molecular proton transfer. Whether a glutamate anion serves this role remains to be determined; however, carboxylate ions can promote enolizations *via* general base catalysis.[14] From the dependence of V_{max} on pH, Rose[12] has calculated that the basic group has a pK of 6.5; and, from chemical studies, Burton and Waley[15] have suggested that the group is histidine.

[14] W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, Chapter 3.

[15] P. M. Burton and S. G. Waley, *Biochem. J.*, 100, 702 (1966).

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1-Phenyl- and 1,3-Diphenyl-2-indanones from the Reaction of α-Halo Ketones and Sodium Methoxide in Methanol

Sir:

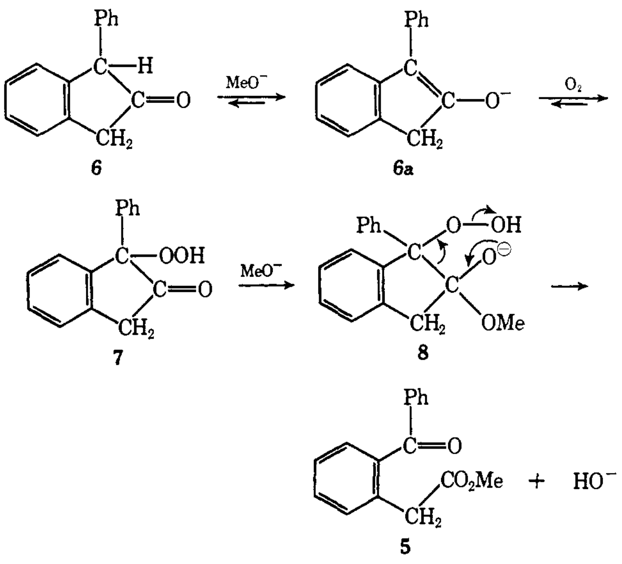
The isomeric diphenyl-α-halopropanones $Ph_2CXCOCH_3$ (**1**) and $Ph_2CHCOCH_2X$ (**2**) react with 0.05 M sodium methoxide in methanol to give essentially quantitative yields of Favorskii ester $Ph_2CHCH_2CO_2Me$ (**3**). Slow addition of 0.05 M NaOMe–MeOH to a methanol solution of **1** gave, however, only 48% **3**; 16% 1-methoxy-1,1-diphenylpropanone (**4**) and 19% methyl *o*-benzoylphenylacetate (**5**) were then formed.

Methanolysis of **1** under these conditions is too slow to account for the formation of more than about one-fourth of the amount of **4** obtained. Methanolysis of an intermediate enol allylic chloride[1] is suggested as the major source of **4**.

When the inverse addition experiment with **1** was carried out under nitrogen, 1-phenyl-2-indanone (**6**) was isolated in place of **5**. Methoxide ion converted **6** (p$K_a \cong 15$ in methanol) almost completely to its enolate ion **6a** (λ_{max} 300 nm) which was found to react at a moderate rate with oxygen to form **5**. The rate of this reaction was followed spectrophotometrically by observing the disappearance of **6a** and also by observing the appearance of **5**. A (pseudo) first-order transformation of **6** to **5** was observed. The mechanistic sequence of Scheme I is suggested, based on this kinetic result and analogy with the mechanistic evidence available from studies of the oxidative cleavage of acyclic ketones.[2]

The novel part of this mechanistic scheme is cleavage of the α C–C bond in the keto hydroperoxide **7** by addition of methoxide ion to the carbonyl group and fragmentation of the resulting adduct (**8**). (The C–C and O–O bonds need not be broken simultaneously in the fragmentation reaction.) This mode of cleavage represents an alternative to that suggested previously for such compounds, namely, the decomposition of a tautomeric form of the α-keto hydroperoxide (a four-membered-ring α-hydroxy peroxide).[3]

Scheme I



Reaction of **2** (X = Cl) under inverse addition gave **3** and **5**, but no **4**. The ratio of **3** to **5** was identical, within experimental error, with that from **1** (X = Cl). An identical **3**:**5** ratio was also obtained from **2** (X = Br). This is strong evidence for a common intermediate from **1** and **2** which gives rise to both **3** and **5**, since it would be highly unlikely that **3** and **5** would be formed in an identical ratio from all three substrates if they were being formed from each substrate by separate, individual reactions.

Judging from previous work with $PhCHXCOCH_3$ and $PhCH_2COCH_2X$ systems, which has shown that halide ion is lost from a carbanion (enolate ion) intermediate in a rapid step having a high degree of ionic character in the transition state,[4] formation of dipolar ion intermediate **9** from **1** or **2** is reasonable. The common intermediate referred to above could then be an equilibrium mixture of **9** and the corresponding cyclopropanone (**10**).[5–7] Indanone **6** can be visualized as coming from **9** and ester **3** can be visualized as coming from **10**.

Formulation of proton removal as the slow step in the reaction of **1** or **2** with methoxide ion (as shown) is supported by the observation of a relatively small $k_{Br}:k_{Cl}$ leaving group effect in each instance (3.4:1.0 for **1** and 4.2:1.0 for **2**). (Leaving group effects of the order of *ca.* 100:1 are expected when complete pre-equilibrium is established.[4]) With 0.05 M sodium methoxide the conversion of **10** (or its hemiketal) to **3** is the predominant reaction, but at low methoxide ion concentrations this second-order reaction suffers competition from the first-order transformation of **9** to **5**. At high methoxide ion concentrations only **3** is obtained.

Reaction of $Ph_2CXCOCH_2Ph$ or its isomer $Ph_2CHCOCHXPh$ in a nitrogen atmosphere with either

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[1] F. G. Bordwell, A. C. Knipe, and M. W. Carlson, *J. Amer. Chem. Soc.*, 91, 3949 (1969); F. G. Bordwell and M. W. Carlson, *ibid.*, 91, 3951 (1969).

[2] G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, Advances in Chemistry Series, No. 51, American Chemical Society, Washington, D. C., 1965, pp 112–171.

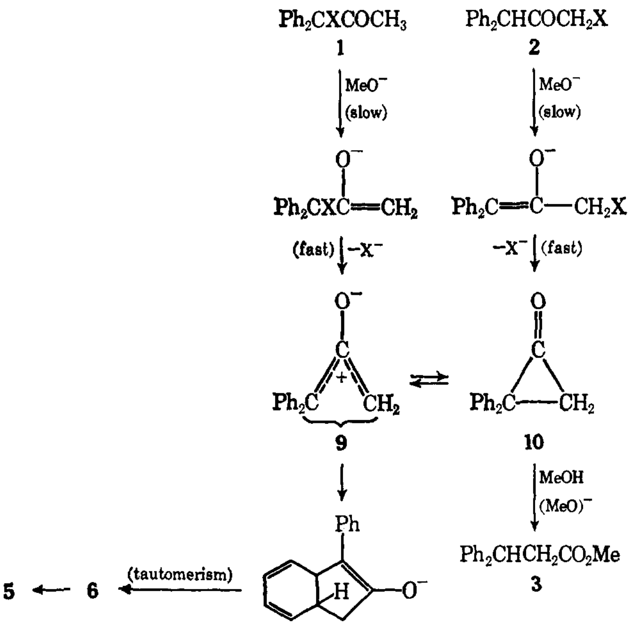
[3] W. E. Doering and R. M. Haines, *J. Amer. Chem. Soc.*, 76, 482 (1954).

[4] See F. G. Bordwell, R. G. Scamehorn, and W. R. Springer, *ibid.*, 91, 2087 (1969), and references cited therein.

[5] For calculations of the relative energies of cyclopropanones and the corresponding dipolar ions see J. G. Burr, Jr., and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954); R. Hoffmann, *J. Amer. Chem. Soc.*, 90, 1475 (1968).

[6] Cycloaddition reactions of cyclopropanones appear to be best explained by assuming reaction *via* a dipolar intermediate [N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, *ibid.*, 91, 2283 (1969)].

[7] N. J. Turro and W. B. Hammond, *Tetrahedron*, 24, 6017 (1968), have shown that cyclopropanones exist in methanol solution largely in the form of their methyl hemiketals.



low or high concentrations of sodium methoxide gave 1,3-diphenyl-2-indanone to the apparent exclusion of the usual Favorskii product. Perhaps in this instance the hemiketal ⇄ cyclopropanone ⇄ dipolar ion equilibrium strongly favors the latter species.

Acknowledgment. This work was supported by the National Science Foundation (GP 7065).

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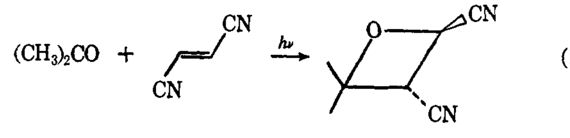
Stereoelectronic Requirements for the Photoaddition of an Electron Deficient Olefin to Cyclohexanones[1]

Sir:

Evidence has recently been presented indicating that the stereospecific photoaddition of acetone to the electron-deficient olefin *trans*-dicyanoethylene (*t*-DCE) (eq 1) proceeds *via* an initially formed complex between the ketone excited singlet state and the olefin.[2] Subsequent partitioning of this complex leads to both oxetane formation and dissociation to give ground-state acetone and *t*-DCE. Formation of the complex is envisaged as occurring through an interaction between the nucleophilic three-electron π system of n,π^* ketone singlet state and the electrophilic π system of the ground-state


(1)

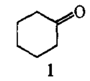
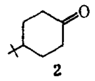
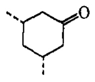
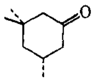
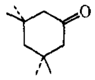
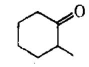
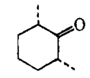
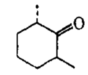
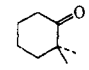
olefin. In the present work, we have measured the rates for quenching of the fluorescence of a series of alkyl-substituted cyclohexanones by *t*-DCE. The results tend to substantiate the previously proposed mechanism and more clearly indicate some of the factors which govern the rate of complex formation.

Slopes of the Stern–Volmer plots for fluorescence quenching, determined for ten cyclohexanones which have been shown to undergo photochemical oxetane formation in the presence of *t*-DCE,[3] are given in Table I. The slope of a Stern–Volmer plot (see eq 2) for the quenching of ketone fluorescence by *t*-DCE equals $k_c\tau_s$, the product of the bimolecular rate constant for complex formation (k_c) and ketone singlet lifetime (τ_s)

$$\frac{\phi_F^0}{\phi_F} = 1 + k_c\tau_s[t\text{-DCE}] \tag{2}$$

in the absence of olefin. Singlet lifetimes (τ_s), measured by monitoring the fluorescence decay *via* the single photon-counting technique,[4] as well as the rate con-

Table I

Ketone	$k_c\tau_s$[a]	τ_s,[b] nsec	k_c, M^{-1} sec^{-1} × 10^{-9} [c]
 1	9.6	2.5	3.8
 2	10.6	2.9	3.6
 3	8.6	2.6	3.3
 4	3.3	2.6	1.3
 5	3.6	3.0	1.2
 6	5.2	3.0	1.8
 7	2.6	2.9	0.9
 8	10.0	4.0	2.5
 9	6.5	3.8	1.7
 10	40.1	8.0	5.0

[a] Slopes of the Stern–Volmer plots for *t*-DCE quenching of fluorescence of acetonitrile solutions of the ketones. [b] Ketone-singlet lifetimes measured by monitoring the fluorescence decay using the single photon-counting technique.[4] [c] Error limits, ±10%.

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[1] (a) Molecular Photochemistry. XXIX. Paper XXVIII: F. D. Lewis, J. C. Dalton, and N. J. Turro, *Mol. Photochem.*, **2**, 67 (1970). (b) The authors wish to thank the Air Force Office of Scientific Research for their generous support of this work through Grant AFOSR-68-1381.

[2] (a) N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Amer. Chem. Soc.*, **90**, 3274 (1968); (b) N. J. Turro, P. A. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, **89**, 3950 (1967); (c) J. C. Dalton, P. A. Wriede, and N. J. Turro, *ibid.*, **92**, in press (1970).

[3] D. M. Pond and J. C. Dalton, unpublished results.

[4] For a discussion of this technique, see J. B. Birks and I. H. Munro, *Progr. Reaction Kinetics*, **4**, 239 (1967).