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]

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(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.

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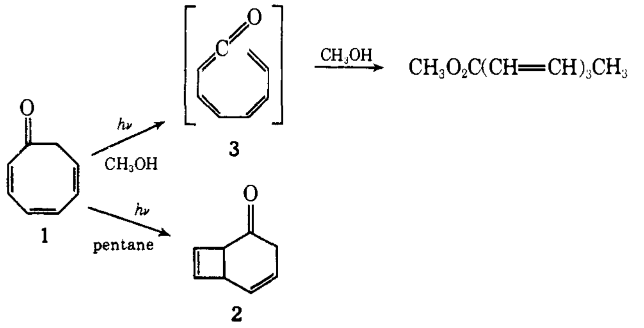
The Photochemistry of 2,4,6-Cyclooctatrienone. *trans,cis,cis*-2,4,6-Cyclooctatrienone[1]

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 (λ >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°,

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(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).

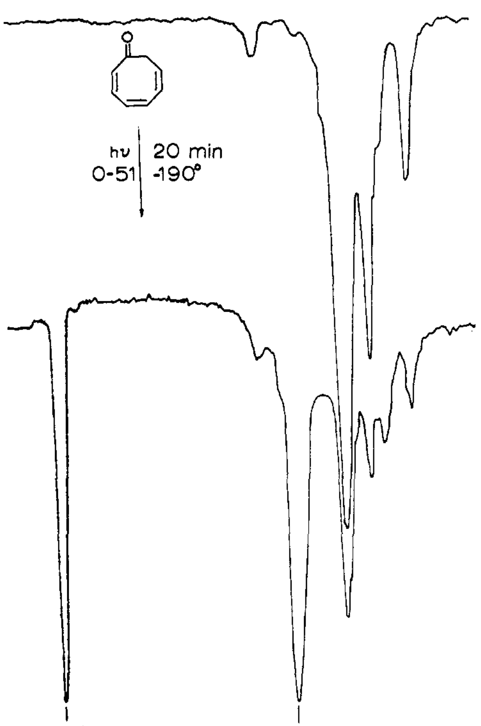


Figure 1. Infrared spectra of the carbonyl and double-bond region of 2,4,6-cyclooctatrienone before and after irradiation (Corning 0-51 filter, λ >360 nm) at −190°.

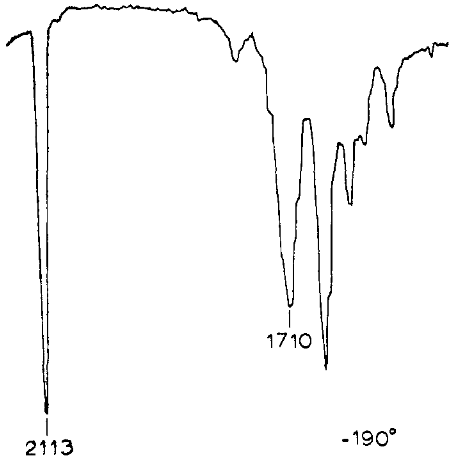
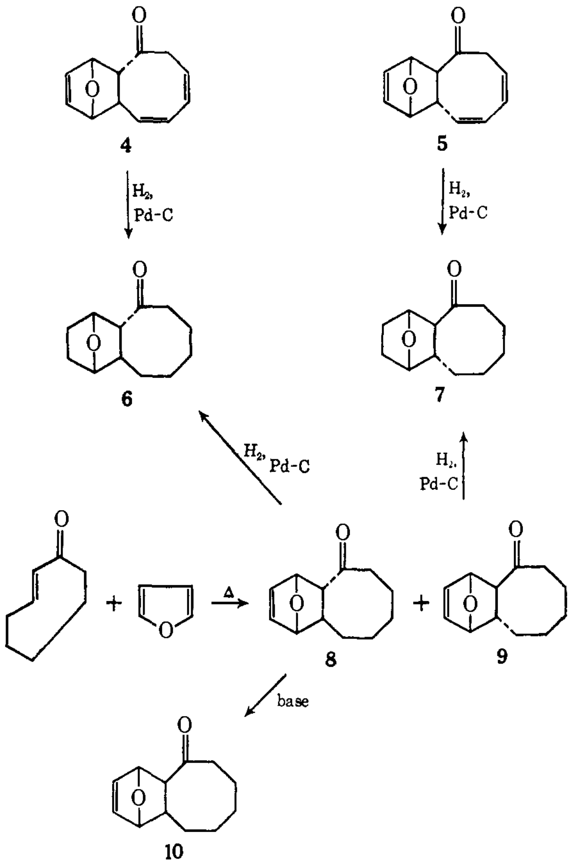


Figure 2. Infrared spectrum of the sample shown in Figure 1 after warming to −95° and recooling to −190°.

the ketene absorption (2113 cm^{-1}) disappeared with a concomitant increase ($\sim$15%) in the absorption bands of 2,4,6-cyclooctatrienone (all intensities were compared at −190°). This shows that the ketene is converted thermally to starting material. Irradiation of 2,4,6-cyclooctatrienone in a glass which contained methanol at −190° gave the ketene which could be observed spectroscopically. Warming converted the ketene to an ester. A similar experiment on a preparative scale gave the ester isolated earlier by Büchi and Burgess.[2]

The high-frequency absorption (1731 cm^{-1}) of the carbonyl group and the high reactivity of the transient together with earlier reports of the low-temperature photoisomerizations of 2-cyclooctenone[6] and 2-cycloheptenone[7,8] suggested that the transient might be *trans,cis,cis*-, *cis,trans,cis*-, or *cis,cis,trans*-2,4,6-cyclooctatrienone. Using a technique applied previously to *trans*-2-cycloheptenone[7,8] we sought to trap the 1731-cm^{-1} transient with furan. Irradiation of 2,4,6-cyclooctatrienone in an ether–isopentane glass containing furan at −190° followed by warming to room temperature gave two adducts. The adducts are formed by a thermal reaction of the 1731-cm^{-1} transient and furan, since the infrared spectrum of the furan-containing glass at −190° did not show the characteristic absorption bands of the adducts. These bands did appear as the glass was warmed in the dark. The structures of the adducts were shown to be **4** and **5**. Reduction of the adducts **4** and **5** gave perhydroadducts **6** and **7** which were compared with authentic samples prepared by reduction of the furan adducts **8** and **9** of photochemically generated *trans*-2-cyclooctenone.[6] One *trans* adduct (**8**) was epimerized by base to the more stable *cis* adduct, **10**. The other *trans* adduct (**9**) underwent more complex transformations on treatment with base. All of the adducts and their reduction products gave satisfactory elemental analyses, mass spectrometric molecular weights, and nmr and infrared spectra.



The high-frequency carbonyl absorption (1731 cm^{-1}) and the structures of the furan adducts **4** and **5** show that the unstable product is *trans,cis,cis*-2,4,6-cyclooctatrienone (**11**).

The bicyclic ketone **2** might be formed either from an excited state of *cis,cis,cis*-2,4,6-cyclooctatrienone (**1**) or

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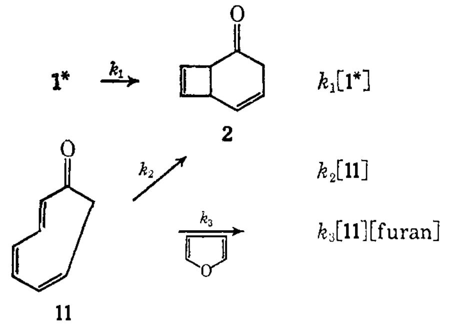
(6) P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, **86**, 2087 (1964).

(7) P. E. Eaton and K. Lin, *ibid.*, **87**, 2052 (1965).

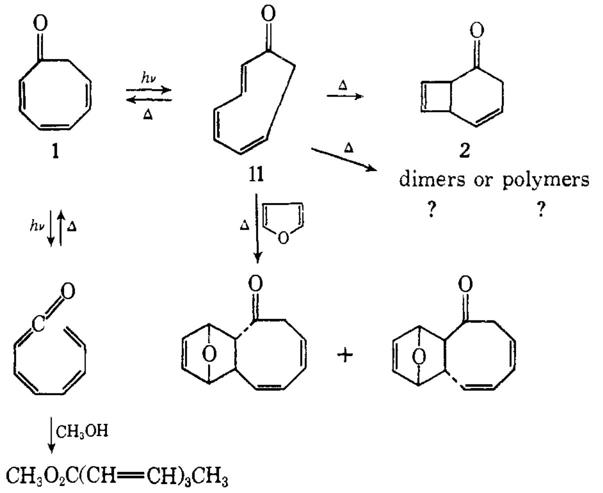
(8) E. J. Corey, M. Tada, R. LaMahieu, and L. Libit, *ibid.*, **87**, 2051 (1965).

by a thermal electrocyclic reaction of *trans,cis,cis*-2,4,6-cyclooctatrienone (**11**).[9] In the first case, the yield of bicyclic ketone will not depend in any way on the concentration of furan. In the second case, the yield of bicyclic ketone in the presence of furan will be given by the ratio $k_2[\mathbf{11}]/k_3[\mathbf{11}][\text{furan}]$; *i.e.*, the yield of



bicyclic ketone **2** will be inversely proportional to furan concentration. Irradiations at room temperature in varying concentrations of furan show that a competition does exist between cycloaddition and the electrocyclic reaction which produces bicyclic ketone **2**. It is clear that furan is not quenching an excited state of 2,4,6-cyclooctatrienone, since the disappearance of starting material is as rapid in the presence as in the absence of furan. The present state of the photochemistry of 2,4,6-cyclooctatrienone may now be summarized as shown in Scheme I.[10a]

Scheme I



Acknowledgment. This investigation was supported by a grant (GM-14305) from the National Institute of General Medical Science, U. S. Public Health Service.

[9] R. S. H. Liu[10] has shown that direct irradiation of *cis,cis*-1,3-cyclooctadiene and thermal isomerization (80°) of *cis,trans*-1,3-cyclooctadiene gives in each case bicyclo[4.2.0]oct-7-ene. Both reactions are orbital symmetry-allowed processes.

[10] R. S. H. Liu, *J. Am. Chem. Soc.*, **89**, 112 (1967).

[10a] NOTE ADDED IN PROOF. J. K. Crandall and R. P. Haseltine (*ibid.*, **90**, 6251 (168)) have trapped an intermediate in the photochemistry of 2,7-cyclooctadienone.

[11] National Aeronautics and Space Administration Trainee, 1965–1968.

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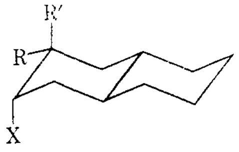
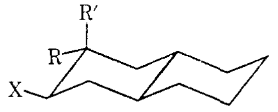
Stereochemistry of Elimination in Deamination of the *trans*-2-Decalylamines[1]

Sir:

Axial cyclohexyl primary amines undergo nitrous acid deamination with extensive elimination, typically 50–80% of the total product, whereas equatorial amines yield only 5–25% of olefin.[2–6] White and Bachelor have reported that a somewhat similar situation obtains in the related decomposition[7] of various N-nitroso amides derived from the epimeric 3-aminocholestanes.[4] We have confirmed this general pattern with respect to decompositions of the N-nitroso carbamates **1a** and **2a** derived respectively from *trans-trans*-2-decalylamine (**1d**) and *trans-cis*-2-decalylamine (**2d**). Decomposition of **1a** in boiling cyclohexane yields a product mixture composed of 80% 1- and 2-octalins and 20% of a mixture of the epimeric ethyl *trans*-2-decalyl carbonates. Under the same conditions, the equatorial epimer **2a** yields a product containing 41% olefin. In acetic acid, the proportions of olefin in the product are 78% from **1a** and 14% from **2a**.



1



2

a, X = N(NO)CO₂Et; R = R′ = H
b, X = N(NO)CO₂Et; R = D; R′ = H
c, X = N(NO)CO₂Et; R = H; R′ = D
d, X = NH₂; R = R′ = H
e, X = NH₂; R = D; R′ = H
f, X = NH₂; R = H; R′ = D

This behavior, particularly with regard to nitrous acid deamination, has been widely attributed[2,8] to the occurrence of an E2 *trans*-diaxial elimination of a proton and a nitrogen molecule from the diazonium ion in the case of the axial amine (see **3**). An alternative explanation[3] involves the removal of the *trans*-axial proton from a carbonium ion, the configurational identity of which is maintained by weak association with a counterion (a vibrationally excited ion pair; see **4**). In the case of the equatorial amine or the derived ion

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[1] This work was supported by Grant AM 06419-05 from the National Institutes of Health.

[2] J. A. Mills, *J. Chem. Soc.*, 260 (1953); C. W. Shoppee, R. E. Lack, and P. Ram, *ibid.*, *C*, 1018 (1966).

[3] E. H. White and D. J. Woodcock, "The Chemistry of the Amino Group," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1968, p 440.

[4] E. H. White and F. W. Bachelor, *Tetrahedron Letters*, 77 (1965).

[5] E. J. Jankowski, Ph.D. Thesis, University of Pittsburgh, 1966.

[6] W. Hückel and K. D. Thomas, *Ann.*, **645**, 177 (1961); W. Hückel and K. Heyder, *Chem. Ber.*, **96**, 220 (1963); K. Schreiber and H. Ripperger, *Ann.*, **655**, 136 (1962); G. Drefahl and S. Huneck, *Chem. Ber.*, **93**, 1961 (1960); A. K. Bose, *Experientia*, **9**, 256 (1953).

[7] (a) E. H. White and J. E. Stuber, *J. Am. Chem. Soc.*, **85**, 2168 (1963); (b) E. H. White and C. A. Aufdermarsh, Jr., *ibid.*, 83, 1179 (1961); (c) R. Huisgen and C. Rüchardt, *Ann.*, **601**, 1 (1956).

[8] D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc.*, 1048 (1951); W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954); A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 2888 (1957); A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, pp 104–105; H. Christol and J. M. Bessière, *Bull. Soc. Chim. France*, 2141 (1968); P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 1, W. A. Benjamin, Inc., New York, N. Y., 1965, p 40; D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963, p 164.