

dd, $J = 7.2, 4.0, 2$ H).¹³ Quantitative thermal conversion of **1** into **2** but not **3** was confirmed by nmr and ir spectroscopy and provided the following kinetic parameters: k (at 10.7°) = $(7.8 \pm 0.3) \times 10^{-5} \text{ sec}^{-1}$; k (at 32.3°) = $(9.3 \pm 0.5) \times 10^{-4} \text{ sec}^{-1}$; $\Delta H^\ddagger = 19 \text{ kcal/mol}$; $\Delta S^\ddagger = -10 \text{ eu}$ (cf. the rate of thermolysis of cyclo-nonatetraene and azonin^{3b,c}). Catalytic hydrogenation (Rh, *vide supra*) of **1** provided **1'** quantitatively. All these results are consistent with the assignment of all-*cis* structure **1** to **Y** and further suggest that **X** is a geometrical isomer, very likely (*cis*)³, *trans*-oxonin (**5**) assuming **X** is a single compound¹⁴ and the selection rule is applicable to the thermolysis.

Preliminary photochemical experiments with the irradiation of **1** and other isomers by 2537-Å light at -80° indicated that a certain number of compounds set up a photochemical "pool," monocyclic tetraenes representing major constituents. Although the exact composition is difficult to estimate due to substantial leakage leading to polymeric material (unlike (CH)₁₀ and C₉H₁₀ hydrocarbons^{3a,b}), geometrical isomerization of a double bond of an oxonin is undoubtedly an important photochemical process.^{3a,b} This situation is very similar to that observed for its nitrogen analog as we found that both **3a** and **6**^{3c,15} provided N-carbethoxyazonin (**1a** and possibly **5a**) upon low-temperature irradiation and that the photolysate upon warming afforded **2a** and **4a**.⁷ Each set of C₉H₁₀, (CH)₁₀, C₈H₈O, and C₈H₈N-R appears to behave photochemically in a similar fashion and the relative thermal stability of all *cis*- and mono-*trans*-monocyclic compounds is comparable in, at least, the first three series.³

Acknowledgment. The authors are grateful to Mr. H. Ona for his skillful technical assistance and to the National Research Council of Canada and Defense Research Board for financial support.

(13) If these nmr signals exhibited by **1** are compared with those of furan (H-2, τ 2.58, H-3, 3.36) (Varian Analytical Instrument Division, High Resolution Nmr Catalog, Sample No. 50, 1962), γ -pyran (H-2, 3.84, H-3, 5.37) [S. Masamune and N. T. Castellucci, *J. Amer. Chem. Soc.*, **84**, 2452 (1962)] and oxepin (3.8, 4.4, 4.86) [E. Vogel, W. A. Böll, and H. Günther, *Tetrahedron Lett.*, 609 (1965)], it is obvious that there is no clear evidence for the presence of any significant diamagnetic ring current.

(14) We have not yet excluded the possibility that a second double bond isomer of **1** in addition to **5** was produced and isomerized to an as yet uncharacterized C₈H₈O compound. The structural assignment of **5** is solely on the basis of the selection rule.

(15) S. Masamune and N. T. Castellucci, *Angew. Chem. Intern. Ed. Engl.*, **3**, 582 (1964).

S. Masamune, S. Takada, R. T. Seidner
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada
Received October 1, 1969

Mechanism of the Reaction of ¹Δ_g Excited Oxygen with Olefins. II. Elimination of the Concerted "Ene" Mechanism as the Route to Allylic Hydroperoxides¹

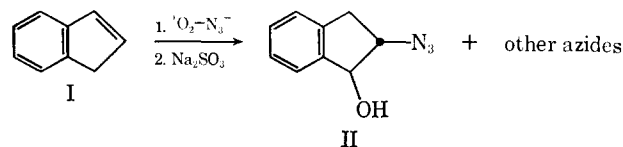
Sir:

In a previous communication we furnished chemical evidence for the existence of 1,2-dioxetanes as inter-

(1) This work was supported by grants from the American Cancer Society, California Division, the National Science Foundation, GP-12050 (to D. R. K.), and the Petroleum Research Fund (to P. R.), administered by the American Chemical Society.

mediates in carbonyl-forming reactions of ¹Δ_g oxygen with olefins.² Subsequently, Kopecky has isolated stable dioxetanes of alkyl-substituted olefins and shown that they thermally decompose to the expected carbonyl fragments.³ We have pointed out that allylic hydroperoxides could arise also from the dioxetane *via* a stereospecific, intramolecular hydrogen abstraction as an alternative route to the generally accepted "ene" mechanism.² In this communication, we show conclusively that allylic hydroperoxides are not formed *via* a concerted "ene" mechanism and furthermore furnish additional evidence for the existence of a discrete intermediate which leads to the production of allylic hydroperoxides in ¹Δ_g additions to olefins.

Our earlier observation that an intermediate in the dye-sensitized photooxidation of indene could be intercepted by nucleophilic attack of methanol prompted us to examine the effects of other nucleophiles on these reactions. When indene (**I**) was photooxidized with methylene blue at 25° in 40% aqueous acetone, 1.0 *M* in sodium azide, a sensitive mixture of azido hydroperoxides was obtained. Sulfite reduction of the mixture led to the isolation of **II**, *trans*-2-azido-1-indanol,⁵ and two other azide-containing compounds which were not identified. The complete absence of the normal reaction product, homophthalaldehyde, is consistent with the enhanced nucleophilicity of azide ion over methanol.



2,3-Dimethyl-2-butene (**III**) reacts with ¹Δ_g oxygen under a wide variety of conditions to yield only the corresponding rearranged allylic hydroperoxide (**V**),⁶ but when **III** was photooxidized with methylene blue in the presence of sodium azide (1.0 *M* in 40% aqueous methanol) only 3% of **V** was obtained; 97% of the mixture consisted of the azido hydroperoxide **IV**.⁷ **IV** is not a secondary reaction product since **V** was completely unreactive when subjected to the identical conditions required for the formation of **IV**. Photo-reactions of azide ion were also discounted since **III** was

(2) W. Fenical, D. R. Kearns, and P. Radlick, *J. Am. Chem. Soc.*, **91** 3396 (1969).

(3) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969), and personal communication.

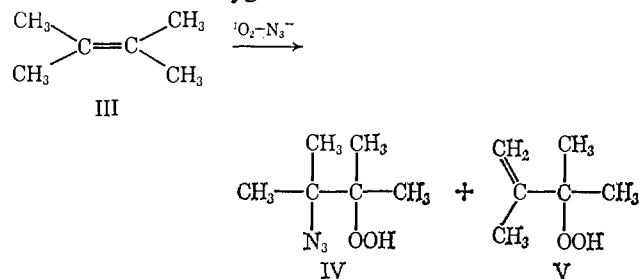
(4) The photooxidations of **I**, **III**, and **VI** were conducted as 0.1 *M* solutions with the described sensitizers and solvent systems. Irradiation times varied from 48 hr with indene to 5 hr with 2,3-dimethyl-2-butene.

(5) The structure of **II** was confirmed as *trans*-2-azido-1-indanol by its infrared absorptions at 3450 and 2140 cm⁻¹ and by its nmr spectrum which consisted of a multiplet at τ 2.80 (4 H), a broad singlet at 5.00 (1 H), a multiplet at 6.08 (1 H), a double doublet ($J = 7.5$ Hz) at 6.77 (1 H), a double doublet ($J = 7.5$ Hz) at 7.30 (1 H), and a broad solvent-dependent band at 7.10 (1 H) (10% solution in CDCl₃).

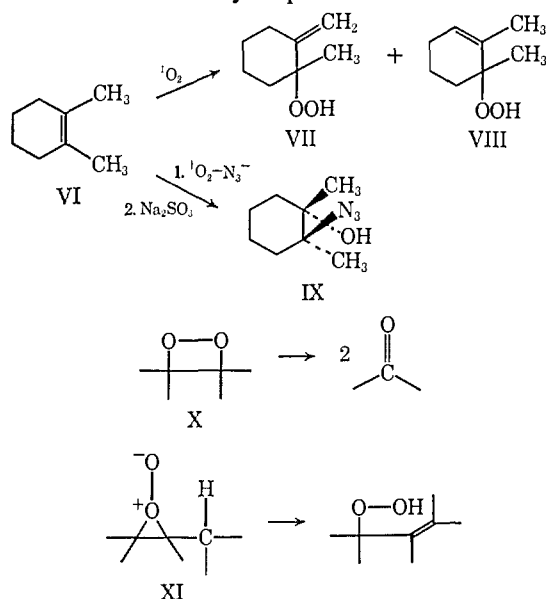
(6) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

(7) The structure of **IV** was indicated by its infrared spectrum with absorptions at 3430 and 2130 cm⁻¹, its nmr spectrum which showed two sharp singlets at τ 8.69 and 8.74, and its reduction with sulfite ion to a new compound, 2-azido-2,3-dimethyl-2-butanol. The latter compound had an nmr spectrum of two equal-intensity singlets at τ 8.71 and 8.82. The azido alcohol was synthesized independently by reaction of 2,3-dimethyl-2,3-epoxybutane with azide ion in aqueous methanol and the two were shown to be identical by comparison of their nmr and infrared spectra.

completely inert when the photolyses were conducted in the absence of oxygen.⁸



The photooxidation of 1,2-dimethylcyclohexene (VI)¹¹ results in a 9:1 mixture of the allylic hydroperoxides VII and VIII.¹⁰ When the photooxidation of VI was conducted with fluorescein in 1.0 M sodium azide solution (40% aqueous acetone) only *trans*-2-azido-1,2-dimethylcyclohexanol (IX; 60%) was obtained after reduction of the azido hydroperoxide mixture.¹¹



These results completely rule out the concerted "ene" mechanism as the route to allylic hydroperoxides. They are consistent only with a reaction path involving an intermediate susceptible to attack by a suitable nucleophile. The stereospecificity of the nucleophilic displacement indicates that the intermediate is either a dioxetane (X) or a perepoxide (XI).^{12,13} Kopecky's

(8) We cannot discount the rather remote possibility that $^1\text{O}_2$ reacts with azide ion to generate a reactive species responsible for these observations.

(9) 1,2-Dimethylcyclohexene was prepared by the method of Hammond; G. S. Hammond and T. D. Nevitt, *J. Am. Chem. Soc.*, **76**, 4121 (1954).

(10) G. O. Schenck, *Angew. Chem.*, **64**, 12 (1952). We have photooxidized 1,2-dimethylcyclohexene in 40% aqueous acetone, 1.0 M in LiCl, and find results identical with those reported by Schenck in ethanol.

(11) The structure of the *trans*-2-azido-1,2-dimethylcyclohexyl hydroperoxide results from its infrared spectrum with bands at 3440 and 2120 cm^{-1} , its nmr spectrum which had peaks at τ 8.45 (broad singlet, 8 H, $-\text{CH}_2-$), 8.70 (singlet, 3 H, CH_3), and 8.78 (singlet, 3 H, CH_3), and its reduction with sulfite ion to *trans*-2-azido-1,3-dimethylcyclohexanol (IX) (purity >95%) which had an nmr spectrum with bands at τ 8.45 (broad singlet, 8 H, $-\text{CH}_2-$), 8.69 (singlet, 3 H, CH_3), and 8.83 (singlet, 3 H, CH_3). The alcohol IX was identical in nmr and infrared spectra with a sample independently prepared by the reaction of 1,2-epoxy-1,2-dimethylcyclohexane with azide ion in aqueous methanol.

(12) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms," Interscience Publishers, London, 1966, p 88.

(13) D. B. Sharp, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, p 79P.

recent observation that the dioxetanes of alkyl-substituted olefins are relatively stable at room temperature and thermally decompose to yield only carbonyl fragments³ rules out dioxetanes as the intermediates in the formation of allylic hydroperoxides.

On the basis of our observations we propose that in the reaction of singlet $^1\Delta_g$ oxygen with olefins, carbonyl products arise from dioxetane intermediates and allylic hydroperoxides arise from perepoxide intermediates as indicated. The question of which intermediate is formed first, and whether or not they are interconvertible, remains unresolved at this time.

(14) Alfred P. Sloan Fellow.

William Fenical, David R. Kearns, Phillip Radlick¹⁴

Department of Chemistry, University of California
Riverside, California 92502

Received August 2, 1969

A Simple Synthesis of a $\text{C}_{10}\text{H}_{10}$ Hydrocarbon and an Explanation of $\text{C}_{10}\text{H}_{10}$ Photochemistry

Sir:

A number of syntheses for $(\text{CH})_{10}$ hydrocarbons have been devised,¹ and many interconversions of these by heat or light discovered.^{1d-k} The early precursors for all these syntheses are polycyclic. The possibility of simply expanding the readily available monocyclic C_9H_5^- ring² has, however, not been explored. The cyclononatetraenyl anion reacts with electrophiles² to give cyclononatetraenes,^{2b,3} and the addition of the CH^+ fragment to the anion might be effected by reaction with methylene chloride and alkyllithium in ether as it is known that the methylene chloride-alkyllithium combination generates the chlorocarbene reagent,^{4,5} that the latter reacts with organolithium compounds to yield alkylcarbene reagents,⁶ and that these undergo 1,2 migrations to yield olefins or add to double bonds.⁶ The fact is that this synthesis can be conducted effectively, that it provides a particularly easy synthesis for one $\text{C}_{10}\text{H}_{10}$ hydrocarbon (I), which previously was known only as a minor product of more difficult syn-

(1) (a) M. Avram, E. Sliam, and C. D. Nenitzescu, *Ann. Chem.*, **636**, 184 (1960); (b) E. E. van Tamelen and B. Pappas, *J. Am. Chem. Soc.*, **85**, 3296 (1963); (c) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964); (d) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966); (e) M. Jones, Jr. and L. T. Scott, *ibid.*, **89**, 150 (1967); (f) M. Jones, Jr., *ibid.*, **89**, 4236 (1967); (g) W. von E. Doering and J. W. Rosenthal, *Tetrahedron Lett.*, 349 (1967); (h) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4804 (1967); (i) S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 2727 (1968); (j) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 5286 (1968); (k) S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969); (l) E. E. van Tamelen and T. L. Burkoth, *J. Am. Chem. Soc.*, **89**, 151 (1967); (m) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *ibid.*, **86**, 3162 (1964).

(2) (a) T. J. Katz and P. J. Garratt, *ibid.*, **86**, 5194 (1964); (b) E. A. LaLancette and R. E. Benson, *ibid.*, **87**, 1941 (1965).

(3) (a) P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969); (b) G. Boche, H. Böhme, and D. Martens, *Angew. Chem. Intern. Ed. Engl.*, **8**, 594 (1969); (c) S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969).

(4) (a) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; (b) G. Köbrich, *Angew. Chem. Intern. Ed. Engl.*, **6**, 41 (1967); (c) G. L. Closs, *Topics Stereochem.*, **3**, 193 (1968).

(5) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

(6) (a) G. L. Closs, *ibid.*, **84**, 809 (1962); (b) G. L. Closs and L. E. Closs, *ibid.*, **85**, 99 (1963); (c) W. Kirmse and B.-G. von Bülow, *Chem. Ber.*, **96**, 3316 (1963); (d) W. Kirmse and D. Grassmann, *ibid.*, **99**, 1746 (1966); (e) M. J. Goldstein and S. J. Baum, *J. Am. Chem. Soc.*, **85**, 1885 (1963).