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**.

$$4 \xrightarrow{\text{H}_2}_{\text{Pd/C}} \quad \xleftarrow{\text{Pb(OAc)}_4} 1 \qquad (3)$$
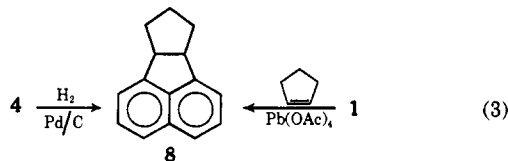
The third adduct (44%) unexpectedly proved to be pentacyclic. Its nmr spectrum (100 MHz) consisted of aromatic protons, τ 2.6 (6 H), a broad unresolved doublet at 6.43 (1 H), a triplet ($J = 10$ Hz) of doublets ($J = 4$ Hz) at 7.16 (1 H), a multiplet, 7.42–8.16 (3 H), and a doublet ($J = 10.5$ Hz) of 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,

(10) This spectrum is reminiscent of that of benzotricyclo[4.1.0.0³,⁷]-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.
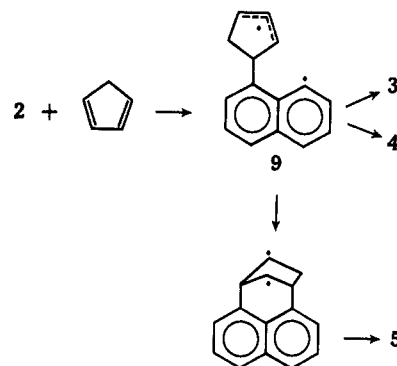
who found that tetracyanoethylene adds readily to 1,3-di-*tert*-butylcyclobutadiene (**10**) to give the dihydrobenzvalene derivative **11** in high yield.[13] In this case, however, the authors feel that a symmetry-allowed cis,trans,trans 2 + 2 + 2 cycloaddition mechanism is operating.
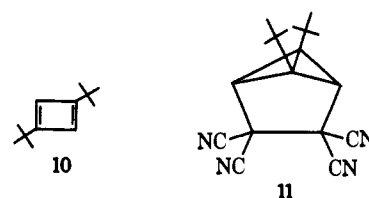
(13) P. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5888 (1969).

J. Meinwald,* G. W. Gruber
Department of Chemistry, Cornell University
Ithaca, New York 14850
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%

(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).

1

2

3

6

5

a, X = H
b, X = D
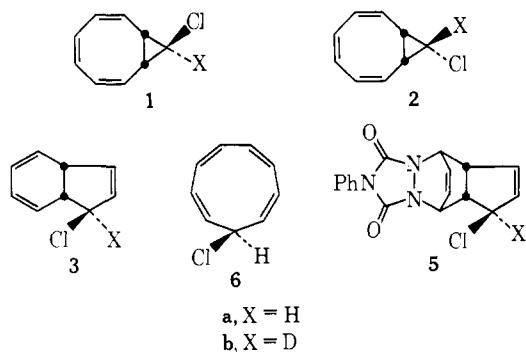
1a and 15% 2a on extension of the photolysis time to 12 hr. In contrast, illumination of the anti counterpart[4] 1a under the same conditions produces no change. This substance does, however, isomerize cleanly when irradiated (through Pyrex in petroleum ether (bp 30–60°) at 0° for 1.5 hr) in the presence of benzophenone, the crude photolysate produced under these conditions consisting (nmr) of ca. 65% 1a and 35% exo-1-chloro-cis-8,9-dihydroindene (3a). The syn isomer 2a responds similarly when subjected to the same photolysis conditions, the photolysate in this case being composed (nmr) of ca. 65% 1a and 35% 3a along with traces of indene. The structural assignment shown in 3a derives chiefly from trapping experiments. These entailed separate treatment of the benzophenone-containing photolysates from 1a and 2a with 4-phenyl-1,2,4-triazoline-3,5-dione (4) at ca. −30° to produce, in each case, a high yield of the same single adduct which proved identical (mixture melting point, nmr, ir) with a synthetic sample of 5a,[5] mp 206–207°, prepared from 4 and authentic 3a.[2] Spectrally, 5a is characterized as follows: m/e 327 (P$^+$); ir (KBr) prominent bands at 1760, 1700, 1400, 1245, and 778 cm^{-1}; nmr (60 MHz, CDCl$_3$) singlets at τ 2.58 (5 H) and 4.20 (2 H), a triplet at 3.60 (2 H), and well-resolved multiplets centered at 4.8 (1 H), 5.0 (1 H), 5.6 (1 H), 6.3 (1 H), and 6.7 (1 H).

In order to gain some insight into the mechanism(s) of the photorearrangements of 1a and 2a we examined the behavior of their deuterated analogs 1b[6] and 2b[7] under the same conditions. The rationale here, of course, is that knowledge of the exact distribution of the label among the products ought to allow for an unambiguous choice between two basic mechanistic alternatives, i.e., a purely skeletal reorganization and a rearrangement resulting from migration of peripheral atoms. In actual fact, irradiation of either 1b or 2b under the conditions described above led to rearrangements entirely analogous to those observed with the protio analogs *without any scrambling of the label;* i.e., the photoproducts invariably contained an intact CDCl function.[8] Hence, *all the reorganizations re-*

(4) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, 86, 5194 (1964).
(5) Correct elemental analysis was obtained for this substance.
(6) We thank Drs. Schleyer and Barborak for supplying us with a sample of 1b.
(7) Prepared by the method of LaLancette and Benson[3] using cyclooctatetraene–methylene-d₂ chloride and methyllithium.
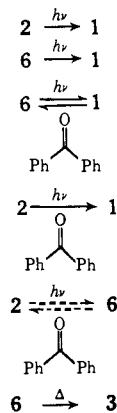(8) The exact position of the deuterium in 1b and 2b was ascertained through direct nmr analysis of the crude photolysates. Similarly, the nmr spectrum of 5b (mp 206–207°, m/e 328 (P$^+$), ν_{CO}^{KBr} 1705 cm^{-1}) prepared from 3b, which in turn was generated from photolysis of either 1b or 2b, was found to be virtually identical with that of 5a except for the complete absence, in the spectrum of 5b, of the 1 H multiplet at τ 5.6 due to the CHCl group.

ported herein are purely skeletal in nature. Formally, such a skeletal process may lead to product either directly or through the intermediacy of "all-cis" 9-chloro-1,3,5,7-cyclononatetraene (6).[9] In order to make a rational choice between these two alternatives, we synthesized the previously unknown monocycle shown in 6 and examined its response to photolysis conditions analogous to those employed with 1 and 2. Thus, treatment of cyclononatetraenide with N-chlorosuccinimide in tetrahydrofuran at −78° produced, in ca. 60% yield, a yellow mobile liquid which was formulated as 6 on the basis of (1) its nmr spectrum (CDCl$_3$; −30°), which consists of a sharp singlet (τ 4.18) with broadened base; (2) its low-temperature (−12°) catalytic (Rh/C) hydrogenation to yield a mixture containing[10] ca. 19% cyclononane (ir) and 67% chlorocyclononane, spectrally identical (ir, nmr, mass spectrum) with an authentic sample prepared from cyclononanol and thionyl chloride; and (3) its thermal conversion, at 0°, to 3.[11] Brief irradiation of 6 in acetone-d₆ through Pyrex and at ca. −15° with a Hanovia light source produced a two-component mixture consisting (nmr analysis at ca. −30°) of ca. 55% 1 and 45% 6. Similarly, illumination of 6 (through Pyrex in 1:1 ether–petroleum ether at ca. −15° for 30 min) in the presence of benzophenone led (work-up and nmr analysis at −30°) to a photolysate consisting of ca. 60% 1 and 40% 6. These findings, coupled with the earlier detection of 3 in the sensitized photolysis of 1 and 2 when work-up and analysis were executed at ambient temperature, prompted a reinvestigation of the benzophenone-induced photobehavior of these substances under the conditions employed for 6. In this manner, 2 produced a photolysate consisting of ca. 65% 1 and 35% 6 along with traces of 2, while 1 led to a two-component mixture consisting of 69% 1 and 31% 6, the composition of this latter photolysate remaining virtually unchanged (67% 1 and 33% 6) upon irradiation under the same conditions for an additional 22 min.

The response of 1, 2, and 6 to low-temperature irradiation clearly establishes that dihydroindene 3 invariably arises from thermal rearrangement of 6 and also that sensitized excitation of 1, 2, or 6 leads to rapid establishment of a photostationary state consisting of ca. 65% 1 and 35% 6. Further, the complete absence of either 3 or 6 among the direct-photolysis products of 1 and 2, coupled with the apparent similarity of the rates controlling the 6 → 1 and 2 → 1 photoisomerizations, strongly suggests that here, as perhaps also in the sensitized process, the conversion of 2 to 1 is not intermediated by 6. The operational implications of our present findings are summarized in Scheme I, where dashed arrows denote uncertain processes.

It now seems proper to elaborate on what appears to be the most striking single feature of the present results, namely, the stereospecific nature of the various

(9) Excited-state interconversion between cis-bicyclo[6.1.0]nona-2,4,6-triene and all-cis-cyclononatetraene is permitted by orbital symmetry [(a) A. G. Anastassiou, *J. Amer. Chem. Soc.*, 90, 1527 (1968)] and was in fact realized recently: (b) A. G. Anastassiou, V. Orfanos, and J. H. Gebrian, *Tetrahedron Lett.*, 4491 (1969).
(10) Analysis of the mixture and isolation of the individual components in the pure state were accomplished by gas chromatography.
(11) This substance was characterized on the basis of its nmr spectrum and through its conversion to 5 (nmr, ir) on treatment with 4.

Scheme I

$$2 \xrightarrow{h\nu} 1$$

$$6 \xrightarrow{h\nu} 1$$

$$6 \underset{\underset{\displaystyle Ph \overset{O}{\underset{\|}{\bigwedge}} Ph}{}}{\overset{h\nu}{\rightleftharpoons}} 1$$

$$2 \underset{\underset{\displaystyle Ph \overset{O}{\underset{\|}{\bigwedge}} Ph}{O}}{\xrightarrow{h\nu}} 1$$

$$2 \underset{\underset{\displaystyle Ph \overset{O}{\underset{\|}{\bigwedge}} Ph}{O}}{\xrightarrow{h\nu}} 6$$

$$6 \xrightarrow{\Delta} 3$$

photoconversions exemplified by the irreversible isomerization of **2** to **1** and also by the rearrangement, be it reversible (sensitized excitation) or irreversible (direct excitation), of **6** exclusively to **1**. The specificity of these processes is, we believe, best accounted for in terms of factors relating to conformation. We note, for example, that excited-state conversion of **2** to **1** most likely results from a 1,7 sigmatropic shift of the CHCl bridge which must pivot about the cyclopropane C–C bond common to both reactant and product if the migration is to conform with the restrictions imposed on the systems by orbital symmetry.[12] Clearly, such a process will invert the configuration of the migrating function relative to the remainder of the molecule, i.e., it will allow for interconversion between **1** and **2**. Within this scheme, the actual irreversibility of the stereoisomerization is, we believe, best reasoned in terms of steric restrictions imposed on the migration by different and rather pronounced conformational preferences inherent in the two molecules. Specifically, we suggest that whereas the syn isomer **2** is sterically constrained to the "extended" arrangement shown in **7**, the anti counterpart **1** exists, for reasons we do not yet fully comprehend, predominantly in the "folded" conformation shown in **8**.[13] Brief scrutiny of these forms reveals that while the extended arrangement **7** may readily accommodate a 1,7 pivotal migration of the bridge, the folded form **8** cannot do so without generating a sterically impossible situation in the form of folded **2**; hence, the observed irreversibility.[14] Furthermore, the conformational arrangements shown in

(12) Orbital symmetry considerations demand that the 1,7 process occur suprafacially in the excited state: R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(13) Strongly suggestive nmr evidence for preferred arrangements 7 and 8 for 2 and 1, respectively, derives from the relative positions of the resonances due to the CHCl proton. In the spectrum of **1a** this resonance appears ca. 50 Hz upfield from the corresponding signal of **2a**.

(14) It should be noted here that isomerization of 2 to 1 through a sequence involving rupture of a peripheral cyclopropane C–C bond followed by rebonding at the same position with inversion also accounts for the observed irreversibility of this process for exactly the same conformational reasons we advanced for the 1,7 shift. For energetic reasons we believe this "topical" stereoisomerization to represent a less likely possibility[15] than the symmetry-controlled 1,7 shift, but cannot, of course, eliminate it entirely as a reasonable mechanistic candidate without further experimentation with properly tagged reactants.

(15) It is interesting to note in this context that 9,9-dimethyl-cis-bicyclo[6.1.0]nona-2,4,6-triene, a substance believed[16] for obvious reasons to be rigidly held in the "extended" form, does appear to undergo topical isomerization upon irradiation, the photoproduct being 9,9-dimethyl-trans-bicyclo[5.1.0]nona-2,4,6-triene: S. W. Staley and T. J. Henry, J. Amer. Chem. Soc., **92**, 7612 (1970).

(16) S. W. Staley and T. J. Henry, ibid., **91**, 1239 (1969).

7 and **8** serve to rationally interpret the specificity of the photoinduced behavior of **6** as well, i.e., the occurrence of a **6** $\rightleftharpoons$ **1** process to the apparent exclusion of a **6** $\rightleftharpoons$ **2** interconversion. In brief, it appears that whereas arrangement **8** may properly generate **6** on symmetry-controlled excited-state rupture of the crosslink, conformation **7** is, for obvious reasons, topologically incapable of doing so. Instead, this latter arrangement ought to lead to a *trans,cis,cis,trans*-cyclononatetraene skeleton under the same conditions.[17,18]
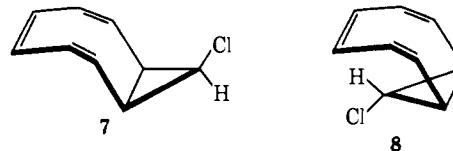
The chemistry of **6** is currently under investigation within our laboratories.

(17) Operationally, the predicted photoconversion of 7 and 8 to geometrically isomeric 1,3,5,7-cyclononatetraenes may be viewed either as a conformationally controlled unidirectional disrotatory motion, corresponding to an inward and outward movement of the bridge protons in the case of 7 and 8, respectively, or simply as a nonrotatory rupture of the cross-link.

(18) One referee commented as follows with regard to the photosensitized interconversion of 6 and 1: "Electrocyclization of polyenes has in general been found to be a singlet reaction. The interconversion of 1 and 6 in the presence of benzophenone raises the interesting question whether the sensitized conversion of 6 to 1 might not proceed by way of trans,cis,cis,cis-9-chloro-1,3,5,7-cyclononatetraene which could cyclize thermally to 1." We fully concur with the underlying principles of this statement, but nonetheless wonder whether one should expect a molecule, as thermally labile as 9-Cl-cis³,trans-CNT might be anticipated to be, to electrocyclize with the high degree of regiospecificity and stereospecificity demanded by our results.

A. G. Anastassiou,* E. Yakali
Department of Chemistry, Syracuse University
Syracuse, New York 13210
Received April 1, 1971

Wavelength Dependency in the Photochemistry of 1,3-Cyclohexadienes. *cis*-Bicyclo[4.3.0]nona-2,4-diene to *cis,cis,trans*-1,3,5-Cyclononatriene Valence Tautomerism[1]

Sir:

Very subtle structural differences in homoannular cyclohexadienes have been shown to play an important role in the rearrangement pathway followed by the molecule upon photoexcitation.[2] We now wish to report that energy of excitation can also be a factor in the cyclohexadiene photochemical dichotomy.

Grimme and Vogel[3] have reported that *cis*-bicyclo-[4.3.0]nona-2,4-diene (**1**) undergoes rearrangement on

(1) This investigation was supported in part by P.H.S. Grant No. 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

(2) (a) D. H. R. Barton, Helv. Chim. Acta, **42**, 2604 (1959); (b) R. J. de Kock, N. G. Minnaard, and E. Havinga, Recl. Trav. Chim. Pays-Bas., **79**, 922 (1960); (c) W. G. Dauben, Chem. Weekbl., **29**, 381 (1964); (d) W. H. Schaller, R. N. Moore, J. E. Hawkins, and R. V. Lawrence, J. Org. Chem., **27**, 1178 (1962); (e) G. J. Fonken and K. Mehrotra, Chem. Ind. (London), 1841 (1963); (f) W. G. Dauben and R. M. Coates, J. Amer. Chem. Soc., **86**, 2490 (1964).

(3) E. Vogel, W. Grimme, and E. Dinne, Tetrahedron Lett., 391 (1965).