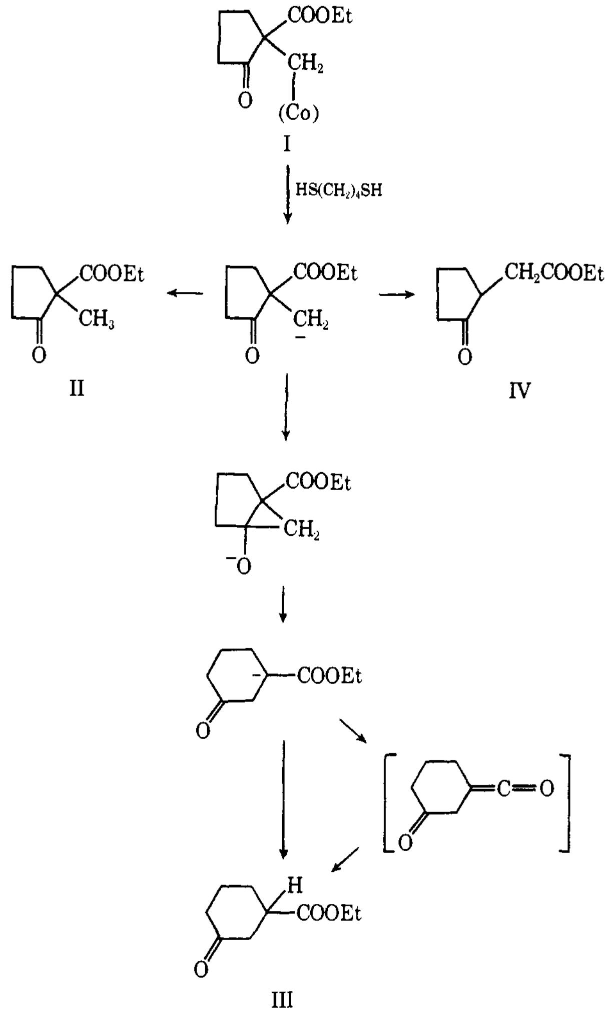
Scheme I



tems have been unsuccessful,[10] presumably because the carbanion adds a proton before the groups are rotated into a position for the carbanion to attack the carbonyl group and rearrange. The orientation is favorable in the cyclic ester. In the enzymatic reaction, the substrate is probably held in the proper position by the enzyme to favor rearrangement through a stabilized homoenolate ion.[11]

Acknowledgment. We gratefully acknowledge the assistance of Drs. Roy Teranishi and Robert Lundin at the Western Regional Research Laboratory. This work was supported by the National Institutes of Health (GM 08285).

[10] (a) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **89**, 1999 (1967); (b) J. Fox, Dissertation, University of California at Davis, 1970.

[11] A. Nickon and J. L. Lambert, *J. Amer. Chem. Soc.*, **88**, 1905 (1966).

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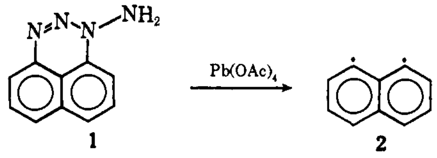
Received April 21, 1971

Addition of 1,8-Dehydronaphthalene to Cyclopentadiene

Sir:

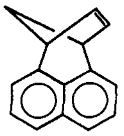
In 1965 Rees and Storr reported that oxidation of 1-aminonaphtho[1,8-*de*]triazine (**1**, eq 1) provides a convenient source of the highly reactive intermediate, 1,8-dehydronaphthalene (**2**).[1] At the same time these



(1)

authors demonstrated that **2** adds 1,2 to olefins, in a stereospecific manner. In contrast, *o*-benzyne undergoes nonstereospecific 1,2 cycloadditions,[2] and prefers to react as a dienophile.[3,4] Recent calculations by Hoffmann and coworkers suggest that the antisymmetric combination of 1,8-dehydro orbitals in **2** is of lower energy than the symmetric combination, and that 1,2 addition to olefins should be favored over 1,4 addition to conjugated diene systems.[5] We wish to report the first study of the reactions of 1,8-dehydronaphthalene (**2**) with a conjugated diene.

When **2** was generated[6,7] by lead tetraacetate oxidation of **1** in a methylene chloride solution of cyclopentadiene, a mixture of three 1:1 adducts was isolated in *ca.* 20% yield. These were purified by chromatography on basic alumina, followed by preparative glpc (5 ft × 1/4 in. HMDS-treated column of 10% SE-30 on 60–80 mesh Chromosorb W at 180°), and identified as **3**, **4**, and **5** on the basis of the evidence presented below.[8]



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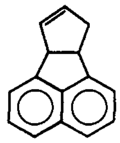

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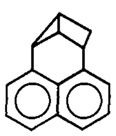

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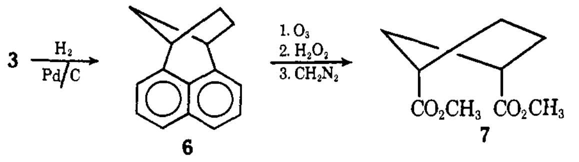
The component of shortest glpc retention time, **3** (9% of the 1:1 products), had the following nmr spectrum (60 MHz): aromatic protons, τ 2.60 (6 H, m), olefinic protons, 3.92 (2 H, broad s), a broad, complex doublet ($J \sim 9$ Hz, 2 H) at 6.28, and a multiplet at 7.7 (2 H). Upon hydrogenation (5% Pd/C), **3** afforded a new compound **6** whose nmr spectrum (60 MHz) consisted of aromatic hydrogens, τ 2.75 (6 H), a broad singlet at 6.67 (2 H), and a broad multiplet (7.7–8.5, 6 H). Ozonolysis of **6**, followed by esterification of the resulting acid with diazomethane, afforded *cis*-1,3-dicarbomethoxycyclopentane (**7**, eq 2),[9] as de-



(2)

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[1] C. W. Rees and R. C. Storr, *Chem. Commun.*, 193 (1965).

[2] See M. Jones, Jr., and R. H. Levin, *J. Amer. Chem. Soc.*, **91**, 6411 (1969), and references cited therein.

[3] G. Wittig, *Angew. Chem.*, **69**, 245 (1957).

[4] R. G. Miller and M. Stiles, *J. Amer. Chem. Soc.*, **85**, 1798 (1963).

[5] R. Hoffmann, A. Imamura, and W. J. Hehre, *ibid.*, **90**, 1499 (1968).

[6] C. W. Rees and R. C. Storr, *J. Chem. Soc. C*, 760 (1969).

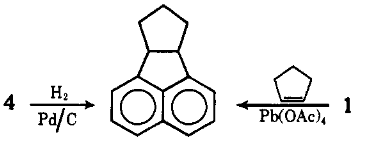
[7] R. W. Hoffmann, G. Guhn, M. Preiss, and B. Dittrich, *ibid.*, 769 (1969).

[8] Mass spectra of samples of **3**, **4**, and **5** confirmed the $C_{15}H_{12}$ formulation. These products were also shown to be stable under the separation and purification conditions.

[9] J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, **93**, 725 (1971).

termined by comparison with authentic material. The structures **6** for the hydrogenation product, and **3** for precursor, follow unambiguously from these data.

The second component (47%) displayed an nmr spectrum (60 MHz) consisting of aromatic protons, τ 2.80 (6 H), olefinic protons, 4.47 (2 H) as an AB multiplet, and resonances at 5.5 (1 H, m), 5.94 [triplet (J = 9 Hz) of doublets ($J \sim$ 4 Hz)(1 H)], and 6.87–7.67 (2 H, m). Upon hydrogenation (5% Pd/C) this compound afforded a dihydro derivative **8** (mp 68–69°), whose nmr spectrum (60 MHz) consisted of transitions at τ 2.71 (6 H, m), 6.02 (2 H, broad singlet), and 7.71–9.12 (6 H, m). Compound **8** was prepared independently by oxidation of **1** in the presence of cyclopentene (eq 3). The second adduct must therefore be **4**.



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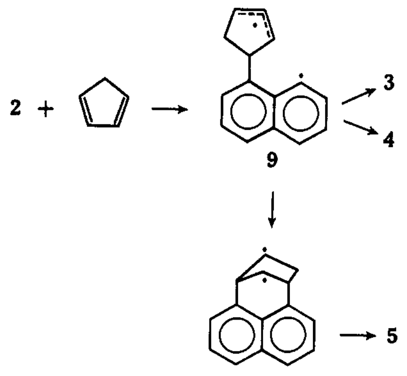
(3)

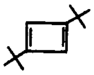
The third adduct (44%) unexpectedly proved to be pentacyclic. Its nmr spectrum (100 MHz) consisted of aromatic protons, τ 2.6 (6 H), a broad unresolved doublet at 6.43 (1 H), a triplet (J = 10 Hz) of doublets (J = 4 Hz) at 7.16 (1 H), a multiplet, 7.42–8.16 (3 H), and a doublet (J = 10.5 Hz) of triplets (J = 2 Hz) at 8.70 (1 H).[10] Upon hydrogenolysis (5% Pd/C) this compound afforded the previously characterized **6**. These observations are best accommodated by structure **5**.

Summing up, we have shown that one of the major 1:1 products derived from 1,8-dehydronaphthalene and cyclopentadiene is the 1,2-adduct **4**, in accord with theoretical expectations.[5] The 1,4-adduct **3** is a minor product in this reaction, as anticipated.[5] The facile formation of a 1,3-adduct **5** in a thermal reaction from cyclopentadiene with accompanying bridging to produce a bicyclo[2.1.0]pentane moiety is unanticipated, and to our knowledge, unprecedented. In contrast, the addition of benzyne to cyclopentadiene occurs with the formation of only benzonorbornadiene, the 1,4 adduct.[11]

Of the three products derived from the addition of **2** to cyclopentadiene, only the formation of **4** corresponds to a symmetry-allowed, concerted process. The formation of **3** and **5** (and perhaps also **4**) can be economically rationalized in terms of intermediate **9** as shown in the following scheme.[12]



While the 1,3 addition of **2** to cyclopentadiene does not appear to have analogy, it is worth noting that the symmetry-allowed product **4** is sterically most unfavorable, while the bicyclo[2.1.0]pentane geometry of **5** appears from molecular models to match the steric requirements of **2** very closely. The only other case of 1,3 addition to a conjugated diene of which we are aware was observed by Reeves, Henery, and Pettit, who found that tetracyanoethylene adds readily to 1,3-di-*tert*-butylcyclobutadiene (**10**) to give the dihydrobenzvalene derivative **11** in high yield.[13] In this case, however, the authors feel that a symmetry-allowed cis,trans,trans 2 + 2 + 2 cycloaddition mechanism is operating.



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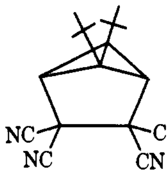

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Acknowledgment. The partial support of this research by the U. S. Public Health Service (Fellowship No. 5 FO2 CA37802-02 to G. W. G.) is acknowledged with pleasure.

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[10] This spectrum is reminiscent of that of benzotricyclo[4.1.0.0^{3,7}]hept-4-ene. See J. R. Edman, *J. Amer. Chem. Soc.*, **88**, 3454 (1966).

[11] L. Friedman, private communication. Also see: L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963); G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958); and T. F. Mich, E. J. Nienhouse, T. E. Farina, and J. J. Tufariello *J. Chem. Educ.*, **45**, 272 (1968).

[12] Many alternatives to this scheme, involving dipolar intermediates, can also be envisaged. In the absence of experimental evidence, detailed discussion of this point is unwarranted.

(13) P. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5888 (1969).

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Received June 1, 1971

Photochemical Behavior of the Stereoisomeric 9-Chloro-*cis*-bicyclo[6.1.0]nona-2,4,6-trienes. Synthesis of 9-Chloro-*cis;cis,cis,cis*-1,3,5,7-cyclononatetraene

Sir:

Recently[1] we recorded the results of a study dealing with the mechanistic details of the thermal bond relocation of *cis*-bicyclo[6.1.0]nona-2,4,6-triene and proposed that molecular reorganization within such systems must be a sensitive function of conformation. In this connection, we presently report on (1) the light-induced rearrangement(s) of the *syn*- and *anti*-9-chloro-*cis*-bicyclo[6.1.0]nona-2,4,6-trienes[2] and (2) on the synthesis and thermal and photochemical bond relocation of 9-chloro-*cis,cis,cis,cis*-1,3,5,7-cyclononatetraene.

Through-Pyrex irradiation of the syn isomer[3] **2a** in acetone and at 0° with a high-pressure Hanovia light source results in a clean mixture consisting (nmr) of *ca.* 33% **1a** and 67% **2a** after 45 min and *ca.* 85%

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(1) A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, **93**, 3083 (1971).

(2) It is pertinent to note here that the two isomeric substances under study were recently shown to thermolyze by different mechanisms: J. C. Barborak, T.-F. Su, P. v. R. Schleyer, G. Boche, and G. Sneider, *ibid.*, **93**, 279 (1971).

(3) E. A. LaLancette and R. E. Benson, *ibid.*, **87**, 1941 (1965).