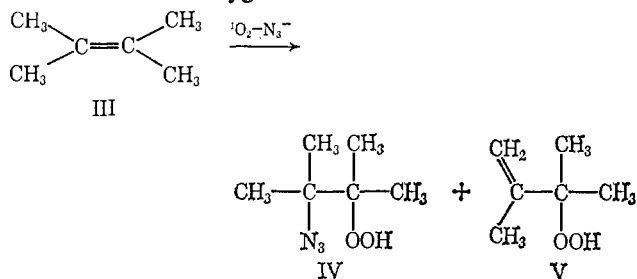
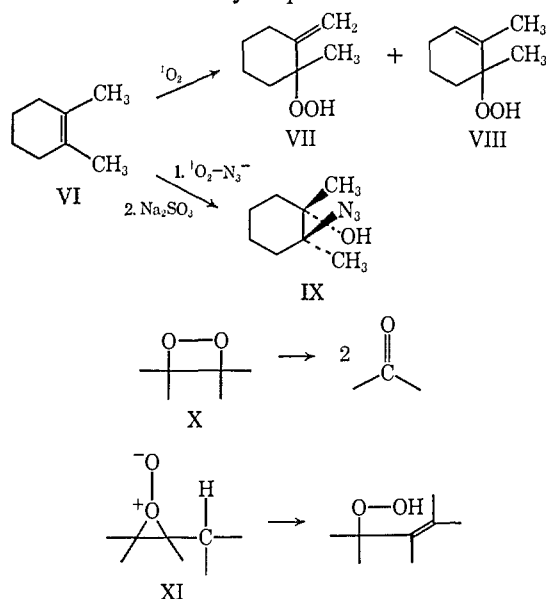


completely inert when the photolyses were conducted in the absence of oxygen.<sup>8</sup>



The photooxidation of 1,2-dimethylcyclohexene (VI)<sup>11</sup> results in a 9:1 mixture of the allylic hydroperoxides VII and VIII.<sup>10</sup> 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.<sup>11</sup>



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).<sup>12,13</sup> 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  $\text{cm}^{-1}$ , its nmr spectrum which had peaks at  $\tau$  8.45 (broad singlet, 8 H,  $-\text{CH}_2-$ ), 8.70 (singlet, 3 H,  $\text{CH}_3$ ), and 8.78 (singlet, 3 H,  $\text{CH}_3$ ), and its reduction with sulfite ion to *trans*-2-azido-1,3-dimethylcyclohexanol (IX) (purity >95%) which had an nmr spectrum with bands at  $\tau$  8.45 (broad singlet, 8 H,  $-\text{CH}_2-$ ), 8.69 (singlet, 3 H,  $\text{CH}_3$ ), and 8.83 (singlet, 3 H,  $\text{CH}_3$ ). 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 fragments<sup>3</sup> 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.

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### 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,<sup>1</sup> and many interconversions of these by heat or light discovered.<sup>1d-k</sup> The early precursors for all these syntheses are polycyclic. The possibility of simply expanding the readily available monocyclic  $\text{C}_9\text{H}_5^-$  ring<sup>2</sup> has, however, not been explored. The cyclononatetraenyl anion reacts with electrophiles<sup>2</sup> to give cyclononatetraenes,<sup>2b,3</sup> and the addition of the  $\text{CH}^+$  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,<sup>4,5</sup> that the latter reacts with organolithium compounds to yield alkylcarbene reagents,<sup>6</sup> and that these undergo 1,2 migrations to yield olefins or add to double bonds.<sup>6</sup> 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).

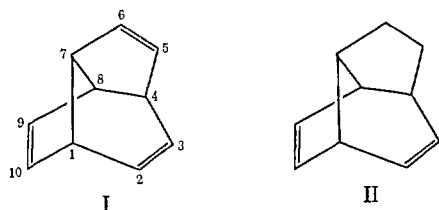
(3) (a) P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969); (b) G. Boche, H. Böhme, and D. Martens, *Angew. Chem. Intern. Ed. Engl.*, **8**, 594 (1969); (c) S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969).

(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).

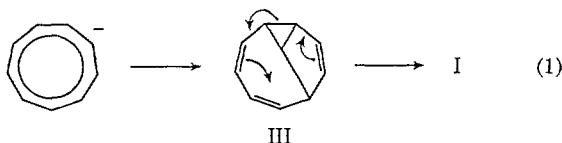
(6) (a) G. L. Closs, *ibid.*, **84**, 809 (1962); (b) G. L. Closs and L. E. Closs, *ibid.*, **85**, 99 (1963); (c) W. Kirmse and B.-G. von Bülow, *Chem. Ber.*, **96**, 3316 (1963); (d) W. Kirmse and D. Grassmann, *ibid.*, **99**, 1746 (1966); (e) M. J. Goldstein and S. J. Baum, *J. Am. Chem. Soc.*, **85**,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

theses,<sup>1d,f,h,i,7</sup> and that the mechanism by which I forms is not only interesting but suggests two unifying intermediates (III and VIII) that have not previously been considered for the transformations of (CH)<sub>10</sub> hydrocarbons.



When lithium cyclononatetraenide (0.27 mol) in ether<sup>8</sup> (600 ml) was mixed with methylene chloride (0.60 mol) at  $-60^{\circ}$ , *n*-butyllithium (0.6 mol) in *n*-hexane then added at  $-30$  to  $-40^{\circ}$ , and the mixture allowed to warm to room temperature overnight, we obtained after extraction and crude distillation 25 g of a fraction containing 48% I by glpc (35% yield), distillation of which gave as the purest fraction 7.3 g of material that was more than 82% I, contaminated with 15% of its dihydro derivative II,<sup>1f,9</sup> and 3% 8,9-dihydroindene.<sup>2</sup> Pure I and II could be isolated by glpc.<sup>11</sup> *trans*-Dihydronaphthalene appeared to be in the higher boiling fractions for its characteristic nmr peaks were observed,<sup>1j,1</sup> and naphthalene<sup>1f,j,10</sup> could be isolated from the distillation residues in a yield of 5% after crystallization and sublimation.

The simplest explanation for the formation of I is that indicated in eq 1: it is formed by the Cope rearrangement<sup>12</sup> of a presumed precursor III. This mech-



anism requires that the corresponding reaction with CD<sub>2</sub>Cl<sub>2</sub> give the hydrocarbon monodeuterated only at C<sub>1</sub>. In fact the product obtained is greater than 98% monodeuterated,<sup>13</sup> the proton nmr resonance of only one of the hydrogens is changed in intensity (by exactly half), and the resonance changed is the one at  $\tau$  7.62, which we attribute to H<sub>1</sub>.<sup>1f,14</sup>

(7) The structure assigned this material in ref 1h is revised in ref 1i.

(8) If ether<sup>8a</sup> is replaced with tetrahydrofuran the yield is much reduced [cf. G. Köbrich and H. R. Merkle, *Chem. Ber.*, **99**, 1782 (1967)].

(9) II is known to form when I is heated,<sup>1f,10</sup> and *trans*-dihydronaphthalene, another product, also seems to effect hydrogenation.<sup>1j</sup>

(10) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **89**, 4534 (1967).

(11) We are grateful to Professor Maitland Jones, Jr., for identifying the spectra of these samples with his.

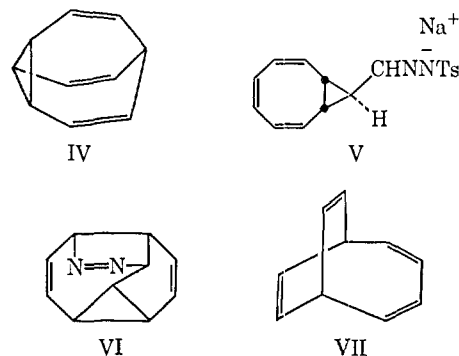
(12) (a) S. J. Rhoads, "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 11; (b) W. von E. Doering *et al.*, *Tetrahedron*, **23**, 3943 (1967).

(13) Mass spectrometry.

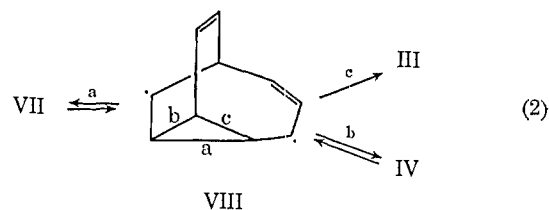
(14) There are two reasons for believing that the peak at  $\tau$  7.62 is due to H<sub>1</sub>. The experiment with CD<sub>2</sub>Cl<sub>2</sub> and proton decoupling experiments show that the 3.3-Hz separation of the peaks at  $\tau$  4.20 is caused by coupling with the proton giving the peaks at  $\tau$  7.62. This is exactly the separation required by the 6.5-Hz coupling [ $J_{1,2}$ ] measured in various bicyclo[3.2.1]octenes.<sup>15</sup> Secondly, the peak at  $\tau$  3.45 is split into a clean doublet while the peak at  $\tau$  4.50 is split into a more complex multiplet by coupling with the protons, causing the  $\tau$  7.62 and 6.90 peaks, respectively. The complexity would be expected from the coupling of the isochronous protons at C<sub>7</sub> and C<sub>8</sub> because they are adjacent.

(15) (a) S. A. Cerefica, unpublished measurements in this laboratory on deuterated bicyclo[3.2.1]octadienes; (b) C. W. Jefford and K. C. Ramey, *Tetrahedron*, **24**, 2927 (1968); (c) H. Tanida, K. Tori, and K. Kitahonoki, *J. Am. Chem. Soc.*, **89**, 3212 (1967).

The hydrocarbon I has previously been obtained in four ways:<sup>16</sup> by photolysis of IV,<sup>1f</sup> of V,<sup>1h</sup> of VI,<sup>1i</sup> and of VII.<sup>1j</sup> As a product of these photolyses it is always accompanied by either IV or VII. Although other ex-

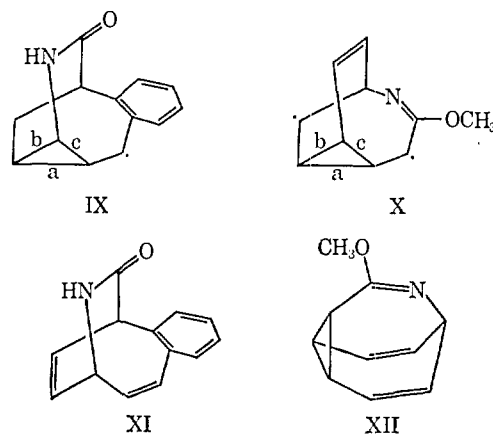


planations have been given for these transformations,<sup>1f,11</sup> all can be formulated as proceeding by way of III, which from V can arise by valence isomerization to the cyclononatetraene and then by carbene addition, and which from IV, VI, and VII can arise from the reasonable<sup>17</sup> precursor VIII (eq 2). Cleavage of bond a in



VIII gives VII, b gives IV, and c gives III. III isomerizes thermally to I. This accounts for the photochemical interconversion of IV and VII and the simultaneous formation of I.

Cleavage of bonds a, b, and c in the analogous intermediates IX and X gives the puzzling products of the photolysis of XI<sup>18</sup> and XII.<sup>19</sup> Related reactions<sup>18,20</sup> can similarly be accounted for.



(16) It is also obtained by photolysis of *cis*-dihydronaphthalene,<sup>1d</sup> but because of the latter's photochemical conversion to VII,<sup>1e,j</sup> the likely precursor of I is VII.

(17) (a) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969); (b) H. E. Zimmerman, R. S. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969); (c) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

(18) (a) L. A. Paquette and J. R. Malpass, *ibid.*, **90**, 7151 (1968); (b) L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, *ibid.*, **91**, 5296 (1969).

(19) L. A. Paquette and G. R. Krow, *ibid.*, **90**, 7149 (1968).

(20) L. A. Paquette and T. J. Barton, *ibid.*, **89**, 5480 (1967).

**Acknowledgments.** We are grateful to the National Institutes of Health (MH-08912) for its support and Badische Anilin und Sodafabrik, A.G., for gifts of cyclooctatetraene.

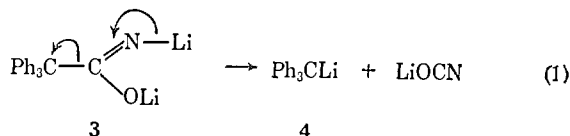
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New York, New York 10027  
Received October 1, 1969

### A Novel Decarboxamidation of Certain Primary Carboxamides by Means of *n*-Butyllithium<sup>1</sup>

Sir:

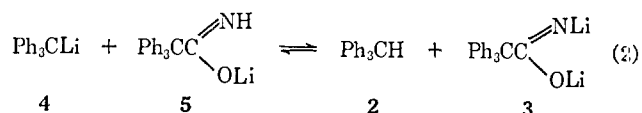
We wish to report that certain primary carboxamides undergo decarboxamidation when treated with *n*-butyllithium. Thus 2,2,2-triphenylacetamide (**1**) in tetrahydrofuran (THF) solution was treated with 1.2 equiv of *n*-butyllithium in hexane. The red solution was refluxed for 6 hr to give, after work-up, a 65% yield of triphenylmethane (**2**) and 21% of recovered **1**. Starting material was quantitatively recovered when less than 1 equiv of the organolithium reagent was used.

Apparently the reaction proceeds by diionization at the carboxamide function<sup>2</sup> to give a species such as **3**, which undergoes carbon-carbon bond cleavage (eq 1)



to give trityllithium (**4**)<sup>3</sup> and lithium cyanate. Lithium cyanate was detected in the reaction mixture as follows. Upon work-up, the water-soluble fraction was freeze-dried to produce a solid residue. All of the bands in the ir spectrum of the residue accorded with those of an authentic mixture of lithium cyanate and lithium hydroxide, and in particular each spectrum exhibited a strong band at 4.46  $\mu$ , ascribed to cyanate.<sup>4</sup>

If dianion **3** is required for cleavage, it is interesting that good yields of **2** are obtained with only 1.2 equiv of *n*-butyllithium. In this case the reaction mixture would be expected to contain mostly monoanion **5**, along with only 20 mol % of dianion **3**. Decomposition of **3** (see eq 1) would produce trityllithium (**4**). Apparently dianion **3** and monoanion **4** are of comparable basicity,<sup>5</sup> and **4** can abstract a proton from monoanion **5** (eq 2).



The additional dianion **3** so produced then decomposes (eq 1), and so on.

(1) Supported by the National Science Foundation.

(2) Trianions previously prepared from phenyl- and diphenylacetamide with *n*-butyllithium [see E. M. Kaiser, R. L. Vaulx, and C. F. Hauser, *J. Org. Chem.*, **32**, 3640 (1967)] involved diionization at the carboxamide function.

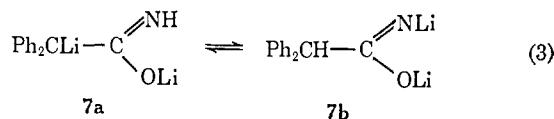
(3) The red color observed in the reaction mixture is characteristic of  $\text{Ph}_3\text{CLi}$  in THF.

(4) See L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958, p 267.

(5) Some support for this assumption is given by the fact that the monoanion of **2** ( $\text{p}K = 33$ ) is expected to be much more basic than the monoanion of **1** ( $\text{p}K \sim 25$ ).

Interestingly, even 2,2-diphenylacetamide (**6**) underwent a similar decomposition. Thus, treatment of **6** in THF with 1.2 equiv of *n*-butyllithium gave a yellow<sup>6</sup> solution which was refluxed 2.5 hr to give diphenylmethane in 86% yield. Again, starting material was quantitatively recovered when less than 1 equiv of *n*-butyllithium was used.

Although the predominant dianion in this case, **7a**, is probably that resulting from loss of the methinyl hydrogen, **7a** apparently is in equilibrium with dianion **7b** which results from diionization at the carboxamide function (see eq 3).<sup>7</sup> Dianion **7b** is considered to



undergo decomposition in a manner analogous to **3**.

Treatment of lithium cyanate with lithium diphenylmethide under typical reaction conditions gave only recovered starting material. The irreversibility of the overall reaction may be due to the insolubility of lithium cyanate in the medium.

Although decarboxylation of acids has often been effected through the anion, the analogous reaction of primary carboxamides has not been reported. The decompositions reported in the present paper appear to be the first examples of decarboxamidation<sup>8</sup> effected through ionization. This novel type of reaction should be useful in synthesis. Further studies are in progress on the scope, mechanism, and synthetic utility of this reaction.

**Acknowledgment.** We thank the National Science Foundation for the award of a Science Faculty Fellowship (to H. A. S.).

(6) The color is characteristic of  $\text{Ph}_2\text{CHLi}$  in THF.

(7) Support for existence of an appreciable quantity of **7b** at equilibrium is afforded by previous results (see Kaiser, *et al.*, ref 2), confirmed in the present study, that treatment of the dilithio salt of **6** with excess deuterium oxide incorporates only 0.7 methinyl deuterium atom per molecule.

(8) Loss of the carboxamide group as urea has been reported for certain  $\alpha,\beta$ -acetylenic carboxamides upon treatment with amide ion [J. C. Craig and M. Moyle, *J. Chem. Soc.*, 4402 (1963)]; however, this cleavage is nucleophilic acyl substitution by amide ion.

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Received October 23, 1969

### Nitrogen Inversion without Retarding Factors<sup>1</sup>

Sir:

Angle strain<sup>2</sup> and electronegative substituents<sup>3</sup> have been widely utilized to bring the rate of nitrogen inversion within the range of dynamic nuclear magnetic resonance (dnmr) methods.<sup>4</sup> Because of the difficulty in

(1) This work was supported by the National Science Foundation (Grant GP-9257) and by the Petroleum Research Fund, administered by the American Chemical Society (PRF 2970-A4,5).

(2) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5126 (1956).

(3) J. M. Lehn, B. Munsch, P. Millie, and A. Veillard, *Theoret. Chim. Acta*, **13**, 313 (1969); D. L. Griffith and B. L. Olson, *Chem. Commun.*, 1682 (1968). The more important factor may actually be the presence of lone pairs on these substituents.

(4) G. Binsch, *Topics Stereochem.*, **3**, 97 (1968). For an alternative procedure, see L. B. Holzman, Ph.D. Dissertation, Yale University, 1968.