Photochemical Transformations of Selected 3-Cycloheptenone Derivatives[1a]

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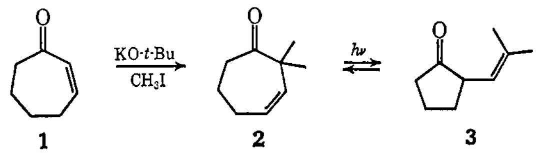
Abstract: The photoisomerization of three selected 3-cycloheptenone derivatives has been examined. 2,2-Dimethyl-3-cycloheptenone (**2**) was shown to rearrange exclusively to 2-isobutenylcyclopentanone (**3**) by a mechanism which probably proceeds from a singlet state. Irradiation of 3,3-dimethylbicyclo[5.1.0]oct-4-en-2-one (**8**) gave rise only to a similar product of 1,3-acyl rearrangement, namely, **10**. No cyclopropyl bond cleavage and no transannular hydrogen abstraction could be detected. Thus, allylic α cleavage is seen to compete effectively with cyclopropyl ring opening. The photolysis of 2,2,7,7-tetramethyl-3,5-cycloheptadienone (**15**) could not be quenched with either piperylene or naphthalene, but was sensitized by benzophenone or acetone. Under either set of conditions, 3-methyl-4-caren-2-one (**16**) was produced. No photodecarbonylation could be detected. The role of the four α,α'-methyl groups in directing the photochemical behavior of the substituted dienone is discussed.

During the last year or two, it has become increasingly apparent that the photochemistry of β,γ-unsaturated ketones has provided an intriguing new source of unusual molecular rearrangements. The general types of phototransformations which have been observed with cyclic and acyclic β,γ-unsaturated ketones have been summarized in a recent paper from this laboratory.[2] As part of a general study of photochemical transformations of unsaturated medium-sized ring ketones,[3,4] we originally reported the gross features of the photorearrangement of 3-cyclooctenones.[4] The present investigation concerned itself with the photochemistry of 3-cycloheptenones and began with three goals: first, a search for possible transannular reactions in the seven-ring systems; secondly, determination of the relative light-induced reactivity of a β,γ-unsaturated carbonyl chromophore and a conjugated cyclopropyl ketone moiety; and thirdly, exploration of the photochemical behavior of a 2,2,7,7-tetrasubstituted 3,5-cycloheptadienone.

Results

2,2-Dimethyl-3-cycloheptenone. The compound selected to provide data regarding the first point at issue was 2,2-dimethyl-3-cycloheptenone (**2**) which was conveniently prepared by dimethylation of 2-cycloheptenone (**1**) with excess potassium *t*-butoxide and methyl iodide according to established procedures.[5] Irradiation of **2** in dilute ether solution using a 450-W Hanovia lamp with a Corex filter was followed by withdrawal of small aliquots at various time intervals and examination of these by vapor phase chromatography (vpc). Careful monitoring of the course of the reaction indicated the formation of a lone volatile photoproduct, **3**. Interestingly, an apparent photostationary state appeared to be reached after approximately 4 hr, at which point the ratio of **3**:**2** was slightly greater than 4:1. Preparative scale vpc separation of such a mixture gave pure **3** which was assigned the isomeric 2-isobutenylcyclopentanone formulation on the basis of its elemental analysis (isomeric with starting material **2**) and spectral data. The infrared spectrum of **3** in carbon tetrachloride solution exhibits strong 1750-cm^{-1} carbonyl absorption characteristic of cyclopentanones and a weak band at 1670 cm^{-1} attributable to a nonconjugated olefinic bond. The photoisomer displays ultraviolet absorption maxima (isooctane) at 295 (80), 310 (90), 325 (70), and 335 mμ (ϵ 25); such enhanced n $\rightarrow$ π^* absorption is characteristic of β,γ-unsaturated carbonyl chromophores. The nmr spectrum exhibits a doublet of septuplets centered at δ 4.90 that was easily recognized as the lone vinyl proton in the molecule. The methyl groups which appeared as slightly broadened singlets at δ 1.76 and 1.68 were considered to be attached to sp^2-hybridized carbon on the basis of their chemical shifts. The remainder of the spectrum consists of a broad multiplet centered at δ 3.0 attributable to the allylic α-carbonyl proton and a six-proton broad absorption at δ 1.6–2.5 due to the methylene protons. From these data and the realization the photoproduct exists in photoequilibrium with **2** (see below), it was clear that the 2-isobutenylcyclopentanone structure (**3**) represented a unique fit to the spectral parameters. At this point, it should be mentioned that two methyl groups were originally introduced at position 2 of the 3-cycloheptenone molecule in order to assist in the stabilization of a 2-vinylcyclopentanone derivative if such a molecule were produced. In contrast to simple 2-vinylcyclohexanone and 2-vinylcyclooctanone[6] derivatives which are rapidly isomerized into conjugation during attempted purification by gas chromatography,[4,7] **3** was found to be completely stable to such



1 **2** **3**

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[1] (a) The authors are grateful to the Army Research Office (Durham) and the Alfred P. Sloan Foundation for grants which contributed to the financial support of this research; (b) Esso Research and Engineering Fellow, summer 1965; Lubrizol Fellow, 1967–1968.

[2] L. A. Paquette and G. V. Meehan, submitted for publication.

[3] L. A. Paquette and O. Cox, *J. Am. Chem. Soc.*, **89**, 1969, 5633 (1967).

[4] L. A. Paquette and R. F. Eizember, *ibid.*, **89**, 6205 (1967).

[5] For leading references to the alkylation of α,β-unsaturated ketones see H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 190–192.

[6] R. G. Carlson and J. H. Bateman, *Tetrahedron Letters*, 4151 (1967).

[7] J. K. Crandall, J. P. Arrington, and J. Hen, *J. Am. Chem. Soc.*, **89**, 6208 (1967).

conditions indicating that such substitution had accomplished its intended purpose.

As expected from the results described above and earlier,[2,4,7] irradiation of pure **3** led rapidly to the formation of **2**; the ratio of the two components at the photostationary state was virtually identical with that already encountered.

Irradiation of **2** in ether solution containing piperylene, or in neat piperylene as solvent, was studied (see Table I). On the basis of the ultraviolet spectrum of piperylene, it can be shown that this diene was absorbing only a minimal portion of the incident light under the conditions employed. The results clearly indicate that the photolysis of **2** is not quenched by piperylene (E_T^{trans} = 59 kcal/mol, E_T^{cis} = 57 kcal/mol).[8]

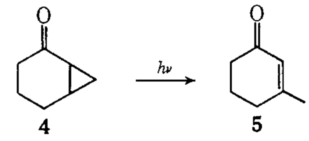
Table I. Representative Time and Percentage Composition Values for the Photorearrangement of 2,2-Dimethyl-3-cycloheptenone (**2**)[a]

Solvent	Time, min	Photolysate compn, %[b] **2**	**3**
Ether	30	41	33
	60	22	46
Ether (0.16 *M* in added benzophenone)[c]	60	82	4
	120	49	27
	180	34	43
	240	19	47
	300	11	50
Acetone[d]	60	82	10
	120	43	9
	180	25	9
	240	14	9
Ether (containing 33% by volume of piperylene)	60	42	39
	120	24	47
Piperylene	60	41	40
	120	25	46

[a] All runs were performed with a 450-W Hanovia immersion lamp fitted with a Corex (absolute cutoff point ~2580 Å) filter. [b] Cyclooctane was added throughout at the beginning of each photolysis for the purpose of internal standardization (see Experimental Section). The percentage composition values reflect the true composition of the reaction mixture and are free of all normalization. [c] The concentration of benzophenone was such that this ketone absorbed approximately 85% of the incident light. [d] Acetone was absorbing greater than 95% of the incident radiation.

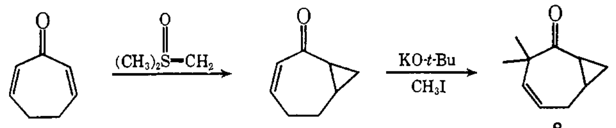
The photolysis of **2** was likewise found not to be sensitized by benzophenone (E_T = 68.5 kcal/mol)[8,9] or acetone (E_T = ~82 kcal/mol).[9,10] Thus, irradiation through Vycor of an ether solution of **2** containing sufficient benzophenone to absorb >85% of the incident light resulted in a substantial reduction in the rate of formation of **3**. Irradiation of **2** in acetone solution under conditions where the concentration of acetone was sufficiently high to absorb greater than ~95% of the light likewise significantly diminished the rate of production of **3**. In this latter experiment, however, significant quantities of **2** (and perhaps also **3**) appeared to be slowly destroyed by polymer formation as the reaction time was extended.

3,3-Dimethylbicyclo[5.1.0]oct-4-en-2-one. The photolability of conjugated cyclopropyl ketones, first recognized by Pitts and Norman in 1954,[11] has been the object of frequent study in recent years. The propensity of such molecules for *cis–trans* photoisomerization[12] or for conversion to α,β-unsaturated ketones[11,13] is now quite well established. In many cyclopropyl-conjugated ketones, the two proximate cyclopropyl bonds generally do not overlap equally well with the carbonyl π lobes with the result that selective, and sometimes specific, cleavage of the geometrically favored bond is observed.[13] For example, irradiation of **4** yields 3-methyl-2-cyclohexenone (**5**) as the major volatile photoproduct.[13f]



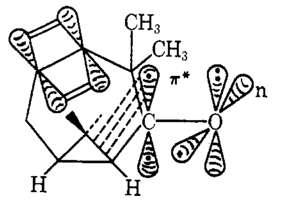
4 **5**

In an effort to relate the primary photochemical process exemplified in the conversion of **4** → **5** to the 1,3-acyl rearrangement observed, for example, with **2**, 3,3-dimethylbicyclo[5.1.0]oct-4-en-2-one (**8**) was selected for study. A convenient two-step synthesis of **8** was devised, beginning with the known 2,6-cycloheptadienone (**6**). Reaction of **6** with 1 equiv of dimethyloxosulfonium methylide[14] in dimethyl sulfoxide solution led to the isolation of **7** in 35% yield. Dialkylation of **7** with potassium *t*-butoxide and methyl iodide in *t*-butyl alcohol[5] readily gave rise to **8**.



6 **7** **8**

Upon irradiation, the n → π* state of the carbonyl group of **8**, *viz.*, **9**, may: (a) rearrange exclusively by means of the 1,3-acyl rearrangement pathway to yield **10**, (b) undergo selective fission to produce **11**, or (c)



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(8) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964); 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, *ibid.*, **86**, 3197 (1964).

(9) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 298; (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York N. Y., 1965, pp 132–179.

(10) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

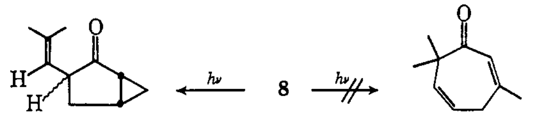
(11) J. N. Pitts, Jr., and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954).

(12) (a) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *ibid.*, **85**, 1001 (1963); (b) R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 144 (1964); (c) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964); (d) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *ibid.*, **87**, 1410 (1965); (e) W. G. Brown and J. F. Neumer, *Tetrahedron*, **22**, 473 (1966).

(13) (a) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963); (b) R. Beugelmans, *Bull. Soc. Chim. France*, 3087 (1965); (c) C. H. Robinson, O. Gnoj, and F. E. Carlon, *Tetrahedron*, **21**, 2509 (1965); (d) L. D. Hess and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **89**, 1973 (1967); (e) R. E. K. Winter and R. F. Lindauer, *Tetrahedron Letters*, 2345 (1967); (f) W. G. Dauben and G. W. Shaffer, *ibid.*, 4415 (1967).

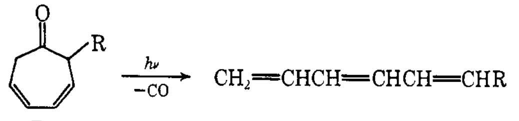
(14) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965).

partition itself between these two extremes. At play, therefore, is a direct intramolecular competition between π^*-assisted C_1–C_8 cyclopropane bond fission, which bond is oriented for maximum overlap with the π^* orbital (*cf.* **9**), and Norrish type I cleavage to produce a biradical (if such a rearrangement is nonconcerted), the acyl fragment of which is subject to rebonding at the alternate terminus of the allylic radical moiety. When a pentane solution of **8** was irradiated directly with a 450-W Hanovia lamp through Corex optics (absolute cutoff point at 2580 Å), a single photoisomer was formed in high yield. This lone ketonic product was easily identified as **10** on the basis of its spectra. The infrared carbonyl absorption at 1735 cm^{-1} gave the first hint that the cyclopropane ring had been retained in conjugation with a five-ring ketone. Also, portions of the nmr spectrum of **10** are remarkably similar to that of **3**. For example, the isobutenyl side chain appeared as a one-proton multiplet centered at δ 4.93 and two methyl groups seen at 1.76 and 1.59. In addition, the presence of the cyclopropyl group was unmistakably evident (see Experimental Section). The stereochemical relationship of the isobutenyl side chain to the cyclopropyl ring in **10** was not apparent from the available data and was not studied further. The material did, however, exhibit only one peak when subjected to gas chromatography on several columns. Thus, the photoexcited state of **8** (**9**) prefers to rearrange by means of path a.



10 **11**

2,2,7,7-Tetramethyl-3,5-cycloheptadienone. 1,3-Cycloheptadiene derivatives, whether carbocyclic[15] or heterocyclic,[16] are well known to undergo valence-bond isomerization when exposed to ultraviolet light. The generality of such transformations has been well established, with the exception of two 3,5-cycloheptadienones. When **12a** and **12b** were photolyzed in ether solution with a broad-spectrum lamp in Pyrex vessels, carbon monoxide and the isomeric trienes **13a** and **13b**, respectively, were produced.[17] Such results may be considered unusual in view of the many examples which follow the general reaction pathway and in light of the fact that cyclic ketones do not usually undergo photodecarbonylation in solution.[18] The anomalous behavior of **12a** and **12b** was originally attributed to the noncoplanarity of their diene functions which presumably causes such molecules to show properties more reminiscent of nonconjugated than conjugated dienes.[17b] However, Mislow and Gordon[19] have noted that this claim is in error and that the two double bonds are stereochemically and spectroscopically equivalent. That is to say, ketones **12a** and **12b** possess an axis which passes through the carbonyl group and is twofold symmetric with respect to either the entire molecule or the dienone chromophore.

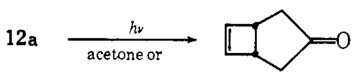


$$\xrightarrow[-CO]{h\nu} CH_2{=}CHCH{=}CHCH{=}CHR$$

12a, R = H
b, R = CH_3

13a, R = H
b, R = CH_3

Very recently, Schuster and coworkers[20] have clearly established that the photodecarbonylation of **12a** results exclusively from reaction through the singlet excited state. In sharp contrast, the sensitized photolysis of **12a**, which of necessity must proceed through a triplet state, was found to yield only valence bond isomer **14**.



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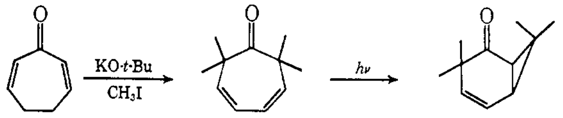
Independent work in this laboratory has also been concerned with this interesting phenomenon. The photochemistry of 2,2,7,7-tetramethyl-3,5-cycloheptadienone (**15**) was of particular interest because of its inherent C_2 symmetry, its structural similarity to **2** and **8**, and for several additional reasons associated with secondary steric effects which will be made apparent in the Discussion.

Ketone **15** was prepared by treating 2,6-cycloheptadienone (**6**) with excess potassium *t*-butoxide and methyl iodide. Initially, the direct irradiation of **15** in ether solution with a 450-W Hanovia lamp through Vycor optics was examined and was found to give rise to a lone major photoproduct. Preparative scale vpc separation of the irradiation mixture provided a pure colorless liquid isomeric ketone which was found to be identical in all respects with an authentic sample of pure 3-methyl-4-caren-2-one (**16**). A time–concentration curve for a typical irradiation under these conditions is shown in Figure 1. The photodecomposition of **16** in the later stages of these experiments is congruent with the known lability of this ketone upon irradiation.[21]



6 **15** **16**

The effect of added naphthalene (E_T = 61 kcal/mol)[8] and piperylene as possible triplet quenchers on the photorearrangement of **15** was examined (Tables II and III). No quenching was observed over a concentration range of three powers of ten. In actual fact, the rate of disappearance of the starting ketone

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[15] For reviews of this topic, see (a) O. L. Chapman, *Advan. Photochem.*, **1**, 323 (1963); (b) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 43–50; (c) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y., 1967, pp 122–130, 224–230; (d) D. J. Pasto in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, Chapter 4; (e) K. F. Koch, *Advan. Alicyclic Chem.*, **1**, 257 (1966).

[16] L. A. Paquette and J. H. Barrett, *J. Am. Chem. Soc.*, **88**, 1718 (1966), and pertinent references cited therein.

[17] (a) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961); (b) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).

[18] In contrast, vapor phase photodecarbonylation of cyclic ketones is a well-known phenomenon: R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).

[19] K. Mislow and A. J. Gordon, *J. Am. Chem. Soc.*, **85**, 3251 (1963).

[20] D. I. Schuster, B. R. Sckolnick, and F.-T. H. Lee, *ibid.*, **90**, 1300 (1968). We wish to thank Professor Schuster for making his results known to us prior to publication.

[21] A. J. Bellamy and G. H. Whitham, *J. Chem. Soc.*, 4035 (1964).

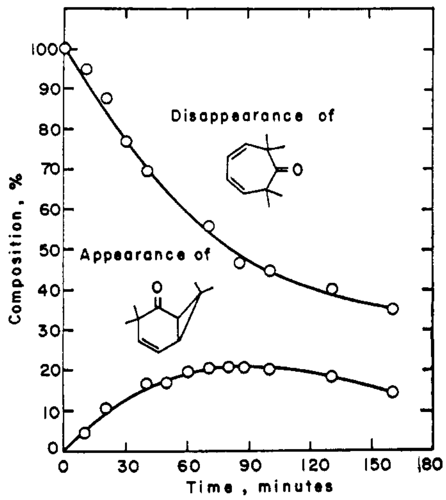


Figure 1. Concentrations of **15** and **16** *vs.* time during the irradiation of **15** through Vycor optics (dilute ether solution, 450-W Hanovia lamp).

(**15**) remained roughly constant in the various runs,[22] but the quantity of **16** formed was consistently greater in the presence of the hydrocarbons.

Sensitized irradiation of **15** in acetone solution or in ether solution containing benzophenone under conditions where the sensitizers were absorbing >85% of the incident light *led again to the formation of* **16** *and at greatly increased rates* (Tables II and III). From the preparative point of view, we have found it most convenient to prepare substantial quantities of **16** of quite high purity directly by irradiating gram quantities of **15** in acetone solution through Corex.

Table II. Representative Time and Percentage Composition Values for the Photorearrangement of 2,2,7,7-Tetramethyl-3,5-cycloheptadienone (**15**) Using Pyrex Optics

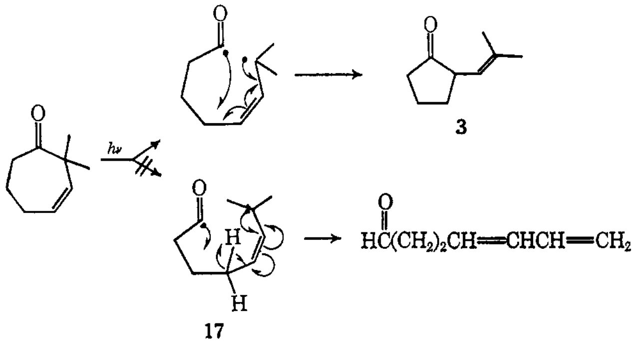
Solvent	Time, min	Photolysate compn, %[a] **15**	**16**	A[b]	B[b]
Ether	60	94	0.6	t[c]	t
	120	85	1.0	t	t
	180	79	1.4	t	t
	240	66	1.5	t	t
	300	61	1.5	t	t
Ether (8×10^{-2} *M* in naphthalene)	60	92	2.1	t	t
	120	81	11	t	t
	180	70	16	t	0.5
	240	48	17	t	0.8
	300	41	19	t	1.0
Ether (0.3 *M* in naphthalene)	60	92	6.0	t	t
	120	83	7.5	t	0.3
	180	76	10	t	0.6
	240	65	18	t	0.7
	300	61	21	t	1.0
Ether (2.7×10^{-2} *M* in piperylene)	60	92	8	t	t
	120	73	12	t	t
	180	70	17	t	0.8
	240	53	21	t	1.5
	300	48	22	t	3.2
Ether (2.7 *M* in piperylene)	60	71	10	..	1
	120	66	23	..	2
	180	53	25	..	5
	240	45	22	..	8
	300	38	29	..	12
Piperylene	60	90	6	..	t
	120	74	13	..	1.8
	180	61	16	..	1.3
	240	53	20	..	6
	300	50	18	..	10
Acetone	30	79	12	..	t
	60	62	25	..	t
	90	43	35	..	t
	120	27	46	..	2.0
	150	20	50	..	4.0
Ether (1.27 *M* in benzophenone)	10	42	62	..	..
	20	20	80	..	..
	30	13	82	..	t
	60	6	82	..	t

[a] Cyclooctane was added throughout at the beginning of each photolysis for the purpose of internal standardization (see Experimental Section). The percentage composition values reflect the true composition of the reaction mixture and are not normalized. [b] Photoproducts A and B (not characterized) were shown in separate experiments to arise from **16**. [c] t = trace.

Discussion

In an earlier communication dealing with the photochemistry of 3-cyclooctenones,[4] we proposed an initial Norrish type I reaction from the n → π* excited state to account for the observed products. This mechanism is in agreement with the general concept that n → π* excited states which are comprised of partially occupied, electron-deficient p_y orbitals are capable of hydrogen abstraction[23] and of attacking π systems.[24] In the case of **2**, it is interesting to note that the intermediate acyl radical appears to react exclusively by bonding at the alternate terminus of the allylic radical moiety and does not seem to become involved in transannular hydrogen abstraction of the type (five-centered transition state) shown in structure **17**. By comparison, approximately 10% intramolecular hydrogen abstraction (six-centered transition state) occurs in the 3-cyclooctenone examples.[4] However, in view of the fact that the total yields of **2** and **3** from irradiation of **2** in ether account for only 75–85% of the total material, it is possible that the diene aldehyde was formed in small amounts but escaped detection because of its instability under the conditions of irradiation.

The photoconversion of **2** → **3** could neither be quenched by piperylene nor sensitized by benzophenone. The latter result was not considered surprising since the E_T of benzophenone is recognized to be slightly above that of α,β-enones and below that of saturated ketones. The failure of piperylene to quench the rearrangement signifies either that the reaction proceeds *via* singlet species or that the rate of intramolecular rearrangement of a triplet intermediate is more rapid than diffusion control.



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[22] The slightly greater rates observed in the case of piperylene are definitely out of the range of experimental error and probably are the result of discrete amounts of adduct formation.

[23] (a) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (b) M. Kasha, *Radiation Res. Suppl.*, **2**, 243 (1960).

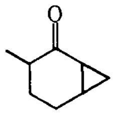
[24] H. E. Zimmerman, *Science*, **153**, 837 (1966).

Table III. Representative Time and Percentage Composition Values for the Photorearrangement of 2,2,7,7-Tetramethyl-3,5-cycloheptadienone (**15**) Using Corex Optics

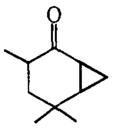
Solvent	Time, min	Photolysate compn, %[a]			
		15	**16**	A[b]	B[b]
Ether	30	84	9.0	2.5	2.9
	45	75	14	2.0	3.3
	75	55	17	2.2	4.6
Pentane	30	86	10	1.3	1.3
	45	82	16	2.2	2.2
	75	69	21	2.5	5.0
	105	51	23	3.3	7.0
Methanol	30	78	7.5	2.2	2.2
	45	64	9.0	2.6	1.8
	75	59	15	2.3	2.3
	105	49	17	2.2	2.6
Ether (1.2 *M* in naphthalene)	30	92	8.0	0.5	1.6
	45	88	10	1.0	3.3
	75	71	10	1.4	2.9
Piperylene	30	81	17	...	5.1
	45	64	18	...	6.5
	75	53	26	...	11
Acetone	30	26	54	0.9	2.7
	45	14	67	1.0	4.5

[a] Cyclooctane was added throughout at the beginning of each photolysis for the purpose of internal standardization (see Experimental Section). The percentage composition values reflect the true composition of the reaction mixture and are not normalized. [b] Photoproducts A and B (not characterized) were shown in separate experiments to arise from **16**.

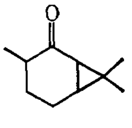
With regard to **8**, our experiments establish that *allylic* α cleavage competes effectively with cyclopropyl ring opening. These data may be compared with the recent independent results of Dauben and Shaffer[13f] who demonstrated a gradation in the primary photochemical behavior of bicyclo[4.1.0]heptan-2-ones which ranged from exclusive cyclopropyl ring opening in the case of **4** to exclusive α cleavage with preservation of the cyclopropane function in ketones **18** and **19**. Ketone **20**, upon irradiation, yielded products derived from both cyclopropyl ring opening and α cleavage.



18.



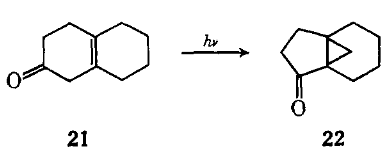
19



20

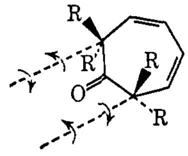
As with **2**, transannular hydrogen abstraction was not detected during the photolysis of **8**.

It now becomes possible to make the generalization that the principal photochemical transformation of medium-sized cyclic β,γ-unsaturated ketones involves 1,3-acyl rearrangement and migration of the allylic double bond presumably *via* the $n \rightarrow \pi^*$ singlet state.[4,6,7,25] In striking contrast, 3-cyclohexenones such as **21** have not been observed to give rise to 2-vinylcyclobutanones;[26] rather, conjugated cyclopropyl ketones (*e.g.*, **22**) result. Unfortunately, the multiplicity in this last reaction has not yet been determined.



21 **22**

Finally, the particular case of 2,2,7,7-tetramethyl-3,5-cycloheptadienone (**15**) must be considered. The photodecarbonylation of its nonmethylated (**12a**) and monomethylated (**12b**) congeners can best be rationalized[20] in terms of a concerted[27] σ-symmetric[28] expulsion of carbon monoxide from an excited singlet state (*cf.* the planar formulation **23**).[29] Two modes of disrotation at the 2 and 7 positions are, of course, possible. Concertedness is allowed in this instance because of the symmetry which obtains in the spin-paired singlet state of such molecules. On the other hand, the C_2 symmetry axis of **12a** is lost when the spin-unpaired triplet state is generated as, for example, in the sensitized irradiation of **12a**; when such is the case, concerted fragmentation is nonallowed and the alternate pathway leading to **14** is followed.[20]



23

Interestingly, despite the fact that **15** possesses a twofold symmetry axis, this ketone does not undergo fragmentation by the σ-symmetric mode; in fact, no carbon monoxide evolution could be detected under the conditions of the irradiation. The exclusive formation of 3-methyl-4-caren-2-one (**16**) is therefore of considerable theoretical interest. We attribute the exceptional behavior of **15** to secondary steric forces operative during the attempted bond reorganization necessary for carbon monoxide expulsion. Thus, as bond rotation (either direction) in **23** commences, two methyl groups are effectively brought into close proximity. The repulsive steric forces generated in this attempted maneuver are apparently sufficient to raise the energy of activation associated with the concerted fragmentation to a level which permits exclusive operation of the alternative rearrangement pathway which leads to **16**. Such an intervention of secondary steric effects has been observed previously in directing the concerted disrotatory cyclization of 2,3-homotropone[3] and its hydrocarbon analog[30] and in retarding the solvolytic reactivity of *cis,cis*-2,3-dimethylcyclopropyl tosylate.[31] The inability of **15** to expel carbon monoxide from its excited singlet state, the presence of which is apparent from our inability to quench the photoisomerization with effective triplet quenchers, is reasonable confirmatory evidence for the concertedness of the formation of **13a** and **13b** from **12a** and **12b**, respectively.

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(25) N. C. Yang and D.-M. Thap, *Tetrahedron Letters*, 3671 (1966).

(26) J. R. Williams and H. Ziffer, *Chem. Commun.*, 197, 469 (1967).

(27) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2511 (1967); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4388, 4389 (1965); H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

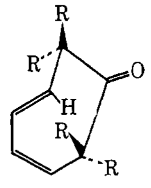
(28) D. M. Lemal and S. D. McGregor, *ibid.*, **88**, 1335 (1966).

(29) Such an argument is strictly dependent on the assumption that the π^* orbital of the carbonyl group is the lowest antibonding molecular orbital of the 3,5-cycloheptadienone system and that the excited state is planar.

(30) W. R. Roth and B. Peltzer, *Ann.*, **685**, 56 (1965).

(31) P. von R. Schleyer, G. W. van Dine, U. Schöllkopf, and J. Paust, *J. Am. Chem. Soc.*, **88**, 2868 (1966); U. Schöllkopf, K. Fellenberger, M. Patsch, P. von R. Schleyer, T. Su, and G. W. van Dine, *Tetrahedron Letters*, 3639 (1967).

The direct conversion of **15** to **16** under conditions of sensitized irradiation again does not parallel the behavior of **12a** under similar circumstances. The production of conjugated cyclopropyl ketones from β,γ-unsaturated ketones with ultraviolet light is, however, not unprecedented.[26,32] If the valence isomerization of **12a** to **14** does in fact occur by conversion of the excited triplet state to the *cis,trans*-3,5-cycloheptadienone **24a** followed by conrotatory thermal cyclization of this twisted ketone, as suggested by Schuster,[20] then the rate of formation of **24b** from **15** can be expected to be severely inhibited because of forbidding intracyclic nonbonded interactions. It may be reasoned that the four methyl substituents in **15** dramatically control the various bond reorganizations and cause isomerization to the cyclopropyl ketone **16** to be the most efficient pathway.



24a, R = H

In the direct photoisomerization of 2,2,7,7-tetramethyl-3,5-cycloheptadienone to 3-methyl-4-caren-2-one, it is clear that the reaction is not quenched by piperylene or naphthalene. Addition of benzophenone or irradiation in dilute acetone solution unequivocally demonstrates that photosensitization is observed. These data indicate that triplet **15** is capable of undergoing rearrangement to **16**; the lack of quenching by piperylene or naphthalene denotes either that singlet **15** can also lead to **16** or that a triplet intermediate is again formed but is rapidly consumed by reaction prior to diffusion.

Experimental Section[33]

2,2-Dimethyl-3-cycloheptenone (2). 2-Cycloheptenone (3.3 g, 0.03 mol)[34] was added to a solution of 10 g (0.09 mol) of potassium *t*-butoxide in 250 ml of absolute *t*-butyl alcohol. To this solution was added 22 g (0.15 mol) of methyl iodide with ice-bath cooling. The reaction mixture was stirred overnight, poured into 200 ml of water, and extracted with three 75-ml portions of ether. The combined organic layers were dried, filtered, and evaporated and the resulting oil was distilled to give 2.9 g of **2**, bp 85–90° (12 mm), of approximately 90% purity. Purification by preparative scale gas chromatography (SE-30 column) afforded 2.5 g (60%) of pure **2** as a colorless liquid, $n^{28}\mathrm{D}$ 1.4678; $\nu_{\max}^{\mathrm{CCl_4}}$ 1720 cm^{-1}; $\lambda_{\max}^{\text{isooctane}}$ 279 mμ (ϵ 20); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 282 mμ (ϵ 41); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.53 (multiplet, 2 H, vinyl protons), 2.62 (broadened triplet, 2 H, α-carbonyl protons), *ca.* 2.0 (multiplet, 4 H, methylene groups), and 1.18 (singlet, 6 H, methyl groups).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.93; H, 10.37.

Irradiation of 2. To a solution of 1.0 g of **2** in 450 ml of anhydrous ether was added 1.0 g of cyclooctane as internal standard. The solution was placed under an atmosphere of nitrogen and was irradiated with a 450-W Hanovia mercury vapor lamp in an immersion-well apparatus fitted with a Vycor filter. The course of the reaction was followed by removing small aliquots at various intervals. After 4.5 hr, a photostationary state consisting of approximately 8% of **2** and 92% of a lone photoproduct, **3**, was attained. The solvent was evaporated at 0°, and the photoproduct was isolated by preparative scale vpc. Molecular distillation at 50° (3 mm) served to provide an analytical sample; $\nu_{\max}^{\mathrm{CCl_4}}$ 1750 (s, carbonyl group) and 1670 cm^{-1} (w, $>C=C<$; $\lambda_{\max}^{\text{isooctane}}$ 295 (80), 310 (90), 325 (70), and 355 mμ (ϵ 25); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 4.97 (doublet of septuplets, J = 9.0 and 1.5 Hz, 1 H, vinyl proton), *ca.* 3.0 (broad multiplet, 1 H, allylic α-carbonyl proton), 1.6–2.5 (broad absorption, 6 H, methylene protons), and 1.76 and 1.68 (singlets, 3 H each, methyl groups).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.06; H, 9.97.

Irradiation of 3. A solution containing 0.0656 g of **3** and 0.0407 g of cyclooctane in 10 ml of anhydrous ether was divided into two portions, and each aliquot was separately irradiated in quartz test tubes affixed to the exterior of the immersion well. Irradiation resulted in rapid establishment of a photoequilibrium with small amounts of **2** in the approximate ratio of 92:8. More prolonged irradiation did not appear to alter the ratio of the two components but gave a poorer recovery of the ketones because of polymer formation.

Bicyclo[5.1.0]oct-3-en-2-one (7). The dimethylsulfoxonium methylide was prepared by the method described by Corey[14] from 2.80 g of sodium hydride (56% in mineral oil) and 14.7 g (0.065 mol) of trimethyloxosulfonium iodide in 70 ml of dry dimethyl sulfoxide (distilled from CaH_2). To the ylide solution cooled to 5° there was added 6.50 g (0.065 mol) of 2,6-cycloheptadienone (**6**)[34] in 25 ml of the same solvent. The reaction mixture which turned yellow immediately was stirred at 0–5° for 20 min, and then at room temperature for an additional 3.5 hr. The brown mixture was poured into 800 ml of distilled water and 500 ml of ether. The two layers were separated, and the aqueous layer was extracted with three 250-ml portions of ether. The combined organic layers were washed with saturated sodium chloride solution, dried, and evaporated to give 6.50 g of a yellow oil. Distillation yielded 2.77 g (35.0%) of liquid, bp 60–82° (0.80–1.2 mm), of approximately 90% purity. An analytical sample of pure **7** was obtained by preparative scale vpc (20% SF-96 on Chromosorb W, 110°); $\nu_{\max}^{\text{neat}}$ 1645 and 1625 cm^{-1}; near-infrared band (in CCl_4) at 1.627 μ (molar absorptivity 0.290); $\lambda_{\max}^{\text{isooctane}}$ 214 (16,800) and 325 mμ (ϵ 76); $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.50–6.54 (complex multiplet, 2 H, vinyl protons) and 0.82–2.57 (complex multiplet, 8 H, methylene and cyclopropyl protons).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.52; H, 8.27.

3,3-Dimethylbicyclo[5.1.0]oct-4-en-2-one (8). A 2.44-g (0.020 mol) sample of **7** (90% purity) was dissolved in 60 ml of dry *t*-butyl alcohol containing 6.73 g (0.060 mol) of potassium *t*-butoxide. To the ice-cooled solution there was added 18.5 g (0.127 mol) of methyl iodide during 20 min. After the mixture had been stirred overnight at room temperature, it was poured into 200 ml of water and extracted with four 75-ml portions of ether. The combined organic layers were washed with water and saturated sodium chloride solution, dried, and evaporated. Distillation of the resulting oil (2.90 g) afforded 2.00 g (66.6%) of **8** as a colorless liquid, bp 52–54° (0.45 mm). An analytical sample of **8** was obtained by preparative scale vpc (15% SE-30 on Chromosorb W, 140°); $\nu_{\max}^{\mathrm{CCl_4}}$ 1705, 1685, and 1645 cm^{-1}; near-infrared band (in CCl_4) at 1.635 μ (molar absorptivity 0.255); $\lambda_{\max}^{\text{isooctane}}$ 208 (1000) and 290 mμ (ϵ 27); $\delta_{\mathrm{TMS}}^{\text{neat}}$ 5.41 (multiplet, 2 H, vinyl protons), 1.30 and 1.10 (singlets, 3 H each, methyl groups), and complex pattern extending between 0.73 and 1.40 (12 H).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.78; H, 9.21.

The semicarbazone of **8** was obtained as white crystals from methanol, mp 166–167°.

Irradiation of 8. A solution of 2.00 g (13.3 mmol) of **8** in 450 ml of purified pentane was irradiated as above under nitrogen but with a Corex filter. After 3.25 hr, the solvent was removed at room temperature and the residual oil (1.93 g) was shown to consist of **8** and **10** in a ratio of 7.5:92.5 (vpc analysis). Preparative scale vpc gave a sample of **10** of 98% purity (20% SF-96 on Chromosorb W, 135°); $\nu_{\max}^{\mathrm{CCl_4}}$ 1735 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 4.93 (multiplet, 1 H, vinyl proton), 0.78–1.41 (multiplet, 2 H, cyclopropyl protons), and 1.52–3.18 (multiplet, 11 H, remaining cyclopropyl and aliphatic protons, including methyl peaks at 1.59 and 1.76).

The semicarbazone of **8** was obtained as white crystals from methanol, mp 190.5–191°.

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[32] L. P. Tenney, D. W. Boykin, Jr., and R. E. Lutz, *J. Am. Chem. Soc.*, **88**, 1835 (1966).

[33] The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were determined with a Cary Model 14 spectrometer and the nmr spectra were recorded with a Varian A-60 spectrometer.

[34] E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965).

Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.79; H, 8.51; N, 20.04.

2,2,7,7-Tetramethylcyclohepta-3,5-dienone (15). A 2.16-g (0.02 mol) sample of 2,5-cycloheptadienone was dissolved in 50 ml of dry *t*-butyl alcohol containing 9.0 g (0.08 mol) of potassium *t*-butoxide. To the ice-cooled solution there was added 14.2 g (0.10 mol) of methyl iodide during 30 min. A work-up similar to that described above gave 2.3 g (70%) of **15**, bp 48–51° (1.5 mm). An analytical sample of **15** was obtained by preparative scale vpc (10% SE-30 on Chromosorb G, 150°); $\nu_{\max}^{\mathrm{CCl_4}}$ 1700, 1660, and 1615 cm^{-1}; $\lambda_{\max}^{\mathrm{isooctane}}$ 235 (5170) and 282 mμ (ϵ 730); $\lambda_{\max}^{\mathrm{CH_3OH}}$ 243 (4680) and 290 mμ (ϵ 710); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ A_2B_2 pattern centered at 5.77 ($J_{AB} = J_{A'B'} = 10$ Hz; $J_{AA'} = 2.8$ Hz; $J_{BB'} = 1$ Hz; 4 H, vinyl protons) and singlet at 1.27 (12 H, methyl groups).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.00; H, 9.83.

Irradiation of 15 on a Preparative Scale. A solution of 1.0 g of **15** in 450 ml of acetone was irradiated as above through Corex optics. After 55 min, the reaction was virtually complete. The solvent was evaporated and the nonpolymeric residue (0.7 g) was subjected to preparative scale vpc. The lone photoproduct was obtained as a colorless oil; $\nu_{\max}^{\mathrm{neat}}$ 1700 cm^{-1}; the nmr spectrum (in $CDCl_3$) displayed singlets at δ 8.73, 8.85, 8.89, and 8.99 (3 H each, methyl groups), a multiplet at 8.26 (2 H, cyclopropyl protons), and a multiplet at *ca.* 4.38 (2 H, vinyl protons). The identity of these spectra with the infrared and nmr spectra of an authentic sample of 3-methyl-4-caren-2-one (**16**)[35] was clearly indicated.

Photolysis Runs. Results of the irradiation of **2** and **15** under a variety of conditions are tabulated in Tables I–III. All of these photolyses were performed in quartz test tubes held in a vertical position on the outer surface of the water-cooled quartz immersion well. In a typical experiment, 250 mg of **15** and 100 mg of cyclooctane (internal standard) were diluted to a specific volume with the solvent of choice (each solvent was purified by appropriate methods until it was homogeneous to vpc). The quartz test tubes were carefully flushed with nitrogen and tightly stoppered with serum caps which permitted withdrawal of aliquots with a microsyringe. An aliquot was removed at time zero and analyzed by vpc.[36] The gas chromatographic unit was carefully calibrated by the procedure utilized in one of our earlier papers.[3] The areas of the various gas chromatographic peaks were determined by cutting and weighing Xerox reproductions of the vpc curves (good quality paper).

In the attempted quenching studies, piperylene (Aldrich) was freshly fractionated prior to use. Naphthalene (reagent grade) was employed as received.

In the sensitized runs, acetone (analytical reagent) and benzophenone (reagent grade) were employed as received.

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[35] We wish to thank Professor Whitham for making available to us the various spectra of authentic **16**.

[36] A 0.125 in. × 10 ft stainless steel column packed with 5% SE-30 on 60–80 mesh Chromsorb W at 155° was employed in conjunction with an Aerograph Hi-Fy Model 600D gas chromatograph equipped with a flame ionization detector.

The Interception of Homoallylic Cations by Neighboring Hydroxyl

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Abstract: The silver ion induced cyclization of selected *cis*- and *trans*-iodohydrins in which the iodine substituent occupies a homoallylic position has been investigated. Evidence is presented which supports the fact that ring closure proceeds by way of intermediate homoallylic cations which are subject to intramolecular nucleophilic attack by the neighboring hydroxyl group. The ambient electrophilic nature of homoallylic cations is considered in light of the demonstrated selectivity for HO-*n* participation exclusively at only one of the two available sites. In the cases studied, the capability for cyclization is seen to be independent of the geometry of the double bond in the iodohydrin precursor in certain examples, but totally dependent on geometry in other instances. Explanation of these experimental findings in terms of the steric demand imposed by the particular transition state, in turn controlled by relative rates of cyclization, is presented.

Of the various effects which can be exerted by a substituent on the reactions of an organic molecule, that which involves direct or partial bonding of the substituent to the developing or completely unfolded reaction site continues to attract widespread interest.[1] The propensity of such groups as amino,[2] thioether,[3] carboxyl,[4] and alkoxyl[5] for neighboring group participation in certain simple systems has been recognized for some years. In contrast, the neighboring hydroxyl group as such has been little studied,[6] although alkoxide ions produced from such alcohols in alkaline solution have received considerable attention.[1] The great majority of the cases examined have been acyclic and cyclic compounds where the substituent had but one reactive site with which to interact intramolecularly. It was our intent in this work to investigate systems in which a hydroxyl substituent could avail itself of two widely differing sites in the course of intramolecular cyclization. Such a study forms part of our continuing program designed to examine new aspects of oxygen[7] and sulfur[8] neighboring group effects.

[1] B. Capon, *Quart. Rev.* (London), **18**, 45 (1964).

[2] (a) H. Freundlich and K. Kroepelin, *Z. Physik. Chem.*, **122**, 39 (1926); (b) G. Salomon, *Helv. Chim. Acta*, **16**, 1361 (1933).

[3] (a) G. M. Bennett, F. Heathcoat, and A. N. Mosses, *J. Chem. Soc.*, 2567 (1929); (b) G. M. Bennett and E. G. Turner, *ibid.*, 813 (1938); (c) see also W. E. Truce, W. W. Bannister, and R. H. Knopse, *J. Org. Chem.*, **27**, 2821 (1962).

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[6] H. W. Heine, A. D. Miller, W. H. Barton, and R. W. Greiner, *ibid.*, **75**, 4778 (1953).

[7] (a) L. A. Paquette, *Tetrahedron Letters*, 1291 (1965); (b) L. A. Paquette and H. Stucki, *J. Org. Chem.*, **31**, 1232 (1966); (c) L. A. Paquette and R. W. Begland, *J. Am. Chem. Soc.*, **87**, 3784 (1965); (d) R. W. Begland and P. C. Storm, unpublished observations in this laboratory.

[8] (a) L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, **89**, 6659 (1967); (b) L. D. Wise, results as yet unpublished.