the five-membered ring exists in a twist-envelope conformation resulting in different POCH dihedral angles for the two protons.[4] We favor the latter explanation since it is difficult to explain the larger POCH coupling constant in Ic compared to Ib on the basis of overlap with the lone pair on phosphorus. Examination of a model of Ic indicates that the POCH dihedral angle approaches 180° with increasing twist of the ring. The methyl group in Ic should cause some steric interactions, compared to Ib, resulting in a larger twist in the five-membered ring. Furthermore, the chemical shifts and coupling constants for Ic and analogous phosphite esters are temperature dependent with $J_{P-H_{13}}$ changing by as much as 1.0 Hz over a temperature range of 150°.[7] This observation indicates rapid equilibration of Ic between two or more twist envelope conformations. Further work is in progress on the nmr spectra and will be reported in the future.

(7) R. H. Cox, M. G. Newton, and B. Campbell, unpublished results.

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Photochemistry of 8-Methyl-1-hydrindanones and 9-Methyl-1-decalones

Sir:

In the photochemistry of aliphatic ketones in solution, nonradiative decay always plays a substantial role among the behaviors of excited states. Ketones which do not undergo type II and related processes undergo the type I process in the gas phase with a quantum efficiency approaching unity.[1] However, ketones such as *tert*-butyl ketones may also undergo the type I process in solution, but the combined quantum efficiencies for all modes of ketone decomposition fall short of unity.[2,3] It has been suggested by Franck and Rabinowitsch that cage recombination of dissociated radicals in solution may account for the decrease in quantum efficiency,[4] but such a process has not been demonstrated in a definitive and quantitative manner. The current communication deals with the photochemistry of both cis and trans isomers of 8-methyl-1-hydrindanones (**1a** and **1b**) and 9-methyl-1-decalones (**2a** and **2b**) and its implication on the nature of nonradiative decay processes of their excited states. The systems were chosen because (1) the cage recombination of biradicals initially generated in the photolysis may lead to cis–trans isomerization of the starting ketone;[5] (2) the intersystem crossing efficiency of these ketones may be estimated by the method of Lamola and Hammond,[6] which is not applicable to acyclic *tert*-alkyl ketones, owing to the high concentration of radicals generated; and (3) the photochemistry of these ketones may provide interesting information concerning conformational effects on photochemistry.

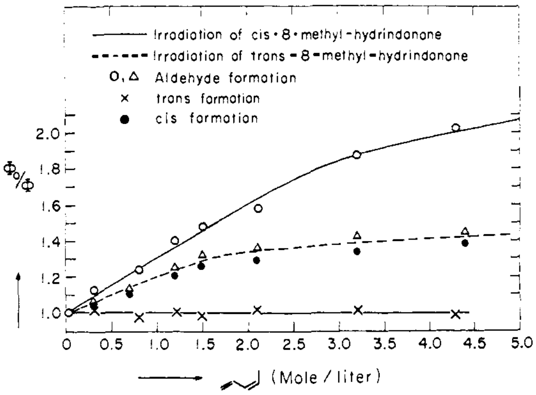


Figure 1.

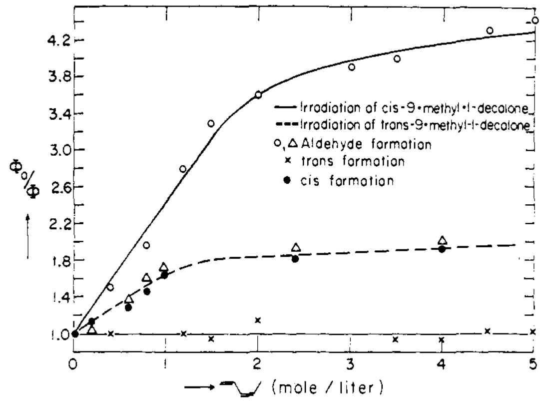
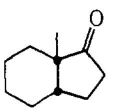
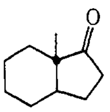


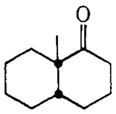
Figure 2.



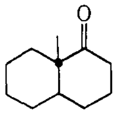
1a



1b



2a



2b

Isomeric 8-methyl-1-hydrindanones were prepared according to the method of Johnson,[7] and isomeric 9-methyl-1-decalones were prepared as a mixture following the procedure of Ireland and Marshall[8] and separated by preparative vpc. Irradiation of these compounds in hexane yielded the corresponding isomer and an unsaturated aldehyde (**3**) as the only detectable products by vpc. The unsaturated aldehydes were isolated by preparative vpc and characterized.[9] When the irradiation of these compounds in hexane (*ca.* 0.3 *M*) at 313 nm was followed quantitatively in an apparatus previously described[10] using ferrioxalate actinometry and 2-hexanone as the secondary standard, the decomposition of these ketones followed zero-order kinetics up to 15% conversion. The irradiations of these ketones were then carried out in the presence

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(1) For a review on photochemistry of aliphatic carbonyl compounds, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 377–399.

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(5) The cis–trans isomerization of 2,6-dimethylcyclohexanone in the gas phase has been reported, but no quantum yields were given and the nature of reactive states was not analyzed: R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

(6) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(7) W. S. Johnson, *J. Amer. Chem. Soc.*, **66**, 215 (1944).

(8) R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

(9) All compounds reported have been characterized by elemental analysis, crystalline derivative, and uv, ir, and nmr spectra.

(10) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

Table I

		1a	1b	2a	2b
ϕ_{ketone}		0.39 ± 0.02	0.83 ± 0.02	0.40 ± 0.02	0.56 ± 0.02
ϕ_{aldehyde}	Total	0.31 ± 0.01	0.27 ± 0.01	0.25 ± 0.01	0.25 ± 0.01
	Singlet	0.19	0.22	0.07	0.15
	Triplet	0.12	0.05	0.18	0.10
ϕ_{isomer}	Total	0.02 ± 0.01	0.46 ± 0.01	0.05 ± 0.01	0.16 ± 0.01
	Singlet	0.02	0.37	0.05	0.10
	Triplet	0.00[a]	0.09	0.00[a]	0.06
ϕ_{isc}		0.13 ± 0.05	0.13 ± 0.05	0.75 ± 0.05	0.39 ± 0.05

[a] Less than 0.002.

of various concentrations of *cis*-1,3-pentadiene in order to analyze the nature of reactive states in these reactions. Stern-Volmer plots for the hydrindanones and the decalones are presented, respectively, in Figures 1 and 2. Except for the isomerizations of **1a** and **2a**, which exhibit a linear plot with zero slope, all other processes studied exhibit nonlinear plots. Assuming that the behaviors from the triplet state will be affected by the presence of a diene, while those from the singlet excited state will be relatively unaffected, the nonlinear plots were analyzed as composites of two linear plots derived from two reactive states. The quantum yield for the individual process from the singlet excited state was determined from the intercept by extrapolating the linear plot of the less quenchable state to zero quencher concentration, while the quantum yield from the triplet state was obtained as the difference between the total quantum yield and that from the singlet excited state. The intersystem crossing efficiency was determined by the method of Lamola and Hammond using *cis*-1,3-pentadiene (1.5 *M*) as the energy acceptor.[6] All these results are summarized in Table I.[11] We found three particularly interesting experimental observations: (1) isomerization from the *cis*-ketones **1a** and **2a** to the *trans*-ketones **1b** and **2b** is not affected by the presence of diene, (2) the intersystem crossing efficiency increases in the order **1a** ~ **1b** < **2b** < **2a**, and (3) isomerization from the *trans*-ketones **1b** and **2b** proceeds with a much higher quantum efficiency than that from the *cis*-ketones **1a** and **2a**.

Judging from the figures, we found that aldehyde formation and isomerization from the *trans*-ketones **1b** and **2b** exhibit Stern-Volmer plots within experimental errors of each other. The results indicate that these two processes occur from both excited states of **1b** and **2b** but mainly from the singlet excited state. On the other hand, aldehyde formation and isomerization from the *cis*-ketones **1a** and **2a** exhibit different Stern-Volmer plots. The isomerization exhibit plots with a zero slope, while the aldehyde formations exhibit nonlinear plots. The results suggest that isomerization occurs virtually all from the singlet excited state,[12] while aldehyde formation occurs from both excited states. On the basis of conformational analysis, the *cis*-ketones **1a** and **2a** may exist in two conformations, *e.g.*, **1c** and **1d** for **1a** (see Chart I), while the *trans*-ketones **1b** and **2b** can exist only in one conformation with a 1,2-diequatorial ring juncture.[13] The alternative

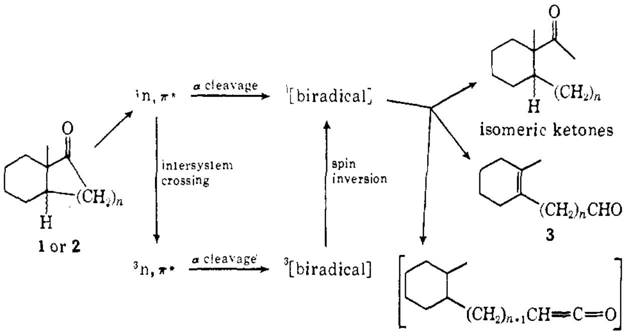
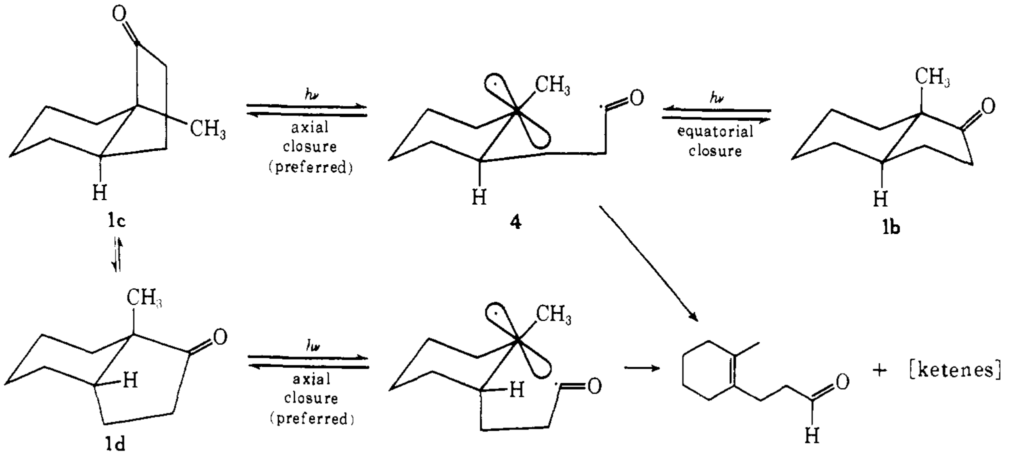


Chart I



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[11] The sum of the quantum yields of isomerization and aldehyde formation is less than that of ketone consumption. The difference may be attributed to the formation of isomeric ketenes which cannot be detected by vpc. However, in the case of **2a** and **2b**, the ketenes formed were readily detected by ir at 4.70 μ with an intensity which would account for the balance of quantum yields qualitatively.

[12] These plots may also exhibit a slight positive slope. Owing to the low quantum efficiencies of isomerization of **1a** and **2a**, a slight slope will be within experimental error of our observation.

1,2-diaxial-trans ring juncture will be too strained to exist under normal conditions. It is reasonable to assume that most photochemical processes are faster than ring inversion in cyclohexane. Therefore, only one of the two conformations of the *cis*-ketones can undergo isomerization without ring inversion (see Chart I), *i.e.*, the one with an axial α-C—C=O (**1c**), which will give **1b** in the normal 1,2-diequatorial conformation. The cleavage of an axial bond in these systems will relieve more steric strain at the transition state than the cleavage of the corresponding equatorial bond, and therefore will proceed with less activation energy or at a faster rate. The photochemistry of these ketones occurs mostly from the singlet excited state, indicating that the rate of α cleavage from the singlet excited state is at least competitive with that of intersystem crossing even with the α-C—C=O group in the equatorial position. The rate of intersystem crossing of *tert*-alkyl ketones is relatively independent of their structure.[3] Therefore, it is not surprising that the rate of α cleavage of an axial α-C—C=O bond will be appreciably faster than the rate of intersystem crossing, and that the α cleavage in **1c** with subsequent ring closure to **1b** occurs virtually all from the singlet excited state. The variation of intersystem crossing efficiencies of these compounds may also be related to the competition between the rates of intersystem crossing and α cleavage. The decalones are thermodynamically more stable than the hydrindanones, and the *cis*-decalone **2a** is more stable than the *trans*-decalone **2b**.[14] The difference in stability among these compounds may be attributed to variation in internal strain, and the relative strain in their excited states may parallel the strain in their ground state. The rate of α cleavage will decrease as the internal strain of these molecules decreases; therefore, the efficiency of intersystem crossing of **1a**, **1b**, **2b**, and **2a** will increase in the order observed.

The quantum efficiencies of isomerization and chemical nonradiative decay of the excited states of these compounds will depend on the stereochemistry of ring closure of the biradical intermediate (**4** from **1a** or **1b**; see Chart I). The intermediate, which is a derivative of the cyclohexyl radical, will give the *cis*-ketone by axial ring closure and the *trans*-ketone by equatorial ring closure. The stereochemistry of reactions of cyclohexyl radicals is known to occur preferentially from the axial side than from the equitorial side.[15] The experimental observation that photoisomerization occurs much more efficiently from *trans*-ketones than from *cis*-ketones, *e.g.*, $\phi_{1b\rightarrow 1a} = 0.46$, $\phi_{1a\rightarrow 1b} = 0.02$, may be readily explained by preferential ring closure of the biradical intermediate from the axial side.

In conclusion, we observed that these ketones (**1a**, **1b**, **2a**, and **2b**) readily undergo photoisomerization from either excited state. The results imply that inefficiency of the type I process of aliphatic ketones in solution may be due to the cage recombination of initially dissociated radicals, and such a process may occur from both the singlet excited and the triplet state.

Acknowledgment. The authors wish to thank the National Science Foundation for the support of this work and Professor Leonard Kaplan for valuable discussions. One of us (R. H. C.) wishes to thank the UniRoyal Co. for a fellowship during the course of this work.

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(16) University Fellow, 1968–1969; UniRoyal Fellow, 1969–1970; William Raney Harper Fellow, 1970–1971.

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Fluorenone-Photosensitized Isomerization of *trans*-Stilbene. Inefficiencies both in Intersystem Crossing and in Triplet Excitation Transfer

Sir:

The quantum yield of isomerization of *trans*-stilbene sensitized in benzene by fluorenone has been reported[1] to be 0.41. This quantum yield is markedly lower than the quantum yield, $\phi_{ST}\alpha$, predicted from the previously measured[2] intersystem crossing quantum yield $\phi_{ST} = 0.93$ for fluorenone in benzene and the known[1] decay fraction $\alpha = 0.59$ for stilbene triplet → *cis*-stilbene. Since other quantum yields reported at the same time[1] have since been shown to be somewhat low,[3] we have repeated this measurement. Our results, surprisingly, indicate that 0.41 is essentially correct. We have performed additional experiments which shed light on the source of this unusual quantum inefficiency. At this time we (1) report the intersystem crossing quantum yields ϕ_{ST} of fluorenone in several solvents; (2) substantiate the previously reported[4] large solvent effect on the rate constant, k_{ST}, for intersystem crossing in fluorenone; (3) demonstrate that internal conversion (k_{IC}) can be significant in the deactivation of fluorenone singlet; and (4) present results which appear to eliminate several possible alternative bimolecular processes and leave decay from a triplet exciplex as the most probable source of the inefficiency in the fluorenone triplet–*trans*-stilbene interaction.

Quantum yields of production of *cis*- and *trans*-diacetoxyethylene (DAE) in the fluorenone-sensitized fragmentation of *trans*-7,8-diacetoxybicyclo[4.2.0]octa-2,4-diene[5] were monitored at 366 nm, relative to parallel and otherwise identical experiments in which benzophenone ($\phi_{ST} \equiv 1.00$) was used as sensitizer. The relative quantum yields (Table I) thus give ϕ_{ST} for fluorenone in the three solvents employed. The value of essentially unity in cyclohexane clearly agrees with the observed[4] low fluorescence yield and the interpretation[4] that k_{ST} is largest here; furthermore, it indicates that there is no

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