## The Effect of α-Methyl Groups on the Photochemistry of 3,4,5,6,7,8-Hexahydronaphthalen-2(1H)-one

*Sir:*

Recent studies in a number of laboratories show that direct irradiation of β,γ-unsaturated ketones generally leads to a 1,3-acyl shift whereas triplet sensitization results in an oxadi-π-methane rearrangement.[1] This difference between singlet and triplet products suggests that, in contrast to saturated ketones,[2] intersystem crossing (isc) is inefficient in β,γ-unsaturated ketones. It is interesting to note that one of the earliest reported[3] oxadi-π-methane reactions was observed on *direct* irradiation of 1 whereas nearly all of the other examples

required triplet sensitization. In this exceptional case, either oxadi-π-methane reaction must proceed from the singlet state or else isc must occur. Comparison of 1 with other compounds in the literature suffers from a lack of close analogies; nevertheless, it is instructive to compare it with 2, another system of fused six-membered rings. The latter exhibits the "normal" behavior for β,γ-unsaturated ketones wherein direct irradiation[4] leads to a 1,3-acyl shift and triplet sensitization to the oxadi-π-methane rearrangement.[1b,5,6] The key structural differences between 1 and 2 are the location of the double bond and the number of methyl groups. In order to isolate one of the effects, we chose to investigate the photochemistry of α-methylated derivatives of 1.[7]

Our results demonstrate that 1 intersystem crosses to a triplet state which undergoes the oxadi-π-methane reaction but that successive introduction of methyl groups to the α-carbon dramatically increases the importance of singlet 1,3-acyl shift relative to intersystem crossing. Ultimately, the dimethyl compound (4) shows the same behavior as 2 (Scheme I).

Direct irradiation of the ketones[8] 1, 3, and 4 was carried out in benzene solvent under nitrogen with 313-nm light while sensitized irradiations at 313 nm employed acetone as solvent. The quantum yields shown in Table I were determined on a photochemical merry-go-round using 2,3-diazabicyclo[2.2.1]heptene-2

**Scheme I**



Table I. Quantum Yields for β,γ-Unsaturated Ketones

| Compound | Direct[a] | | Sensitized[b] | |
|---|---|---|---|---|
| | $\Phi_{-k}$[c] | $\Phi_p$[d] | $\Phi_{-k}$[c] | $\Phi_p$[d] |
| 1 | 0.15 | 5, 0.05 | 0.18 | 5, 0.05 |
| 3 | 0.28 | 6, 0.15; 7, 0.12[e] | 0.21 | 6, 0.01; 7, 0.06[e] |
| 4 | 0.39 | 8, 0.24 | 0.06 | 9, 0.03 |

[a] In benzene. [b] In acetone. [c] Ketone disappearance. [d] Formation of specified product. We have been unable to detect photochemical reversion of any of the direct irradiation products to starting material. [e] Total for both isomers.

as an actinometer. The cyclobutanone products 6 and 8 were isolated by thick-layer chromatography and were identified by their ir and nmr spectra;[9] moreover, the structure of 6 was confirmed by spectral comparison with authentic material.[10] The structural assignments of cyclopropyl ketones 7 and 9 were based on their spectra[9] and lithium-ammonia reduction to 10 and 11.



10, R = C₂H₅
11, R = (CH₃)₂CH

A mechanistic study revealed that (a) the direct conversion of 1 to 5 is quenched by cis-piperylene with concomitant isomerization to trans, (b) the quantum yield for isc of 1 is greater than 0.5, as determined by cyclohexadiene dimerization, (c) the direct conversion of 4 to 8 is not quenched by cyclohexadiene, and none of the characteristic dimers are formed, and (d) acetone sensi-

(1) Some of the recent papers in this area are (a) N. P. Peet, R. L. Cargill, and J. W. Crawford, *J. Org. Chem.*, 38, 1222 (1973); (b) H. Sato, K. Nakanishi, J. Hayashi, and Y. Nakadaira, *Tetrahedron*, 29, 275 (1973); (c) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, 94, 9252 (1972); (d) J. C. Dalton and H. F. Chan, *ibid.*, 95, 4085 (1973).

(2) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, 5, 92 (1972).

(3) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194, 469 (1967); *Tetrahedron*, 24, 6725 (1968).

(4) (a) L. A. Paquette and G. V. Meehan, *J. Org. Chem.*, 34, 450 (1969); (b) H. Sato, N. Furutachi, and K. Nakanishi, *J. Amer. Chem. Soc.*, 94, 2150 (1972).

(5) Sensitized irradiation was carried out in the steroid series. See ref 1b and 6.

(6) K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Lett.*, 1925 (1969).

(7) Interest in this point is heightened by the recently demonstrated sensitivity of the di-π-methane reaction in 1,4-dienes to substitution at the central carbon. See H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, 94, 6208 (1972); 95, 2957 (1973).

(8) The synthesis of 3 and 4 will be described elsewhere. Spectral data for these compounds were in complete accord with their structure.
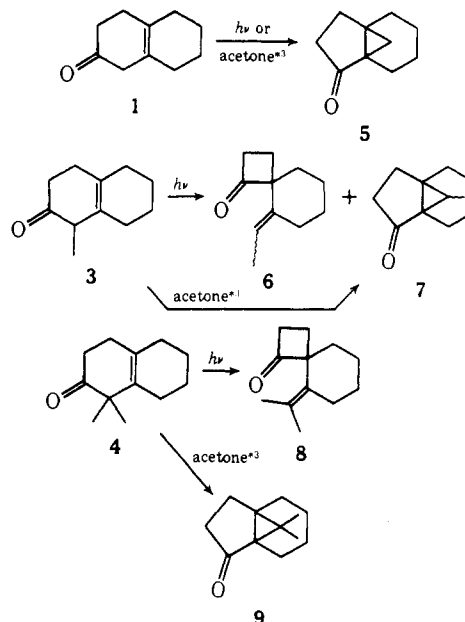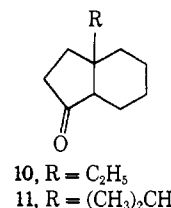
(9) 6: ir 1772 cm⁻¹; δ 1.57 (br, d, J = 7 Hz, CH₃), 2.86 (t, J = 8 Hz, cyclobutanone CH₂), 5.22 (q, J = 7 Hz, olefinic). 8: ir 1770 cm⁻¹, δ 1.63 (s), 1.68 (s) (methyls), 2.94 (distorted t, J = 8 Hz, cyclobutanone CH₂); mass spectral, M⁺· 178.1359 (calcd for C₁₂H₁₈O, 178.1357). 7, isomer a: ir 1700 cm⁻¹; δ 1.13 (d J = 6 Hz, cyclopropyl CH₃); isomer b, ir 1700 cm⁻¹; δ 1.16 (d J = 6 Hz, cyclopropyl CH₃). 9: ir 1713 cm⁻¹; δ 1.11, 1.14 (s cyclopropyl methyls).

(10) We are grateful to Professor Barry M. Trost, University of Wisconsin, for the spectra of authentic 6.

tization of **1** produces **5** with a quantum yield equal to that of direct irradiation (*cf.* Table I). These observations clearly establish that **1** intersystem crosses to a triplet state which rearranges to the cyclopropyl ketone. The acetone results in Scheme I show that a characteristic triplet reaction of all three ketones is oxadi-$\pi$-methane rearrangement. Since addition of methyl groups decreases the amount of triplet product seen under direct irradiation and increases the amount of cyclobutanone, we conclude that these groups must be influencing the competition between isc and singlet 1,3-acyl shift.

The question immediately arises whether the decrease in the isc efficiency observed on introduction of methyl groups is due to a decrease in the rate of isc or to an increase in the rate of 1,3-acyl shift. Based on the following argument, we suggest that the rate of $\alpha$-cleavage is markedly enhanced by $\alpha$-methylation but we cannot rule out small changes in the isc rate. The total quantum yield of all processes (reaction, isc, and decay) originating from the singlet state is unity; that is, $\Phi_r{}^s + \Phi_{isc} + \Phi_d = 1$. In ketone **1** we know that $\Phi_{isc}$ is greater than 0.5 and that $\Phi_r{}^s$ is negligible because no 1,3-acyl shift product was detected. Thus $\Phi_d$ must be less than 0.5 and, from the definition[11] of $\Phi_d$, the inequality $k_r{}^s + k_{isc} > k_d$ must be true. Assuming a detection limit of 2% for 1,3-acyl shift product in the direct reaction, the quantum yield for this product must be less than $0.02 \times 0.15$. The definition[11] of $\Phi_r{}^s$ then allows us to state that $k_{isc} + k_d > 332k_r{}^s$. Adding this inequality to the one derived above leads to the conclusion that $k_{isc} > 165k_r{}^s$ for ketone **1**. A similar argument obtains for compound **4** except that the absence of **9** in the direct irradiation shows the inefficiency of isc; in fact, $\Phi_{isc}$ must be less than 0.26.[12] It follows[11] that $k_r{}^s + k_d > 2.8k_{isc}$. Since $\Phi_r{}^s$ was measured for **4** as 0.24, we calculate that $k_{isc} + k_d = 3k_r{}^s$. Elimination of $k_d$ between these equations shows that $k_{isc} < 1.1k_r{}^s$ for ketone **4**. Since liberal assumptions have been made throughout, it is apparent that the ratio of $k_{isc}$ to $k_r{}^s$ is at least 150 times greater for **1** than for **4**. Turro and Yang[13] have shown that $\alpha$-alkylation causes only small changes in $k_{isc}$ for alkanones and we have no reason to expect otherwise in the present case.[14,15] The variation in this ratio is therefore too great to be accounted for solely by differences in $k_{isc}$; an increase in $k_r{}^s$ upon addition of $\alpha$-methyl groups must be the most important factor.

The behavior of **1** resembles that of cyclohexanone[16] since both compounds intersystem cross and react from

the triplet state; however, introduction of the double bond changes the characteristic triplet reaction from $\alpha$-cleavage to oxadi-$\pi$-methane rearrangement. Ketone **4**, on the other hand, undergoes apparent $\alpha$-cleavage from the singlet state, a reaction which is not generally observed in alkanones.[17] Since even singlet 2,2-dimethylcyclohexanone intersystem crosses before it reacts,[16] it appears that the double bond in **4** increases the rate of the 1,3-acyl shift reaction. If this reaction is concerted,[18] it occurs even though the proposed[1a] criterion of $\epsilon > 150$ is not met; on the other hand, if it proceeds by $\alpha$-cleavage followed by allylic recombination, little stabilization of the incipient allyl radical should be available until after $\alpha$-cleavage and bond rotation.[19]

Other explanations[1a,20] for the difference in photochemical behavior seen in **1**, **3**, and **4** might relate to variations in $\epsilon$ or differences in geometry. However, since both of these factors are similar[15] in all of the ketones, these explanations appear to be inadequate.[21]

(11) The quantum yield for any singlet process equals its rate divided by the sum of the rates for all singlet processes.

(12) This number is derived from the fact that the quantum yield of **9** under direct irradiation equals $\Phi_{isc}$ times the efficiency with which triplet **4** proceeds to product. The latter must be at least as high as the sensitized quantum yield of **9** (0.03). If 2% of **9** could be detected in the direct irradiation, its quantum yield would have to be less than $0.02 \times 0.39$.

(13) (a) J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2564 (1970); (b) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 6974 (1970).

(14) Photoelectron spectra for **1**, **3**, and **4** show that the $\pi$ orbital lies about 0.5 eV above the n orbital in each case (K. N. Houk, unpublished results). Coupled with the similarity of the uv spectra,[15] this implies that introduction of methyl groups causes no change in the relative order of electronic states. Therefore no large difference in rate of isc is expected in these ketones.

(15) Uv data $\lambda_{max}$, nm ($\epsilon$); **1** 285 (19); **3** 283 (70); **4** 278 (55).

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

(17) *tert*-Butyl alkanones undergo some $\alpha$-cleavage from the singlet state; *cf.* ref 13b and N. C. Yang, M. H. Hui, and S. Bellard, *J. Amer. Chem. Soc.*, **93**, 4056 (1971).

(18) 1,3-Acyl shift in a ketone of general structure **2** proceeds stereospecifically; *cf.* ref 4b.

(19) The authors are grateful to Professor R. L. Cargill for stimulating discussion on this point.

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

(21) A recent report by J. C. Hemminger, H. A. J. Carless, and E. K. C. Lee, [*J. Amer. Chem. Soc.*, **95**, 682 (1973)] shows that addition of $\alpha$-methyl groups to cyclobutanone drastically reduces the singlet lifetime by enhancing $\alpha$-cleavage, the same effect postulated in the present study.

**Paul S. Engel,*** Mary A. Schexnayder
*Department of Chemistry, Rice University*
*Houston, Texas 77001*

**Herman Ziffer, Jeffrey I. Seeman**
*National Institutes of Arthritis and Metabolic Diseases*
*National Institutes of Health*
*Bethesda, Maryland 20014*
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**Synthetic Methods and Reactions. I. Selenium Tetrafluoride and Its Pyridine Complex. Convenient Fluorinating Agents for Fluorination of Ketones, Aldehydes, Amides, Alcohols, Carboxylic Acids, and Anhydrides**

*Sir:*

We report that selenium tetrafluoride is a convenient fluorinating agent of general use, particularly suitable for replacement of hydroxyl and carbonyl groups by fluorine. Previously, this reagent was mentioned only in a patent[1] concerned with fluorination of some ketones. Selenium tetrafluoride has a suitable liquid range (bp 106°, mp −10°). It is soluble in halogenated solvents, such as methylene chloride or 1,1,2-trifluorotrichloroethane, in which fluorination can be carried out with ease in the liquid temperature range of the solvents, generally with yields of 70% or higher. Compared with

(1) P. W. Kent and K. R. Wood, British Patent, 1,136,075; *Chem. Abstr.*, **70**, 88124 (1969).