studies[1e] are irrelevant to the question of nonclassical ions in these solvolysis reactions.

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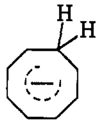
Acid–Base Behavior of Excited States. The Photochemistry of Cyclooctatetraene Dianion

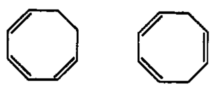
Sir:

As part of a continuing investigation[1] of the photochemistry of carbanionic species, we report our observations of the photochemical behavior of cyclooctatetraene dianion (COT^{2-}). COT^{2-} (I) when irradiated[2] in the presence of weakly acidic proton donors such as amines and terminal acetylenes abstracts a proton to give the cyclooctatrienyl anion (II). This ion eventually is further protonated to give cyclooctatrienes (III) or deprotonated to produce COT^{2-} again. The reaction is easily observed by formation of cyclooctatrienes (and their photoproducts),[4] a reaction which occurs only with irradiation in the presence of weak acids. When 1-hexyne-1-d_1 was present, deuterium incorporation was observed in both COT^{2-} and in the cyclooctatrienes.[5] The deuterium distribution was not statistical, but appreciable quantities of polydeuterated starting materials and products were observed, indicating that cyclooctatrienyl anion (II) is deprotonated at a rate comparable to its further protonation. Thus II has the property, unusual for a hydrocarbon, of acting both as an acid and as a base under the same reaction conditions. No deuterium incorporation in COT^{2-} was observed in the absence of irradiation, indicating that the first step must be photochemically initiated. Proton transfer occurs from both acetylenes and amines, with acetylenes being more effective. That proton transfer and not hydrogen atom transfer is occurring is demonstrated by generation of butyl acetylide from 1-hexyne[5] during the reaction and lack of reaction with nonterminal acetylenes. Proton removal from the cyclooctatrienes does not occur either in the dark or with irradiation. Thus, we observe that the basicity of COT^{2-} is appreciably enhanced in its excited state.[6] The subsequent reactions are visualized as ground-state protonation and deprotonation of II.


I



II


III

The excited-state behavior of acids and bases has been discussed in empirical terms.[7] In this analysis, the energies of the excited states are estimated from absorption and fluorescence spectral data; compounds can be catagorized according to whether they show blue or red spectral shifts on being transformed to their corresponding conjugate base (or acid).[8] The theory is limited, however, since it is necessary to obtain the spectra of both the acid and base in order to predict the photochemical behavior. Thus, since the spectrum of the cyclooctatrienyl anion is not known, the enhanced basicity of COT^{2-} could not have been predicted on the basis of this type of analysis.

It is clear, however, that if the long-wavelength absorption maxima of all pertinent species could be calculated, one could apply the above reasoning and predict the effect of electronic excitation on acidity and basicity. This has, in fact, been done for neutral hydrocarbons,[9,10] and the calculated results agree, at least qualitatively, with experiment.

Although Hückel calculations do not generally give good quantitative correlations with spectra[11] (particularly in the case of highly symmetric and, thus, degenerate molecules), it is nevertheless possible to make use of such calculations to provide qualitative predictions of photochemical acid–base behavior. Thus, it has been possible for us to rationalize[12] quali-

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(1) For previous work in this area see: (a) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Am. Chem. Soc.*, **87**, 4964 (1965); (b) *ibid.*, **89**, 5073 (1967).

(2) Cyclooctatetraene dianion (0.05 *M*) was prepared by addition of a solution of cyclooctatetraene in freshly distilled THF to a stirred suspension of potassium chunks in THF at 25°.[3] All solutions were dry, oxygen free, and maintained under a positive pressure of nitrogen. Weak acids were added neat to the reaction mixture which was kept in the dark until photolysis. Irradiations were carried out using a 450-W Hanovia high-pressure mercury arc lamp. Conversion was *ca.* 30% complete after 12 hr under these conditions.

(3) H. P. Fritz and H. Keller, *Z. Naturforsch.*, **16b**, 231 (1961); T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88**, 3832 (1966), and references therein.

(4) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964), and references therein.

(5) Photolysis and control reaction mixtures were worked up by the addition of these solutions to dry, neat methyl iodide in a nitrogen atmosphere. Dimethylcyclooctatrienes, which correspond to remaining cyclooctatetraene dianion, and cyclooctatrienes were isolated by preparative gas chromatography using an 8 ft × 0.25 in. 10% Ucon 50 LB550X on 60–80 Chromosorb column at at flow rate of 100 cc/min. These products were then analyzed by mass spectrometry. When methyl iodide was added to the reaction mixtures, a complex mixture of dimethylated and polymethylated cyclooctatrienes was obtained. In experiments where 1-hexyne was converted to butyl acetylide, 2-heptyne was produced in this work-up.

(6) Cyclopentadienide, the only *bona fide* carbanion previously examined, appears to undergo the unusual reaction of hydrogen atom abstraction from hydroxyl in protic solvent.[1b]

(7) T. Förster, *Z. Elektrochem.*, **54**, 42 (1950).

(8) A. Weller, *Progr. Reaction Kinetics*, **1**, 189 (1961). Also, see R. Grinter, E. Heilbronner, M. Godfrey, and J. N. Murrell, *Tetrahedron Letters*, 771 (1961).

(9) For example, see J. P. Colpa, C. MacLean, and E. L. Mackor, *Tetrahedron, Suppl.*, **2**, 65 (1963); M. G. Kuz'min, B. M. Uzhinov, and I. V. Berezin, *Zh. Fiz. Khim.*, **41**, 446 (1967); *Chem. Abstr.*, **67**, 32233 (1967).

(10) R. L. Flurry, Jr., and R. K. Wilson, *J. Phys. Chem.*, 71, 589 (1967).

(11) See, for example, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 8.

(12) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press Ltd., Oxford, 1965; A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. 1 and 2, Pergamon Press Ltd., Oxford, 1965. Predictions of relative basicity can be made by calculating the total π energy of the ground and first excited states of the base and its conjugate acid. We assume that protonation of the ground state yields the ground state and protonation of the excited state yields the excited state. Basicity of the ground state should be proportional to the π-energy change on protonation of the ground state;[13] basicity of the excited

tatively the photochemical behavior of COT^{2-} as well as that of previously observed types of compounds (phenols, ketones, amines, hydrocarbons).[8] The acidity of the cyclooctatrienes is predicted not to be greatly enhanced in the excited state, again in accord with experimental observations. It is to be expected that this simple theory will work in many cases since, although quantitative correlations of spectra are fairly poor, qualitative results have significance and one can often predict the direction of the spectral shift on going to the corresponding conjugate acid (or base). Since the electronic differences are large and may be responsible for pK changes of the order of 5–30,[7–10] it is clear that even a crude estimate is likely to give at least the correct direction of the change.

Hückel calculations suggest that carbanions probably cannot be treated as a general class. In contrast to COT^{2-}, anions of the benzylic type are predicted to be less basic when irradiated, which is also expected from the typical bathochromic shift of these anions relative to their conjugate acids.[14]

The limitations of this approach should be recognized. When calculated differences are small, they should be considered judiciously, and special care should be taken with highly symmetrical systems and those with nonbonding electrons. Nevertheless in many cases the predictions will be unambiguous, and the ease with which these calculations can be carried out makes this an attractive method for approaching new systems.[15]

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state should be proportional to the π-energy change on protonation of the excited state.

(13) Reference 11, Chapter 14.

(14) A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963); R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, **60**, 264 (1964).

(15) The same reasoning should be applicable to carbonium ion behavior as well.

(16) National Science Foundation Predoctoral Fellow, 1966–present.

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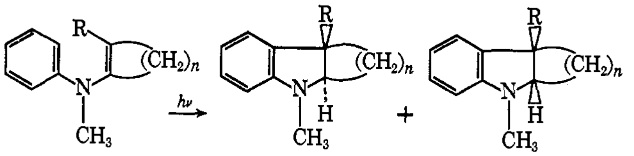
Photochemical Synthesis of 2,3-Dihydroindoles from N-Aryl Enamines[1]

Sir:

Oxidative photocyclizations of *cis*-stilbenes to phenanthrenes are well known.[2] Closely related and noteworthy in the present context are the oxidative cyclizations of diphenylamines to carbazoles and phenylthioethenes to benzothiophenes.[3] Nonoxidative cyclizations, in contrast, are quite rare. Available examples are limited to stilbenes bearing strongly electron-withdrawing substituents in the α,β positions,[4] 2-biphenylisocyanate,[5] and certain acrylic acid anilides.[6] We now report a nonoxidative cyclization of N-aryl enamines which provides a useful two-step synthesis of 2,3-dihydroindoles from ketones and N-alkylanilines.[7] The cyclization proceeds under mild conditions (irradiation in ether solution at room temperature) and should be excellent for labile compounds. The method is suitable for N-aryl enamines derived from cyclic or acyclic ketones and can be used to prepare indole derivatives in which ring C is five, six, or seven membered and offers an entry into the difficultly available *trans*-hexahydrocarbazole series. The method provides a direct means for introduction of angular substituents at C-3 and should find significant application in the synthesis of dihydroindole alkaloids.

Photochemical cyclization of 1-(N-methylanilino)-cycloalkenes (I) gives primarily the *trans* tricyclic product II except for Ia which gives only the *cis* product III.



I II III

	II % yield	III % yield
a, R = H, n = 3		52 (35)
b, R = H, n = 4	71 (55)	3
c, R = H, n = 5	68 (47)	5
d, R = CH$_3$, n = 4	77 (75)	

Degassed ether solutions of the enamine (2.3×10^{-2} M) were irradiated with a Pyrex-jacketed immersion lamp. Products were isolated by chromatography or distillation after removal of the ether. Minor products were separated by vpc. Yields given above are based on vpc analysis using known thermal conductivity ratios and an internal standard. Isolated yields are given in parentheses. Products IIb, IIIa, IIIb, and IIIc were identified by comparison with authentic samples. Product IIc was identified by oxidation to 1-methylcycloheptindole and by its spectroscopic properties.[8,9] The stereochemistry is tentatively considered to be *trans* because the product differs from the isomer available by reduction of the corresponding indole.[10] Product IId shows the expected spectral properties[11] and is not identical with the known *cis* isomer.

(1) Photochemical Transformations. XXVIII.

(2) F. R. Stermitz in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 247.

(3) (a) H. Linschitz and K. H. Grellman, *J. Amer. Chem. Soc.*, **86**, 303 (1964); K. H. Grellman, G. M. Sherman, and H. Linschitz, *ibid.*, **85**, 1881 (1963); (b) S. H. Groen, R. M. Kellogg, J. Buter, and H. Wynberg, *J. Org. Chem.*, **33**, 2218 (1968).

(4) M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, **85**, 2186 (1963); *J. Chem. Soc.*, 5544 (1964).

(5) J. S. Swenton, *Tetrahedron Lett.*, 2855 (1967).

(6) P. G. Cleveland and O. L. Chapman, *Chem. Commun.*, 1064 (1967).

(7) The N-aryl enamines were prepared by an established method (J. Hoch, *C. R. Acad. Sci., Paris*, 200, 938 (1935)). Previously unknown enamines gave satisfactory element analyses and spectra.

(8) IIc: bp 119–120° (0.5 mm); mol wt 201 (mass spectrometry); $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 296 (ϵ 2550), 251 mμ (ϵ 8090); aromatic protons (δ 6.1–7.1, m, 4 H), methine protons (δ 2.6–3.0, m, 2 H), N-methyl protons (δ 2.55, s, 3 H), and methylene protons (δ 1.2–2.4, m, 10 H); 13.36, 13.47 (sh), and 13.78 μ.

(9) All new compounds gave satisfactory elemental analyses.

(10) The isomer obtained by reduction is presumed to be *cis* because reduction of tetrahydrocarbazole and cyclopent[*b*]indole give *cis*-dihydro compounds. In these cases, however, there is a clear thermodynamic preference for the *cis* isomer. The relative thermodynamic stabilities of *cis*- and *trans*-dihydrocyclohept[*b*]indole are not clear.

(11) IId: bp 140° (5 mm); mol wt 201 (mass spectrometry); aromatic protons (δ 6.3–7.2, m, 4 H), N-methyl protons (δ 2.47, s, 3 H), methylene and methine protons (δ 0.9–2.7, m, 9 H), and C-methyl protons (δ 0.95, s, 3 H); 13.48 and 13.96 μ.