Table I

Cycloalkane, n	Rel rate, CsCHA, 100°	Strain per methylene, kcal/mol[d]	$J(^{13}C-H)$, cps
6	1.00	0	124,[e] 124 ± 3[f]
7	0.76 ± 0.09[a,b]	0.9	123[e]
8	0.64 ± 0.06[a,b]	1.2	122[e]
9	1.01 ± 0.07[a]	1.4	124 ± 3[f]
10	0.73 ± 0.05	1.2	118,[e] 121 ± 3[f]
11	0.60 ± 0.03	1.0	122 ± 3[f]
12	0.48 ± 0.05[c]	0.3	123,[e] 121 ± 3[f]
13		0.4	
14	0.345 ± 0.026	0	126 ± 4[f]

[a] At 50°. [b] From ref 1b. [c] 0.48 ± 0.02 at 50°. [d] J. W. Knowlton and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **43**, 113 (1949); S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.*, **71**, 261 (1952); J. Coops, H. van Kamp, W. A. Lambregts, B. J. Visser, and H. Dekker, *ibid.*, **79**, 1226 (1960). [e] C. S. Foote, *Tetrahedron Letters*, 579 (1963). [f] F. J. Weigert and W. R. Young, unpublished results.

thermolyses of bis(azocycloalkylnitriles).[5] In these cases the transition state resembles a planar carbonium ion or radical in which hydrogen opposition strains are reduced. By contrast, the kinetic acidities show comparatively little change along this series. The larger cycloalkanes are somewhat less reactive than cyclohexane toward CsCHA, but the $J(^{13}C-H)$ values

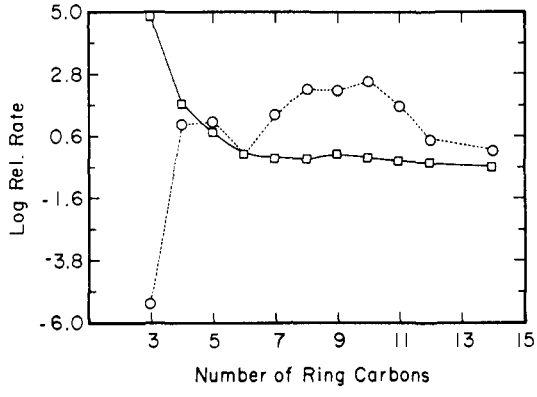


Figure 1. Comparison of relative rate pattern with ring size for acetolysis of cycloalkyl tosylates (broken line, circles) with CsCHA-catalyzed tritiodeprotonation (unbroken line, squares).

tend to be somewhat lower, indicative of less s character in the C–H bonds.[1b] The contrast between the carbanion and carbonium ion reactions is shown in Figure 1 in which the relative rate pattern for the CsCHA exchange reactions is compared to the cycloalkyl tosylate acetolysis rates. We conclude that the transition states for the CsCHA exchange reactions have conformations little different from the ground states and that, therefore, the *carbanion intermediates are pyramidal.* Note that the relatively high primary isotope effect reported previously for cyclohexane[2] implies that the transition state has substantially the structural character of the carbanion intermediate.

(5) C. G. Overberger, H. Biletch, A. B. Firestone, V. Lilker, and J. Herbert, *J. Am. Chem. Soc.*, **75**, 2078 (1953).

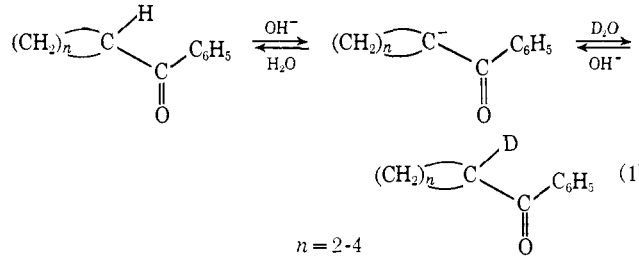
(6) National Science Foundation Predoctoral Fellow, 1964–1967.

Andrew Streitwieser, Jr., William R. Young[6]
Department of Chemistry, University of California
Berkeley, California 94720
Received October 30, 1968

Investigation of Base-Catalyzed Enolization of Cyclopropyl Ketones

Sir:

It has been reported[1] that the first-order rate constants for base-catalyzed isotopic exchange of methine hydrogen of homologous cycloalkyl phenyl ketones in deuterium oxide–triethylamine–dimethylformamide decrease as the ring size increases: three > four > five > six, approaching the open-chain analog isobutyrophenone as an approximate limit (eq 1). The



results obtained from cyclopropyl phenyl ketone are rationalizable on the basis of the s character of the carbon orbital involved in bonding with the potential enolizable hydrogen[2a] (eq 1), the report that the kinetic acidity of cyclopropane is larger than that of its higher and open-chain analogs,[2b] and the observations that base-catalyzed deuterium exchange occurs considerably faster in 2-2-diphenylcyclopropyl cyanide than in 2-methyl-3,3-diphenylpropionitrile[2c] and in cyclopropyl phenyl sulfone than in isopropyl phenyl sulfone.[2d] The behavior of cyclopropyl phenyl ketone is inconsistent, however, with experiments that reveal that nitrocyclopropanes resist neutralization and base-catalyzed deuterium exchange and are much weaker protonic acids than are their homologous or acyclic analogs,[3] and salts of cyclopropanecarboxylic acid do not undergo isotopic exchange in deuterium oxide at temperatures in which deuterium incorporation into its higher homologs and to salts of isobutyric acid is extensive.[4]

The above results have led to investigation of possible deuterium exchange for methine hydrogen in cyclopropyl phenyl ketone, isobutyrophenone, dicyclopropyl ketone, and diisopropyl ketone as catalyzed by deuteroxide ion at 60° in deuterium oxide and purified dimethylformamide. Samples of the kinetic mixtures, as

(1) By R. Dessy, Y. Okuzumi, and A. Chen in H. Shechter and M. J. Collis, and R. Dessy, Y. Okuzumi and A. Chen, *J. Amer. Chem. Soc.*, **84**, 2905 (1962).

(2) (a) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949); (b) E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 28, and references therein; (c) H. M. Walborsky, A. A. Youssef, and J. M. Motes, *J. Amer. Chem. Soc.*, **84**, 2465 (1962); (d) R. Breslow, J. Brown, and J. J. Gajewski, *ibid.*, **89**, 4383 (1967).

(3) H. B. Hass and H. Shechter, *ibid.*, **75**, 1382 (1953); (b) H. Stone, Ph.D. Dissertation, The Ohio State University, 1950; (c) P. W. K. Flanagan, Ph.D. Dissertation, The Ohio State University, 1957; (d) H. W. Amburn, Ph.D. Dissertation, The Ohio State University, 1968.

(4) (a) A. P. Bottini and A. J. Davidson, *J. Org. Chem.*, **30**, 3302 (1965); (b) J. G. Atkinson, J. J. Csakvary, G. T. Herbert, and R. S. Stuart, *J. Amer. Chem. Soc.*, **90**, 498 (1968).

taken periodically, were extracted with pentane, washed rapidly with water, concentrated, examined gas chromatographically to ensure that complicating structural alteration had not occurred, and then analyzed isotopically by nmr integration and low-voltage mass spectrometric methods. Each system was studied in duplicate or under similar conditions and the results obtained are in satisfactory agreement.

Investigation of cyclopropyl phenyl ketone (1.2 *M*) in dimethylformamide containing NaOD (0.17 *M*) and D_2O (10 *M*) reveals that deuteration is resisted in 14 hr at 60°; under identical conditions isobutyrophenone is 55–58% exchanged ($k_1 \sim 1.2 \times 10^{-5}$ sec^{-1}) in 17.5 hr.[5] Dicyclopropyl ketone (1.5 *M*) does not deuterate in NaOD–D_2O–dimethylformamide (NaOD 0.17 *M*, D_2O 10 *M*) in 30 hr at 60°, whereas diisopropyl ketone (1 *M*) in NaOD–D_2O–dimethylformamide (NaOD 0.13 *M*, D_2O 8.3 *M*) is ~40% monoexchanged ($k_1 \sim 7 \times 10^{-6}$ sec^{-1}) in 20 hr. Direct nmr analysis of reaction mixtures of dicyclopropyl ketone (1.2 *M*) in NaOD–D_2O–dimethylformamide (NaOD 0.6 *M*, D_2O 17 *M*) for 120 hr and dicyclopropyl ketone (1.4 *M*) in *t*-butyl alcohol-d_1–potassium *t*-butoxide (0.21 *M*) for 480 hr at 35°, experimental systems in which a protonic quench is avoided, did not reveal deuterium exchange into the cyclopropyl groups.[6]

The present results thus indicate that base-catalyzed deuteration of methine hydrogen in cyclopropyl ketones is resisted in spite of the s character of the exocyclic bonding orbitals. It is apparent that enolization in these systems is repressed because of steric inhibition of delocalization in their transition states. The results of this independent investigation are in agreement with that of Rappe and Sachs[7] who have found that isobutyrophenone and isopropyl methyl ketone undergo base-catalyzed deuterium exchange for methine protons whereas deuteration is resisted in cyclopropyl phenyl ketone and cyclopropyl methyl ketone.[8,9]

(5) Attempts to study base-catalyzed enolization of cyclopropyl phenyl ketone by bromination methods in acetic acid–sodium acetate have been unsuccessful. The system is complicated by rapid absorption of bromine, possibly involving cleavage of the cyclopropane ring.

(6) (a) Deuterium exchange in cyclopropyl phenyl ketone was previously studied in triethylamine–D_2O–dimethylformamide at 60°. These conditions are not exactly that of the present study. Since the active base in the former investigation is deuterioxide ion,[6b] it is clear that the present results apply directly to that of the previous study.[1] (b) R. E. Dessy, Y. Okuzumi and A. Chen, *J. Amer. Chem. Soc.*, **84**, 2899 (1962). (c) In the prior study deuterium exchange was determined spectrophotometrically from the DOH produced. It is likely that impurities in the cyclopropyl phenyl ketone led to the misleading exchange.

(7) (a) Private communication, University of Uppsala. The results of this study are in C. Rappe and W. H. Sachs, *Tetrahedron*, in press. (b) The nmr study of the resistance of dicyclopropyl ketone and cyclopropyl phenyl ketone to base-catalyzed deuterium exchange was conducted in our laboratory in 1965–1966. Upon learning of the results of Rappe and Sachs with cyclopropyl phenyl ketone using competitive nmr techniques, we reinvestigated dicyclopropyl ketone and cyclopropyl phenyl ketone by mass spectrometric methods. We acknowledge the informative exchange of information with Dr. Rappe.

(8) For further study and discussion of base-catalyzed enolization of cyclopropyl phenyl ketone as related to antiaromaticity in cyclopropenyl anions, see ref 2d.

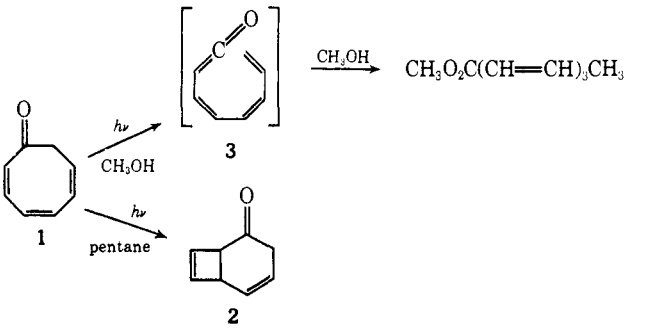
(9) We thank the National Institutes of Health, the Office of Ordnance Research, and the National Science Foundation for support of this research.

Hershel W. Amburn, Karl C. Kauffman, Harold Shechter
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
Received September 13, 1968

The Photochemistry of 2,4,6-Cyclooctatrienone. *trans,cis,cis*-2,4,6-Cyclooctatrienone[1]

Sir:

In 1962, Büchi and Burgess[2] reported that irradiation of 2,4,6-cyclooctatrienone (**1**) in methanol gave a mixture of methyl octatrienoates whereas irradiation in pentane gave a bicyclic isomer (**2**). These authors



suggested that the ester mixture was formed by methanol addition to an intermediate triene ketene (**3**). We now wish to report direct evidence for formation of the ketene **3**, recyclization of **3** to 2,4,6-cyclooctatrienone (**1**), and formation of a new product which is the precursor of the bicyclic ketone **2**.

Irradiation ($\lambda > 360$ nm) of 2,4,6-cyclooctatrienone (**1**) at −190° in a liquid nitrogen cooled infrared cell led to formation of two primary products with carbonyl absorption at 2113 and 1731 cm^{-1}, respectively.[3] After irradiation for 20 min at −190°, the 1731-cm^{-1} band was the most intense band in the spectrum (Figure 1). When the cell was warmed above −130°, the 1731-cm^{-1} band decreased in intensity with concomitant appearance of a new band at 1709 cm^{-1} and an increase in the absorbance of the carbonyl band (1668 cm^{-1}) of 2,4,6-cyclooctatrienone. The cell was allowed to warm to −95° (the 1731-cm^{-1} band had disappeared) and then cooled to −190° for comparison spectra (Figure 2). No change in the intensity of the ketene absorption at 2113 cm^{-1} was observed. The species with the 1731-cm^{-1} band clearly goes thermally to a new product(s) with a band at 1709 cm^{-1} and to 2,4,6-cyclooctatrienone but not to the ketene under these conditions. This is significant because the short-lived transient (presumably a stereoisomer of 1,3,5-cyclooctatriene) produced on flash photolysis of 1,3,5-cyclooctatriene goes thermally to 1,3,5,7-octatetraene.[5] The 1709-cm^{-1} band, although it is the correct frequency for the carbonyl group of bicyclic ketone **2**, has not been identified and could be due to dimers or polymers formed from the 1731-cm^{-1} species. It can be shown definitely (*vide infra*) that the 1731-cm^{-1} species is a precursor of the bicyclic ketone in solution at room temperature. When the cell was warmed above −80°,

(1) Photochemical Transformations. XXIX.

(2) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **84**, 3104 (1962).

(3) The irradiations were carried out with neat films or rigid glasses as in our earlier studies.[4] Temperatures are given to only two significant figures because of difficulties in measurement of exact temperatures in the cell.

(4) O. L. Chapman and J. D. Lassila, *J. Amer. Chem. Soc.*, **90**, 2449 (1968); L. L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, **90**, 5933 (1968).

(5) T. D. Goldfarb and L. Lindqvist, *ibid.*, **89**, 4588 (1967).