95.

Confirmation of the above nmr chemical shift assignment of δ 2.28 to the acyclic methylene was verified by D-for-H exchange. Reaction of 100 mg (0.601 mmol) of 3-methylene-2,2,5,5-tetramethylcyclohexanone with 100 mg (4.35 mg-atom) of sodium in 2 ml of methanol-*d* for 30 min., followed by quenching with 5 ml of deuterium oxide and extraction into 3 ml of carbon tetrachloride, which was then concentrated, caused >95% depletion of the δ 2.28 nmr resonance.

Photolysis of 3-Methylene-2,2,5,5-tetramethylcyclohexanone. A solution of 8.0 g (48 mmol) of 3-methylene-2,2,5,5-tetramethylcyclohexanone in 220 ml of sodium-dried, redistilled benzene (or, alternatively, dioxane) was irradiated 4 hr under nitrogen in a cylindrical vessel surrounding a quartz immersion well equipped with a 450-W high-pressure mercury lamp (Hanovia) and a corex filter.^{28,29} Monitoring by nmr or glpc (*vide infra*) indicated 50% conversion to a single photoproduct. Further irradiation effected no change. Solvent was removed by rotary evaporation below 40°, and the residue was chromatographed through either a 1.5 ft × 0.375 in. SE-30 (3% on Chromosorb G-DMCS) column at 50° or a 3 ft × 0.25 in. butanediol succinate (10% on Chromosorb G-DMCS) column at 65° to afford 3.3 g (42% isolated) of starting methylene ketone (retention time 3 min, both columns) and 3.2 g (40% iso-

lated) of the photoproduct (retention times 6 and 7 min, respectively).

The photoproduct was identified as 3,3-dimethyl-5-isopropylidene-cyclohexanone, a colorless liquid: *ir* (CCl_4) 3010, 1712, 1670, 1465, 1390, and 1370 cm^{-1} ; *nmr* (CCl_4) δ 0.90 (s, 6 H, 3,3-dimethyls), 1.68 (s, 6 H, isopropylidene), 2.13 (s, $\Delta\nu = 3.5$ Hz, 2 H, $\text{CH}_2\text{C}=\text{O}$), 2.28 (s, $\Delta\nu = 2.6$ Hz, 2 H, $\text{CH}_2\text{C}=\text{C}$), and 2.97 (broad s, 2 H, $\text{C}=\text{CCH}_2\text{C}=\text{O}$); *uv* (C_6H_{12}) absorption with vibrational fine structure at 317 nm (ϵ 56), 307 (103), 298 (118), and 289 (108); mass spectrum identical with that of 3-methylene-2,2,5,5-tetramethylcyclohexanone.

Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.91. Found: C, 79.44; H, 10.97.

Photolysis of 6,6-Dideuterio-3-methylene-2,2,5,5-tetramethylcyclohexanone. Irradiation of a solution of 100 mg (0.601 mmol) of 6,6-dideuterio-3-methylene-2,2,5,5-tetramethylcyclohexanone (*vide supra*) in 3 ml of dry benzene in a Pyrex nmr tube adjacent to the 450-W mercury arc for 4 hr caused 37% conversion to the photoproduct (glpc monitoring). Following removal of benzene at reduced pressure, the residue was dissolved in carbon tetrachloride. Analysis by nmr indicated 37% conversion to 2,2-dideuterio-3,3-dimethyl-5-isopropylidene-cyclohexanone with 95% incorporation of deuterium at C-2 as evidenced by depletion of the δ 2.13 resonance.

Thermal Isomerization of 3,3-Dimethyl-5-isopropylidene-cyclohexanone. Heating 100 mg (0.601 mmol) of 3,3-dimethyl-5-isopropylidene-cyclohexanone at 90° for 3 hr caused total isomerization to 100 mg of 5,5-dimethyl-3-isopropylcyclohex-2-en-1-one, which was isolated by preparative gas chromatography on a 5 ft \times 0.25 in. SE-30 (3% on Chromosorb G-DMCS) column at 115°. A clear, colorless liquid, 5,5-dimethyl-3-isopropylcyclohex-2-en-1-one was identified by *ir* (CCl_4) absorptions at 3020, 1660, 1460, 1380, 1360, 900, 865, and 845 cm^{-1} ; *nmr* (CCl_4) resonances at δ 1.02 (s, 6 H, 3,3-dimethyls), 1.08 (d, 6 H_a, $J_{ab} = 7$ Hz, *i*-Pr methyls), 2.14 (heptet, 1 H_b, $J_{ab} = 7$ Hz, *i*-Pr methine), 2.15 (broad s, 2 H_c, $\text{C}=\text{CCH}_2$), 2.28 (broad s, 2 H, $\text{CH}_2\text{C}=\text{O}$), and 5.77 (q, overlapping d of t, 1 H_d, $J_{bd} = 1$ Hz, $J_{od} = 1$ Hz, vinyl H); *uv* (C_6H_{12}) λ_{max} at 235 nm (ϵ 14,300); and mass spectral peaks at *m/e* 166 (P), 151, 110, 95, 82, 67, 41, 27, and 15; spectra compatible with literature³⁴ values recorded under different conditions.

Ozonolysis of the Photoproduct of 3-Methylene-2,2,5,5-tetramethylcyclohexanone. To 20 ml of diethyl ether in an immersion flask equipped with a fritted glass bubbler was added a solution of 1.00 g (6.00 mmol) of 3-methylene-2,2,5,5-tetramethylcyclohexanone in 2 ml of benzene, which had been irradiated for 14 hr in a Rayonet chamber reactor equipped with RUL-3000 lamps, and analyzed by nmr spectroscopy, indicating 41% conversion to the photoproduct. The flask was cooled to 0°, and electrically generated ozone was bubbled through the solution at a rate of 0.01 lmp. After 15 min the solution was poured into 40 ml of ice-water and a white, crystalline solid precipitated. Collection afforded 0.33 g (2.35 mmol, 39%) of solid 5,5-dimethylcyclohexane-1,3-dione. Evaporation of the ethereal layer *in vacuo* yielded 0.52 g (3.40 mmol, 57%) of white solid 2,2,5,5-tetramethylcyclohexane-1,3-dione, mp 95–96° [lit.¹⁷ mp 98°]. Examination of the aqueous layer by nmr spectroscopy showed acetone was present.

Photolysis of 3,3-Dimethyl-5-isopropylidene-cyclohexanone. To 1.0 ml of benzene in a Pyrex nmr tube was added 100 mg (0.60 mmol) of 3,3-dimethyl-5-isopropylidene-cyclohexanone. The solution was irradiated in a Rayonet reactor equipped with RUL-3000 lamps for 130 hr. Examination of the photolysate by nmr and/or glpc (*vide supra*) showed formation of 3-methylene-2,2,5,5-tetramethylcyclohexanone as the sole photoproduct in a photostationary state ratio of 50:50, as measured by the integration of resonance peaks at δ 2.97 for 3,3-dimethyl-5-isopropylidene-cyclohexanone and δ 4.57, 4.72 for 3-methylene-2,2,5,5-tetramethylcyclohexanone, or by integration of glpc peak areas.

Irradiation of 3-Methylene-2,2,5,5-tetramethylcyclohexanone in the Presence of Piperylene. A solution of 530 mg (3.21 mmol) of 3-methylene-2,2,5,5-tetramethylcyclohexanone and 350 mg (5.15 mmol, 2.6 M) of piperylene in 2.0 ml of benzene was irradiated 90 hr with RUL-3000 lamps in a modified merry-go-round inside a Rayonet reactor, in parallel with a second sample, identical with the first except for the absence of piperylene. Both samples showed 45% conversion to 3,3-dimethyl-5-isopropylidene-cyclohexanone, as measured by nmr spectroscopy and glpc integration.

Attempted Triplet Sensitization of 3-Methylene-2,2,5,5-tetramethylcyclohexanone. To 0.5 ml of benzene in Pyrex nmr tubes was added 3-methylene-2,2,5,5-tetramethylcyclohexanone (50 mg, 0.30 mmol) and enough triplet sensitizer (benzophenone, acetophenone, and xanthone in separate experiments) to absorb greater than 95%

of the incident light. The solutions were irradiated for varying lengths of time with RUL-3000 lamps in a Rayonet chamber reactor equipped with a modified merry-go-round apparatus. No photoproducts were detected by nmr or glpc, even after 120 hr.

Test for Triplet Energy Transfer from Benzophenone to 3-Methylene-2,2,5,5-tetramethylcyclohexanone. In one tube, a solution of 0.831 g (4.56 mmol) of benzophenone and 0.051 g (0.28 mmol) of benzhydryl in 10 ml of benzene was prepared. In another tube identical with the first, 0.039 g (0.23 mmol) of 3-methylene-2,2,5,5-tetramethylcyclohexanone was added. Both tubes were irradiated in parallel at 300 nm in a modified merry-go-round apparatus for 2 hr. Production of benzopinacol was followed by nmr; the amount of pinacol formed in the second tube was 95% of that formed in the first, indicating little, if any, energy transfer.

Test for Triplet Energy Transfer from Acetophenone to 3-Methylene-2,2,5,5-tetramethylcyclohexanone. The procedure was essentially the same as above. Tube A contained 0.549 g (4.57 mmol) of acetophenone and 0.030 g (0.50 mmol) of isopropyl alcohol in 10 ml of benzene. Tube B was identical except that 0.086 g (0.52 mmol) of 3-methylene-2,2,5,5-tetramethylcyclohexanone was added. The tubes were irradiated at 300 nm for 10 hr. Formation of products was followed by nmr spectroscopy, indicating the amount of photoreduction product in tube B was only 6% of that produced in tube A.

3-Ethylidene-2,2,5,5-tetramethylcyclohexanone. To 100 ml of dimethyl sulfoxide (Mallinckrodt, dried over calcium hydride) was added 6.72 g (0.280 mol) of dry sodium hydride, prepared by washing 11.8 g of a 57% mineral oil dispersion (Ventron) with dry pentane under nitrogen.¹⁹ The mixture was heated at 80° under nitrogen until hydrogen evolution had ceased (*ca.* 0.5 hr), then cooled in ice. To the green solution was added 117 g (0.280 mol) of ethyltriphenylphosphonium iodide¹⁸ in 100 ml of warm dimethyl sulfoxide. The solution was stirred at 25° for 0.5 hr. To the dark red solution was then added 33.6 g (0.201 mol) of 2,2,5,5-tetramethylcyclohexane-1,3-dione¹⁷ in 100 ml of dimethyl sulfoxide. The solution was stirred 24 hr at 50°, then poured into 800 ml of water and allowed to stand 2 hr. Precipitated triphenylphosphine oxide was collected and washed with two 150-ml portions of ether. The aqueous filtrate was washed with five 150-ml portions of ether. The combined ether extracts were washed with 10% aqueous sodium hydroxide (3 \times 150 ml) and water (3 \times 200 ml), then dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was distilled at reduced pressure through a short-path apparatus until unreacted 2,2,5,5-tetramethylcyclohexane-1,3-dione began to solidify in the condenser. The distillate was chromatographed at 150° through a 6 ft \times 0.75 in. silicone oil UC-W98 (10% on Chromosorb P) column giving three fractions with retention times of 3.3, 4.4, and 6.0 min. The first fraction (*ca.* 10% of the mixture) appeared from nmr analysis to be 1,3-diethylidene-2,2,5,5-tetramethylcyclohexane, but was not characterized further. The second fraction (*ca.* 10%) was identified as 3-methylene-2,2,5,5-tetramethylcyclohexanone by comparison with authentic material. The third fraction (*ca.* 80%) was distilled *in vacuo* to yield 18.6 g (52%) of clear, colorless 3-ethylidene-2,2,5,5-tetramethylcyclohexanone, bp 78° (2.5 mm), as a 15:85 mixture of *E* (anti) and *Z* (syn) isomers: *ir* (CCl_4) 3050, 1705, 1640, 1455, 1380, and 1365 cm^{-1} ; major mass spectral peaks (rel intensities) *m/e* 181 (5.9), 180 (44, P), 165 (14), 137 (11), 124 (5), 123 (6), 109 (11), 107 (2), 97 (11), 96 (100), 95 (13), 93 (4), 91 (5), 84 (4), 83 (95), 82 (8), 81 (55), 80 (2), 79 (16), 78 (2), 77 (9), 69 (7), 68 (10), 67 (29), 66 (2), 65 (7), 63 (2), 57 (9), 56 (13), 55 (34), 54 (10), 53 (28), 51 (8), 50 (3), 43 (10), 42 (4), 41 (47), 40 (6), 39 (29), 29 (20), 28 (6), 27 (27), 15 (9); precise mass determination, 180.1504 (calcd for $\text{C}_{12}\text{H}_{20}\text{O}$, 180.1514).

Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{O}$: C, 79.94; H, 11.18. Found: C, 80.10; H, 11.01.

Since the isomer mixture could not be resolved, even on a 500 ft \times 0.03 in. i.d. capillary stainless steel column coated with 20:1 SF-96(50)/Igepal,²² structural identification of the isomers was accomplished by nmr analysis of the mixture. The *Z* isomer had nmr (100 MHz, CCl_4) resonances at δ 0.92 (s, 6 H, 5,5-dimethyls), 1.26 (s, 6 H, 2,2-dimethyls), 1.70 (doublet of triplets, 3 H_a, $J_{ab} = 7$ Hz, $J_{ac} = 1$ Hz, $\text{C}=\text{CCH}_3$), 2.04 (s, $\Delta\nu = 3.1$ Hz, 2 H_e, $J_{bc} = 1$ Hz, $\text{C}=\text{CCH}_2$), 2.13 (s, $\Delta\nu = 1.8$ Hz, 2 H, $\text{CH}_2\text{C}=\text{O}$), and 5.26 (quartet of triplets, 1 H_b, $J_{ab} = 7$ Hz, $J_{bc} = 1$ Hz, $\text{C}=\text{CH}$); the *E* isomer had nmr (100 MHz, CCl_4) resonances at δ 0.89 (s, 6 H, 5,5-dimethyls), 1.14 (s, 6 H, 2,2-dimethyls), 1.58 (d, 3 H_a, $J_{ab} = 7$ Hz, $\text{C}=\text{CCH}_3$), 2.18 (s, $\Delta\nu = 2.0$ Hz, 2 H, $\text{CH}_2\text{C}=\text{O}$), 2.27 (s, $\Delta\nu = 2.8$ Hz, 2 H, $\text{C}=\text{CCH}_2$), and 5.41 (quartet, 1 H_b, $J_{ab} = 7$ Hz, $\text{C}=\text{CH}$). Structural assignment of the δ 2.13 and 2.18 nmr reso-

nances to the acyclic methylenes and the resonances at δ 2.04 and 2.27 to the allylic methylenes of (*Z*)- and (*E*)-3-ethylidene-2,2,5,5-tetramethylcyclohexanone, respectively, were verified by noting selective depletion (*ca.* 95%) of the δ 2.13 and 2.18 resonances in a 100-mg isomer mixture after treatment with 200 mg of sodium in 3 ml of methanol-*d*₁, quenching with 5 ml of deuterium oxide, and extracting into carbon tetrachloride.³²

The ultraviolet spectra (C₈H₁₂) of mixtures of (*Z*)- and (*E*)-3-ethylidene-2,2,5,5-tetramethylcyclohexanone of differing isomer ratios (produced by photosensitization, *vide infra*) and analyzed for isomer distribution by nmr (*vide supra*) allowed calculation of the individual isomers' spectra. Vibrational fine structure $n-\pi^*$ maxima were recorded at 318 nm (ϵ 22), 307 (44), 298 (54), and 289 (49) for the *Z* isomer, and at 318 nm (ϵ 47), 307 (93), 298 (104), and 289 (95) for the *E* isomer.

Direct Irradiation of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone. A solution of 4.00 g (22.2 mmol) of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone (as a 15:85 *E:Z* mixture) in 30 ml of sodium-dried benzene was irradiated 35 hr in a Rayonet apparatus equipped with RUL-3000 lamps. The reaction was monitored by glpc and by changes in the nmr spectrum until the spectrum indicated no further change and showed 32% conversion (photo-stationary state) to a single photoproduct. Solvent was removed by distillation under reduced pressure and the residue was chromatographed at 65° through a 3 ft \times 0.25 in. butanediol succinate (10% on Chromosorb P-DMCS) column to afford 2.41 g (60%) of recovered starting material (retention time 5.4 min) and 1.04 g (26%) of 3-isopropylidene-2,5,5-trimethylcyclohexanone (retention time 11.3 min), a clear, colorless liquid: ir (CCl₄) 1705, 1665, 1450, 1380, and 1365 cm⁻¹; nmr (60 MHz, CCl₄) δ 0.78 and 1.08 (two s, 3 H each, C₃-methyls), 1.14 (d, 3 H_a, J_{ab} = 7 Hz, C₂-methyl), 1.68 and 1.72 (two s, 3 H each, C=C(CH₃)₂), 2.24 (m, 4 H, CH₂C=O and C=CCH₂), and 3.27 (quartet, 1 H_b, J_{ab} = 7 Hz, C₂-methine); ultraviolet (C₈H₁₂) $n-\pi^*$ fine structure at 320 nm (ϵ 44), 309 (88), 299 (113), and 291 (104); mass spectral peaks at *m/e* 180 (P), 165, 96, 83, and 81.

Anal. Calcd for C₁₂H₂₀O: C, 79.94; H, 11.18. Found: C, 79.73; H, 11.33.

A solution of 270 mg (1.50 mmol) of the photoproduct (*vide supra*) in 5 ml of ether was saturated with ozone (electrically generated, 0.01 lpm) for 25 min at 0°. Analysis by glpc indicated *ca.* 90% of the theoretical amount of acetone. Extraction of the ethereal solution with 5 ml of 10% aqueous sodium carbonate, followed by neutralization with hydrochloric acid, back-extraction into 20 ml of ether, and evaporation yielded 220 mg (95%) of 2,5,5-trimethylcyclohexane-1,3-dione, mp 159–160° [lit.¹⁷ mp 158–159°].

Determination of the Singlet Steady-State Ratio of *Z* and *E* Isomers of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone. A 50-mg sample of a 15:85 *E:Z* isomer mixture of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone in 0.5 ml of sodium-dried benzene was irradiated with a Pyrex-filtered 450-W mercury lamp (Hanovia). Periodic monitoring by nmr indicated that isomerization to 3-isopropylidene-2,5,5-trimethylcyclohexanone reached a photo-stationary value of 32% after *ca.* 80 hr. This ratio did not change upon further irradiation; however, the percentage of *E* isomer of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone to *Z* isomer steadily increased, approaching 100% (98% *E* after 260 hr).

Direct Irradiation of 3-Isopropylidene-2,5,5-trimethylcyclohexanone. A 100-mg (0.556 mmol) sample of 3-isopropylidene-2,5,5-trimethylcyclohexanone in 1.0 ml of sodium-dried, redistilled benzene was irradiated with a corex-filtered 450-W mercury lamp. Monitoring by glpc (3 ft \times 0.25 in. 10% butanediol succinate on Chromosorb P-DMCS at 65°) and nmr indicated formation of (*E*)-3-ethylidene-2,2,5,5-tetramethylcyclohexanone as the only detectable photoproduct. A stationary state was reached after 45 hr in which (*E*)-3-ethylidene- and 3-isopropylidene ketones were present in a 68:32 ratio. Further irradiation caused no change, and no formation of (*Z*)-3-ethylidene-2,2,5,5-tetramethylcyclohexanone was detected.

Photosensitization of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone. To a solution of 3.00 g (16.6 mmol) of a 15% *E:85%* *Z* mixture of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone isomers in 40 ml of sodium-dried benzene was added 1.50 g (7.64 mmol) of xanthone (Aldrich, recrystallized twice from 95% ethanol), calculated to absorb greater than 98% of the incident light at 350 nm. The solution was photolyzed for varying periods of time to 48 hr in a Rayonet reactor equipped with RUL-3500 lamps. Examination of the solution by nmr during the course of irradiation showed that the sole detectable photoreaction was *cis*-*trans* isomerization of the two isomers with the *E* isomer concentration steadily increas-

ing at the expense of the *Z* isomer, to a pseudo-steady-state value of 78% *E:22%* *Z*.

Ozonolysis of the Photolysate from Sensitized Irradiation of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone. A 2.715-g sample (15.06 mmol) of a 15% *E:85%* *Z* isomer mixture of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone in 40 ml of sodium-dried benzene, and containing 1.50 g (7.64 mmol) of xanthone (Aldrich, recrystallized twice from 95% ethanol), was irradiated through Pyrex for 20 hr at 350 nm. The ultraviolet absorption spectrum of the mixture indicated that a minimum of 99% of total incident light was absorbed by xanthone. At the end of the irradiation period, nmr analysis indicated the composition of the photolysate was 46% *E:54%* *Z*. The solution was concentrated and the residue distilled *in vacuo* to give 2.401 g (13.32 mmol) of clear liquid which was analyzed as still a 46% *E:54%* *Z* isomer mixture by nmr. The liquid was dissolved in 30 ml of ether, cooled to 0°, and ozone was bubbled through the solution at a rate of 0.01 lpm for 30 min. It was then poured into 10 ml of 10% hydrogen peroxide solution and the layers were separated. The ethereal layer was concentrated to yield 2.125 g (12.63 mmol, 95% based on distillate) of 2,2,5,5-tetramethylcyclohexane-1,3-dione.¹⁷ Analysis of the aqueous phase by nmr spectroscopy accounted for acetic acid (*ca.* 60% of theoretical) as the only other detectable product.

Triplet Sensitization of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone. To 1.0 ml of sodium-dried benzene in a Pyrex nmr tube was added 100 mg (0.556 mmol) of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone, as a 15% *E:85%* *Z* isomer mixture. Enough triplet sensitizer (*vide infra*) was added to absorb a minimum of 95% (greater where possible) of the incident light. The solutions were irradiated in a Rayonet reactor in a modified merry-go-round with either RUL-3000 or RUL-3500 lamps, and monitored during irradiation for extent of isomerization by nmr spectroscopy. Isomerization of the *Z* isomer to *E* isomer was observed with the following sensitizers: xanthone, E_T = 74 kcal/mol; acetophenone, E_T = 74 kcal/mol; benzophenone, E_T = 69 kcal/mol; 10-thioxanthone, E_T = 65 kcal/mol; phenanthrene, E_T = 62 kcal/mol; and anthraquinone, E_T = 62 kcal/mol. However, Michler's ketone, E_T = 61 kcal/mol; 2-acetonaphthone, E_T = 59 kcal/mol; and 1-acetonaphthone, E_T = 56 kcal/mol, produced no detectable isomerization (irradiation time 7 days for Michler's ketone).

Quantum Yield Measurements. Quantum yields were determined by parallel and/or consecutive irradiation of sample and actinometer in matched cuvettes (either 5-ml with 1-cm optical path or 2-ml with 0.4-cm optical path) held in a carousel centered in a chamber reactor (Rayonet) of eight RUL-3000-Å lamps. The potassium ferrioxalate actinometer of Hatchard and Parker⁴⁶ was employed, but was checked against the uranyl oxalate actinometer of Leighton and Forbes.⁴⁷ Stray light was eliminated by use of a solution filter of 1.0 *M* cobaltous sulfate and 1.0 *M* nickelous sulfate in 5% sulfuric acid contained in a Pyrex vessel of 0.5-cm optical path; the filter was preirradiated several hours before use. This filter transmitted *ca.* 75% of incident light in the range of 290–320 nm. Concentrations of both actinometer and sample solutions were adjusted to absorb all incident light, and were checked by uv spectroscopy before and after irradiation. Analysis of actinometer was by absorbance of the 1,10-phenanthroline complex of ferrous ion at 510 nm; analysis of organic photoproducts was by glpc (3 ft \times 0.25 in. butanediol succinate column, 10% on Chromosorb P-DMCS, 65°), checked by nmr, for direct irradiations and by nmr for sensitized irradiations. In the latter case, quantum yields at higher conversions were used to obtain the quantum yield at zero conversion by extrapolation.

Quenching of Acetophenone Phosphorescence by 3-Methylene- and 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone. A series of solutions was prepared with acetophenone (0.308 g, 2.56 mmol, 0.051 *M*) in ethanol (50 ml) and weighed increments of 3-methylene-2,2,5,5-tetramethylcyclohexanone, with concentrations of the latter ranging from zero to 5.76×10^{-2} *M* over nine solutions. The phosphorescence spectra at 77°K were recorded; a linear Stern-Volmer plot of Φ_0/Φ_Q vs. [Q] was obtained with $k_{q\tau} = 6.4 M^{-1}$. Similarly, the phosphorescence spectra of eight solutions of 0.650 g (5.40 mmol, 0.054 *M*) of acetophenone and weighed increments of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone (range zero to 1.6×10^{-2} *M*) in 100 ml of ethanol were recorded at 77°K, and were found to give a linear plot of Φ_0/Φ_Q vs. [Q], with $k_{q\tau} = 65 M^{-1}$.

Phosphorescence Spectra and Lifetimes of 3-Methylene- and 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone. The phosphorescence spectrum of 3-methylene-2,2,5,5-tetramethylcyclohexanone

(0.1 M) in ethanol glass at 77°K had vibrational fine structure as follows: 405 nm, 0-0 band; 427, 0-1, λ_{\max} ; 445, 0-2; 475, 0-3; and 481 nm, 0-4 band. By use of a Tektronix 564B Storage oscilloscope equipped with a polaroid camera, the mean phosphorescent lifetime was 205 msec with excitation at 300 nm (near the $n-\pi^*$ λ_{\max}). Similarly, the phosphorescence spectra of 3-ethylidene-2,2,5,5-tetramethylcyclohexanone (15% E:85% Z, 0.1 M) in ethanol and isopentane glasses were recorded at 77°K. In both solvents spectra were diffuse, making the following band assignments somewhat uncertain. With excitation at 300 nm, band positions were: 0-0 band, 418 nm in ethanol, 412 nm in isopentane; λ_{\max} , 443 nm in ethanol, 450 nm in isopentane. The mean radiative lifetime was 156 msec (ethanol glass). Authenticity of the phosphorescence spectra was indicated by comparison of the excitation and absorption spectra. Additionally, capillary glpc analysis indicated purity of samples at $\geq 99.9\%$.

Sensitized Irradiation of 3-Ethylidene-2,2,5,5-tetramethylcyclohexanone at 77°K in Isopentane. To 0.50 ml of Spectrograde iso-

pentane in a Pyrex 5-mm nmr tube was added 50.0 mg (0.278 mmol) of the ethylidene ketone as a 15% E:85% Z isomer mixture and 15.0 mg (0.076 mmol) of xanthone (Aldrich, recrystallized twice from ethanol). The solution was immersed in a Pyrex dewar at 77°K and irradiated with an external 450-W mercury lamp. After 5 hr, no visible change could be detected by 100-MHz nmr spectroscopy. When irradiation was continued under identical conditions except at room temperature, only 4 hr irradiation produced a 30% E:70% Z mixture of isomers, as analyzed by nmr.

Acknowledgment. Financial support furnished by the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grants 1409-G1 and 5860-AC3, and a predoctoral stipend in 1971 to R. O. G.), and by the University of California Committee on Research is gratefully acknowledged. We also thank Mr. Philip L. Wylie for technical assistance.

The Continuous Diradical as Transition State. Internal Rotational Preference in the Thermal Enantiomerization and Diastereoisomerization of *cis*- and *trans*-1-Cyano-2-isopropenylcyclopropane

W. von E. Doering* and Krishna Sachdev

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received June 22, 1973

Abstract: Of the three most rapid rearrangements undergone by the disubstituted cyclopropanes of the title, the two geometrical isomerizations cannot be concerted in the usual sense of continuous overlap of orbitals and are thus able to reveal differences among the internal rotations requisite to the rearrangement. The three rearrangements are independent of each other, proceed at their maximum rates at the beginning of the reaction, and can be accommodated only inadequately (32%) by a conventional diradical intermediate within which only one internal rotation at a time is permitted. In our estimation this is the first example of the opening of a three-membered ring which has been so labeled by substituents and optical activity as to reveal the need for a change in mechanistic hypothesis. In the dynamic aspects of bond breaking we believe to have found the basis for a consistent conceptual scheme, that of the continuous diradical as the internally rotationally coupled extension of stretching vibrational modes. Incapable of being trapped, the continuous diradical represents families of energetically and orbitally not concerted transition states the stereochemical differences among which originate in energetic preferences among the observationally independent, internally rotational components.

Singlet trimethylene was put forward many years ago to rationalize the constitutional isomerization of cyclopropane to propylene.¹ This simple mechanistic hypothesis has had the undeniable merit of compatibility with the subsequently discovered *cis*-*trans* geometrical isomerization² and racemization of optically active cyclopropanes,^{3,4} as well as with the varied re-

arrangements of cyclopropanes substituted by one⁵ or two vinyl groups,⁶ by a carbonyl function, or by a combination of carbonyl and vinyl groups.^{7,8}

Recent years have seen major attention directed toward a more precise definition of the nature and role of trimethylene.^{9,10} Is it an intermediate of sufficiently long life to be trapped in a second-order or pseudo-

(1) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966); H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); K. J. Laidler, "Comprehensive Chemical Kinetics," Vol. 5, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, Amsterdam, 1972.

(2) (a) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958); (b) E. W. Schlag and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **82**, 5996 (1960); (c) D. W. Setser and B. S. Rabinovitch, *ibid.*, **86**, 564 (1964); (d) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 5717 (1963); (e) C. S. Elliott and H. M. Frey, *ibid.*, 900 (1964); (f) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc., Ser. A*, **257**, 122 (1960); **260**, 424 (1961); (g) M. R. Willcott III and V. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967); (h) M. R. Willcott III and V. H. Cargle, *ibid.*, **91**, 4310 (1969).

(3) (a) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968); (b) J. A. Berson and J. M. Balquist, *J. Amer. Chem. Soc.*, **90**, 7343 (1968).

(4) W. L. Carter and R. G. Bergman, *J. Amer. Chem. Soc.*, **90**, 7344 (1968); R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969).

(5) For references, see W. von E. Doering and E. K. G. Schmidt, *Tetrahedron*, **27**, 2005 (1971); W. von E. Doering and J. B. Lambert, *ibid.*, **19**, 1989 (1963).

(6) W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 115 (1963).

(7) C. L. Wilson, *J. Amer. Chem. Soc.*, **69**, 3002 (1947); R. M. Roberts and R. G. Landolt, *ibid.*, **87**, 2281 (1965); R. M. Roberts, R. N. Greene, R. G. Landolt, and E. W. Heyer, *ibid.*, **87**, 2282 (1965); D. E. McGreer, N. W. K. Chiu, and R. S. McDaniel, *Proc. Chem. Soc., London*, 415 (1964).

(8) E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **2**, 1 (1963).

(9) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(10) (a) L. Salem, *Accounts Chem. Res.*, **4**, 422 (1971); (b) J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *J. Amer. Chem. Soc.*, **94**, 279 (1972); (c) Y. Jean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, *Proc. Int. Congr. Pure Appl. Chem.*, **23rd**, 1, 197 (1971); (d) L. Salem and C. Rowland, *Angew. Chem.*, **84**, 86 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).