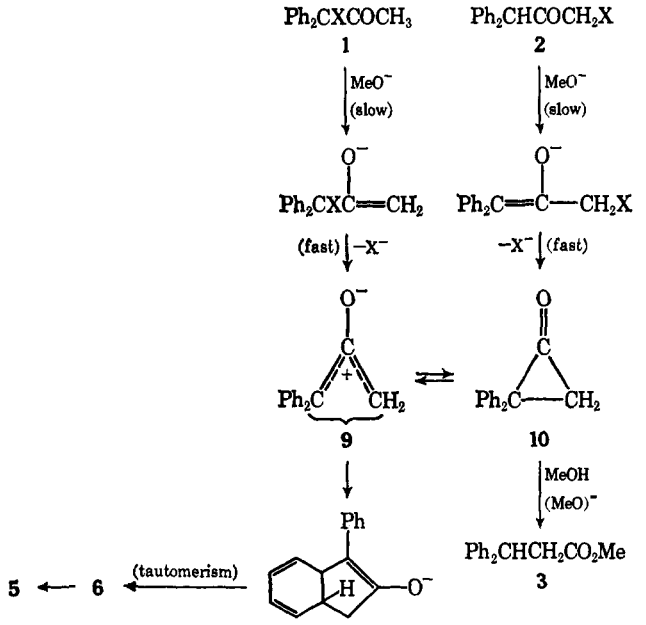

low or high concentrations of sodium methoxide gave 1,3-diphenyl-2-indanone to the apparent exclusion of the usual Favorskii product. Perhaps in this instance the hemiketal ⇄ cyclopropanone ⇄ dipolar ion equilibrium strongly favors the latter species.

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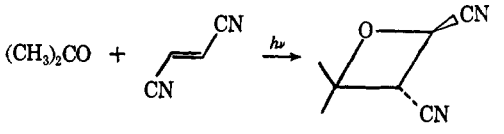
Stereoelectronic Requirements for the Photoaddition of an Electron Deficient Olefin to Cyclohexanones[1]

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)

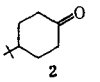
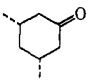
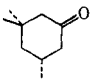
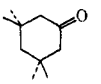
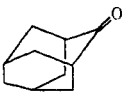
olefin. In the present work, we have measured the rates for quenching of the fluorescence of a series of alkyl-substituted cyclohexanones by *t*-DCE. The results tend to substantiate the previously proposed mechanism and more clearly indicate some of the factors which govern the rate of complex formation.

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)

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

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%.

(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.

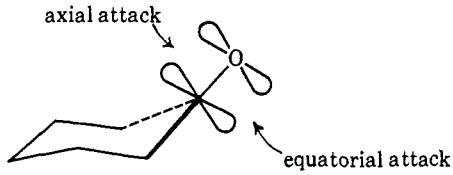
(2) (a) N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Amer. Chem. Soc.*, **90**, 3274 (1968); (b) N. J. Turro, P. A. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, **89**, 3950 (1967); (c) J. C. Dalton, P. A. Wriede, and N. J. Turro, *ibid.*, **92**, in press (1970).

(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).

stants for complex formation are also given in the table.

Attention is first drawn to cyclohexanones substituted in the three, four, and five positions. We see from **1–3** that additions of methyl groups equatorially in the three and five positions, or an equatorial *t*-butyl group in the four position has little effect on k_c. These observations are consonant with the idea that equatorial substitution at these carbons will not hinder approach to the nucleophilic π system of the carbonyl n,π^* excited singlet, and that the excited state is related to the chair conformation of cyclohexanone. On the other hand, comparison of the k_c values for **3** and **4** demonstrates the adverse effect on the rate of complex formation of an axial methyl substitution at the three or five position. The addition of a second axial methyl group (**5**) has no additional effect on k_c. Axial substituents in the three and five positions should interfere with access to the carbonyl from the same side as the substituents, thus making *axial attack* less favorable while having no effect on *equatorial attack* (see structure I). The constancy



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of k_c in going from **4** to **5** then implies that one axial methyl group in the three or five position is sufficient to block nearly all the axial attack.

Looking next at the two- and six-substituted cyclohexanones (**6–10**) we see from a comparison of k_c values for **1**, **6**, and **7** that the introduction of equatorial methyl groups in these positions causes a significant decrease in the rate constant for complex formation. Models suggest that this decrease is primarily due to steric inhibition of axial attack on the ketone excited singlet. The enhancement of the rate constant for complex formation with the *substitution* of axial methyls for equatorial methyls in the two or six position (see **7**, **8**, and **10**) lends further support to this hypothesis. In addition, however, a comparison of the k_c values for **6**, **8**, and **10** suggests that the *introduction* of axial substituents at these carbons actually leads to an increase in the overall rate constant for complex formation. This may mean that the introduction of an axial methyl group in the two or six position results in a subtle change in the electronic distribution in the n,π^* excited state causing an increase in the nucleophilicity of the ketone singlet and a faster rate of complex formation.[5]

The sensitivity of k_c to steric factors is consistent with "steric approach control" of the rate of attack on the nucleophilic π system of the cyclohexanone n,π^* excited singlet. Similar steric effects have been observed on the rates of reduction of substituted cyclohexanones by nucleophilic metal hydrides,[6] a ground-state process now thought to be governed by "steric approach control."

Work is currently in progress to determine whether the oxetanes formed upon photolysis of the cyclohexanones with *t*-DCE are those resulting from axial or equatorial attack.

(5) Cyclohexanones substituted with axial methyl groups in the two or six position have both longer fluorescence lifetimes (τ_s) and larger extinction coefficients ($\epsilon_{\lambda_{max}}$) than the analogous cyclohexanones with equatorial methyls. Also in cyclohexyl radicals, significant interaction between hydrogens in the two and six positions and the radical center is observed only for axial hydrogens. See M. C. R. Symons, *Nature*, **198**, 1196 (1963).

(6) See, for example, J. Klein, E. Dunkelblum, E. L. Eliel, and Y. Senda, *Tetrahedron Lett.*, 6127 (1968).

(7) National Institutes of Health Predoctoral Fellow, 1966–1970.

(8) Alfred P. Sloan Fellow, 1965–1970.

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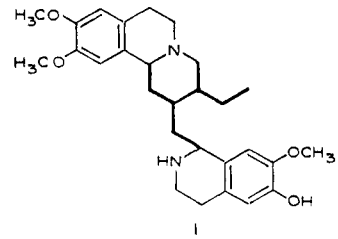
Studies on Indole Alkaloid Biosynthesis. V.[1] The Role of Glycine

Sir:

It has been established that the labeled carbon of glycine-2-^{14}C can be utilized by plants as a "C_1" source. For example, *Nicotiana rustica* L. incorporates the α carbon of glycine into the N-methyl group of nicotine as efficiently as the methyl group of methionine or choline, and ten times as rapidly as formate.[2] It has also been shown that glycine-1-^{14}C is utilized in the formation of the fungal metabolite, echinulin.[3] More recently Gear and Garg reported that glycine-2-^{14}C is a specific precursor of the $C_{9\text{-}10}$ unit in cephaeline (I,



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darkened lines), while glycine-1-^{14}C is a very poor precursor.[4] It was this latter publication which was of particular interest to us since the $C_{9\text{-}10}$ unit present in cephaeline is identical with the unrearranged nontryptophan moiety (darkened lines in II) in the Corynanthe alkaloids, for which mevalonoid origin has been established.[5] The question of glycine involvement in the biosynthesis of these indole alkaloids was therefore undertaken.

Glycine-1-^{14}C and -2-^{14}C of the same specific activity were fed to mature *Vinca rosea* L. plants by means of the cotton wick method over a period of 9 days. Isolation of the alkaloid ajmalicine (II) revealed no incorporation with glycine-1-^{14}C but reasonably good incorporation with glycine-2-^{14}C.

In order to determine the location of label in the alkaloid derived from the glycine-2-^{14}C experiment, a systematic degradation of the active ajmalicine was performed as outlined in Scheme I. The incorpora-

(1) Part IV: J. P. Kutney, V. R. Nelson, and D. C. Wigfield, *J. Amer. Chem. Soc.*, **91**, 4279 (1969).

(2) R. U. Byerrum, R. L. Hamill, and C. D. Ball, *J. Biol. Chem.*, 210, 645 (1954).

(3) A. J. Birch, G. E. Blance, S. David, and H. Smith, *J. Chem. Soc.*, 3128 (1961).

(4) J. R. Gear and A. K. Garg, *Tetrahedron Lett.*, 141 (1968).

(5) (a) For a general review and a collection of references see A. R. Battersby, *Pure Appl. Chem.*, **14**, 117 (1967); (b) for more recent references, see A. R. Battersby, A. R. Burnett, and P. G. Parsons, *J. Chem. Soc., C*, 1187 (1969).