

servative through the consequences of configuration interaction.^{6,11-16} It accounts for a variety of thermal structural isomerizations of cyclopropanes in a unified and theoretically plausible way. It does not provide a mechanism for the thermal epimerization of cyclopropanes, a reaction shown by many unconstrained cyclopropanes which is most simply treated as an independent competitive process.^{17,18}

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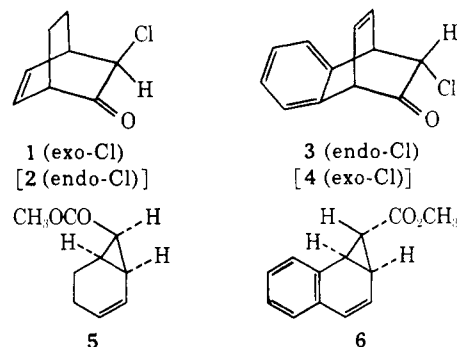
Stereoelectronic Control in the Photorearrangement of α -Chloro Ketones. Mechanistic Studies in Organic Photochemistry¹

Sir:

The current interest in photolysis of organic halides has prompted us to communicate our results on the photochemistry of a series of α -chloro ketones. Generally, irradiation of α -halo ketones leads to the photolysis of the carbon-halogen bond.²⁻⁶ Attempted mechanistic rationales have concentrated on two possible modes of C-X bond breaking, (1) homolytic^{2,4,5} and (2) heterolytic,^{3,5,6} based on the nature of the products obtained (radical abstraction or coupling *vs.* nucleophilic substitution). Recently, examples of intramolecular photorearrangements of α -halo ketones suggest that bridging occurs between the incipient electron-deficient carbon and a nonconjugated π -system.^{5,6}

Four chloro ketones (1-4) were chosen to investigate the influence of aromatic *vs.* double bond participation⁷ and the stereoelectronic requirements⁸ for rearrange-

ment. Irradiation of *exo*-2-chlorobicyclo[2.2.2]octen-3-one (1)⁹ in methanol at 300 nm gave *endo*-7-carbomethoxy- Δ^2 -norcarene (5)¹⁰ in 55% yield as the only major product.¹¹ Similarly, photolysis of *endo*-2-chlorobenzobicyclo[2.2.2]octadien-3-one (3)⁹ gave the $\Delta^{2,4}$ -norcaradiene rearrangement product 6¹² in 60% yield

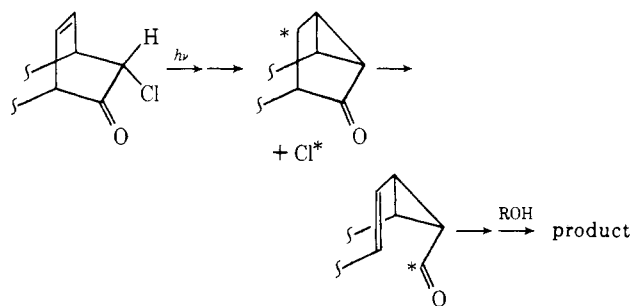


along with minor amounts of naphthalene (7, 13%) and methyl 1-naphthylacetate (8, 3%).

Contrasting results were found when *exo*-2-chlorobenzobicyclo[2.2.2]octadien-3-one (4)⁹ was irradiated. The relative yield of the $\Delta^{2,4}$ -norcaradiene (6) dropped significantly to 34% and the naphthyl ester (8) yield increased to 26%. Although the $\Delta^{2,4}$ -norcaradiene remains the major product, the competitive pathway to 8 is of equal importance in this rearrangement. Even more striking are the contrasting results for the *endo* isomer 2 which gave no Δ^2 -norcarene (5) under identical conditions.¹¹

The major products from chloro ketones 1, 3, and 4 probably arise from a carbon skeleton reorganization described in Scheme I. The results from the product

Scheme I. A Possible Rearrangement Pathway for Chloro Ketones 1 and 3



studies clearly indicate a stereoelectronic influence from the backside of the carbon-chlorine bond by the carbon-carbon double bond at some stage prior to product formation.¹³

Table I gives the results from quantum yield and multiplicity studies of chloro ketones including *exo*-2-chloronorbornenone (9).⁶ Unfortunately, the *endo* isomer was not studied for comparison of stereoelec-

(9) Synthetic details will be given in our full paper. All new compounds gave satisfactory elemental analyses.

(10) J. A. Berson and E. S. Hand, *J. Amer. Chem. Soc.*, **86**, 1978 (1964).

(11) A number of minor products were detected by vpc. None of these were characterized and were present in less than 10% yield. A substantial amount of polymeric material (ca. 15%) was formed.

(12) W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

(13) In the case of chloro ketone 4, the phenyl ring is probably functioning like the double bonds in 1 and 3. The lower efficiency of phenyl *vs.* olefin participation is seen in several photochemical studies (for example, see ref 7).

(1) For Part X, see R. G. Carlson, R. L. Coffin, W. W. Cox, and R. S. Givens, *J. Chem. Soc., Chem. Commun.*, 501 (1973).

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(4) A. N. Strachan and F. E. Blacet, *J. Amer. Chem. Soc.*, **77**, 5254 (1955).

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(8) Kaplan and Hartwig (ref 6) suggested a possible stereoelectronic requirement in the rearrangement of 9 (*vide infra*), but no evidence was provided for it.

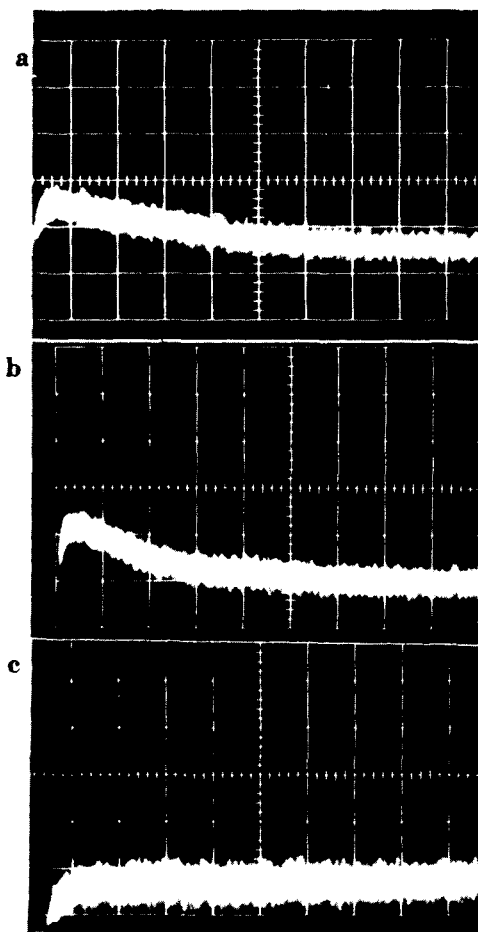


Figure 1. (a) Transient decay at 390 nm for 5.4×10^{-4} M KI in 90% H_2O –10% *tert*-butyl alcohol flashed at >250 nm. (b) Transient decay at 385 nm for 5.0×10^{-4} M phenacyl chloride and 6.0×10^{-3} M KI in 90% H_2O –10% *tert*-butyl alcohol at >300 nm. (c) Trace at 385 nm for 5×10^{-4} M **3** and 6.0×10^{-3} M KI in 90% H_2O –10% *tert*-butyl alcohol flashed at >300 nm. All scans are at 500 $\mu\text{sec}/\text{cm}$ horizontal sweep and 0.02 V/cm vertical sweep. All studies were at ambient temperature in degassed solutions in a 20×2 cm cell. The duration of the photoflash was a few μsec .

tronic effects on both the product yields and reaction efficiency. The multiplicity of the excited state leading to the rearrangement must be the singlet, since the re-

Interestingly, these results show that the stereochemistry of the halogen does not greatly alter the reactivity of the individual ketones as evidenced by the magnitude of the disappearance quantum yields for all of chloro ketones. However, competitive rates must differ accounting for the partitioning of the excited state among a number of other pathways.

The nature of the carbon–chlorine bond fission was explored by flash photolysis using iodide ion as a probe. Flash studies on aqueous potassium iodide and mixed potassium iodide–potassium bromide solutions by Grossweiner and Matheson¹⁵ have demonstrated the presence of an unstable transient identified as the diiodide radical ion (I_2^-) formed by the reaction of photo-generated halide atoms, X^\cdot (Cl^\cdot , Br^\cdot , or I^\cdot), with I^- .

Solutions were flashed with light from a xenon lamp (1600 J) through a nickel sulfate–copper sulfate filter solution and observed at 385 or 390 nm with the output from an EMI 9659 QBM photomultiplier displayed on a Tektronix 535A oscilloscope. Under these conditions, a 5.4×10^{-4} M solution of KI gave the trace in Figure 1a.

Figure 1b demonstrates the ability of iodide ion to capture transient chlorine atoms, when a solution of 5×10^{-4} M phenacyl chloride¹⁶ and 6.0×10^{-3} M KI was flashed employing a Pyrex filter.¹⁷ Under identical conditions, chloro ketone **3** gave no observable transient (Figure 1c).

The absence of the I_2^- spectrum clearly demonstrates that chlorine atoms (or any other species capable of oxidizing I^-) are not available to iodide ion. The question of heterolysis *vs.* homolysis is narrowed, therefore, to the possibility of formation of either a tight radical pair which disproportionates before solvent separation or initial heterolysis directly to the ionic intermediates. Although there is currently no evidence bearing directly on this point, recent studies on the photolysis of a large number of benzyl and substituted benzyl systems,¹⁸ alkyl^{18,19} and aryl halides,²⁰ esters,²¹ and peresters²² as well as the thermal decomposition of peroxides²³ and peresters²⁴ support, and are often best explained by, the tight radical pair–ion pair hypothesis.²⁴ Further studies on some of these reactions employing

Table I. Quantum Yields^a for Direct, Sensitized, and Quenched Photoreactions of Chloro Ketones **1–4** and **9**

Chloro-ketone	Φ_{app}	Φ_s	Φ_q	Nor-carene	Φ_{dis}	Φ_s	Φ_q
1	0.12			5	0.22		
2	<0.01			5	0.44		
9	0.8 ^b				0.8		
3	0.21 ^c	$<0.01^d$	0.2 ^c	6	0.35	0.03	0.35
4	0.11 ^e	$<0.01^d$	0.12 ^e	6	0.32	0.09	0.33

^a Irradiations were carried out by placing a 0.35 mM sample of the ketone and eicosane (standard) in 10 ml of solvent (methanol–ether (direct), methanol–ether–2.4 M piperylene (quenched), or methanol–ether–0.5 M acetophenone (sensitized)), degassing, and irradiating in a merry-go-round apparatus. Samples were withdrawn and analyzed by vpc. Light intensity (0.46 mE/hr) was determined by the method of C. A. Parker and C. G. Hatchard, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956). ^b Assumed to equal the reported disappearance quantum yield. ^c For **7**, $\Phi_{\text{app}} = 0.04$ and **8**, $\Phi_{\text{app}} = 0.01$. ^d Too small to measure. ^e For **7**, $\Phi_{\text{app}} = 0.04$ and **8**, $\Phi_{\text{app}} = 0.09$.

action was neither quenched by piperylene nor sensitized by acetophenone.¹⁴

(14) At this concentration, $>99\%$ of the light was captured by acetophenone. Energy transfer was demonstrated since the normally observed photoreduction was completely quenched by the chloro ketones.

(15) L. I. Grossweiner and M. S. Matheson, *J. Chem. Phys.*, **23**, 2443 (1955); *J. Phys. Chem.*, **61**, 1089 (1957).

(16) The photochemistry of phenacyl derivatives in aqueous and alcohol solutions has been reported by T. Laird and H. Williams, *J. Chem. Soc. C*, 1863 (1971). The major products (dibenzoylthane in water and acetophenone in alcohol irradiations) are formed *via* radical coupling reactions.

(17) This assured that the organic ketone absorbed the incident light. Since KI solutions did not absorb above 260 nm, transients were not observed for KI solutions flashed through a Pyrex filter. Also, no transient was observed at 390 nm when phenacyl chloride alone was flashed.

(18) See M. A. Ratcliff, Jr., and J. K. Kochi, *J. Org. Chem.*, **36**, 3112 (1971).

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the flash technique described in this article are in progress. In general, however, the application of this flash-scavenging technique should provide valuable information concerning the nature of short-lived intermediates in the photolysis of complex organic systems.

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Photochemistry of Carbonyl Compounds through the Enol Form. Studies on the Photorearrangement of 3-Carbomethoxyisochromanone¹

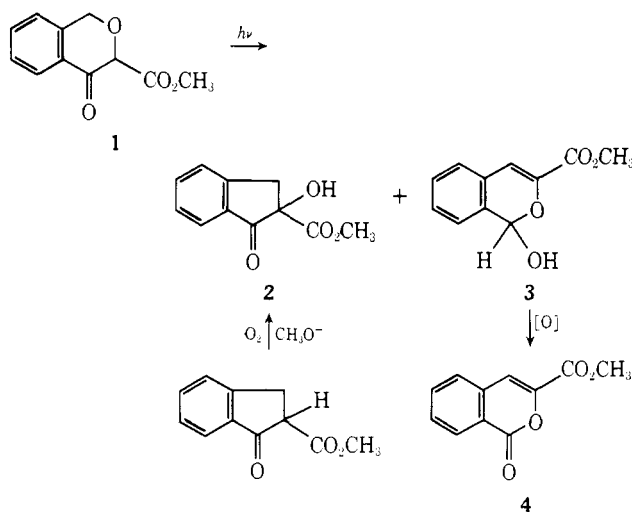
Sir:

The concept of internal photoactivated hydrogen transfer (photoenolization) was originally postulated to explain the apparent lack of bimolecular photoreduction of 2-alkyl-, 2-amino-, and 2-hydroxybenzophenones.^{2,3} Recently, a number of widely scattered and isolated reports⁴⁻⁹ have appeared which indicate that 1,3-tautomerization of certain ketones can also occur upon electronic excitation.¹⁰ Usually, the enol and enolate anions formed from the excited-state either emit phosphorescence or undergo reketonization.^{4-9,11} Of special significance and interest is the possibility of observing further photochemistry from the excited enol (or enolate) when the keto tautomer is the absorbing species. Outside of several examples of intermolecular photocycloaddition of conjugated enols,¹²⁻¹⁵

the behavior of excited state enols has not been studied in any detail. As part of a program directed toward determining the scope and limitations of the photoenolization process, we have discovered a novel intramolecular photorearrangement of a cyclic β -keto ester which involves the enol form. In this communication we describe some of the salient features associated with this reaction.

Using procedures similar to those described for the preparation of other isochromanones, 3-carbomethoxyisochromanone (**1**), mp 47–48°, was prepared in high yield from the corresponding carboxylic acid.¹⁶ The nmr spectrum of **1** in a carbon tetrachloride solution indicates the existence of an equilibrium between the keto (47%) and enol (53%) forms.¹⁷ As the polarity of the solvent increased, the concentration of the enol form increases (i.e., acetone-*d*₆, enol/keto = 1.86). The uv spectrum of **1** in methanol showed absorption maxima at 342 (ϵ 4500) and 247 nm (ϵ 9250) suggesting that, even in a dilute solution, the concentration of the enol form is substantial.¹⁸

Irradiation of **1** in methanol at 25° for 8 hr under an argon atmosphere with Pyrex-filtered light gave a 95% yield of a mixture of two compounds, **2** and **3**, in nearly equal amounts. The two components were separated by thick-layer chromatography. Elemental analysis, the ultraviolet spectrum (methanol, 227, 233, and 296 nm (ϵ 8900, 8000, and 16,300)), and the nmr spectrum (100 MHz, τ 6.15 (s, 3 H), 5.20 (broad s, 1 H), 3.43 (s, 1 H), 2.90 (s, 1 H), and 2.65 (m, 4 H)) suggested 1-hydroxy-3-carbomethoxyisochromene (**3**), mp 110–111°,



as the structure of the slower moving component. Chemical confirmation was obtained by oxidation of **3** to 1-oxo-3-carbomethoxyisochromene (**4**) which was, in turn, independently synthesized.¹⁹ Spectral and ana-

(1) Photochemical Transformations of Small Ring Carbonyl Compounds. LIV. For LIII see A. Padwa and J. Smolanoff, *Tetrahedron Lett.*, 33 (1974).

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(10) Whether the photoenolization can be viewed simply as an allowed [1,3] sigmatropic shift is a question which is currently being pursued in our laboratories.

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(16) C. N. Chefnay, *Bull. Soc. Chim. Fr.*, 1351 (1971).

(17) The nmr spectrum (100 MHz) of the keto tautomer showed signals at τ 6.25 (s, 3 H), 5.2 (s, 1 H), 4.7–5.25 (q, 2 H, J = 14.0 Hz), 2.0–3.2 (m, 4 H) while that of the enol form contained signals at τ 6.18 (s, 3 H), 6.1 (s, 2 H), 2.0–3.2 (m, 4 H), and -0.2 (s, 1 H, exchanged with D_2O).

(18) The $n \rightarrow \pi^*$ absorption associated with the keto tautomer of **1** should resemble acetophenone and consequently would be expected to have a very low extinction coefficient at 342 nm.