

Elution with 10% methanol–methylene chloride gave 861 mg of 2:1 adduct (99% total recovery): nmr ( $\text{CDCl}_3$ )  $\delta$  5.88 (t,  $J = 3.7$  Hz).

**Reaction of the 1:1 Adduct Mixture with PTAD.** To a solution of 200 mg (0.52 mmol) of the combined 1:1 adducts in 5 ml of dichloromethane was added 30 mg (0.17 mmol) of PTAD dissolved in 3 ml of dichloromethane. The color of the PTAD was discharged slowly (10 min at 25°), after which the solvent was removed and the residue was separated by chromatography as described above.

**1:1 Adduct Fraction.** Integration of the nmr spectrum showed the presence of 40% **11**, 15% **12**, 33% **13**, and 12% **14**.

**2:1 Adduct Fraction.** The nmr spectrum ( $\text{CDCl}_3$ ) showed triplets at  $\delta$  5.88 and 5.94 ( $J = 3.7$  Hz) in an intensity ratio of  $\sim 2.7:1.0$ .

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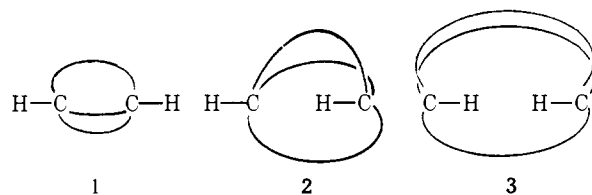
## Cycloadditions to Cyclic 1,3-Dienes. A Diels–Alder Route to Inside–Outside Bicyclics<sup>1</sup>

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**Abstract:** The *cis,cis*-, *cis,trans*-, and *trans,trans*-1,3-cyclododecadienes have been prepared and characterized. The reaction of *cis,trans*-1,3-cyclododecadiene with hexafluoro-2-butyne has been studied in detail. The major product of this reaction was found to be a  $[2\pi + 4\pi]$  cycloadduct, which appeared to form in the traditional Diels–Alder sense. No  $[2\pi + 4\pi]$  cycloadducts could be detected or identified from exploratory reactions of perfluoro-2-butyne with either *cis,cis*-1,3-cyclododecadiene or *trans,trans*-1,3-cyclododecadiene. The minor product of the reaction of perfluoro-2-butyne with *cis,trans*-1,3-cyclododecadiene was found to be an unusual “ene” type product. The structures of both products were established through the extensive use of  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^1\text{H}$  magnetic resonance spectroscopy and mass spectrometry. The  $[2\pi + 4\pi]$  cycloaddition to *cis,trans*-1,3-cyclododecadiene provided a simple route to inside–outside (i,o) bicyclics. The rearrangement of 11,12-bis(trifluoromethyl)-(i,o)-bicyclo[8.2.2]-tetradeca-11,13-diene in the presence of base and *n*-bromosuccinimide is discussed.

In line with our general interest in the effect of bond distortion on chemical reactivity, we have investigated various aspects of the chemistry of compounds containing small rings. As part of our overall concern with this relationship between C–C bond distortion and chemical behavior, we questioned whether highly reactive “bent” carbon–carbon  $\sigma$  bonds might exist in aliphatic systems which did not contain any small rings.<sup>3,4</sup> In order to achieve such a goal, a molecular type would be required in which the bonds between carbon atoms are distorted as a result of the total molecular geometry. In principle, it seemed likely that bicyclic molecules with inverted bridgeheads might fulfill our desires. Theoretically, bridged bicyclic molecules can exist in any one of three categories relative to the stereochemistry at the bridgehead carbons. These can be classified as outside–outside (o,o), inside–outside (i,o), and inside–inside (i,i) bicyclics, which are represented by the general formulas **1**, **2**, and **3**, respec-



tively.<sup>5</sup> If the chains connecting the bridgeheads are small enough, the nonbonded steric interaction of the inverted bridgehead(s) with the rest of the molecule should cause significant perturbations in the bonding in certain parts of the molecule. Thus, we embarked on an exploration of the synthetic routes to inside–outside and inside–inside bicyclics. This paper provides a detailed report of our initial investigations.

At the inception of our studies, several examples of inside–outside and inside–inside bicyclics had already appeared in the literature. However, these were almost entirely limited to macrobicyclic systems having nitrogen at both bridgeheads.<sup>2,6,7</sup> Upon quaternization, these diazamacrobicyclic systems gave double salts which could exist in all three possible stereo-

(1) Paper XLIII on “The Chemistry of Bent Bonds.” For the previous paper in this series see P. G. Gassman and E. A. Armour, *J. Amer. Chem. Soc.*, **95**, 6129 (1973).

(2) (a) To whom correspondence concerning this investigation should be addressed at the Department of Chemistry, University of Minnesota, Minneapolis, Minn. 55455. (b) The Ohio State University Postdoctoral Fellow, 1971–1972; National Institutes of Health Postdoctoral Fellow, 1972–1973.

(3) Some unusual reactivity has been noted for the paracyclophanes. For a review see B. H. Smith, “Bridged Aromatic Compounds,” Academic Press, New York, N. Y., 1964.

(4) Cyclic trans olefins such as *trans*-cyclooctene and *trans*-cycloheptene might also be expected to exhibit some characteristics of molecules containing “bent” carbon–carbon  $\sigma$  bonds. Unfortunately, the reactivity of the olefinic linkage overshadows any chemical reactivity of the rest of the molecule which might be associated specifically with strained  $\sigma$  bonds.

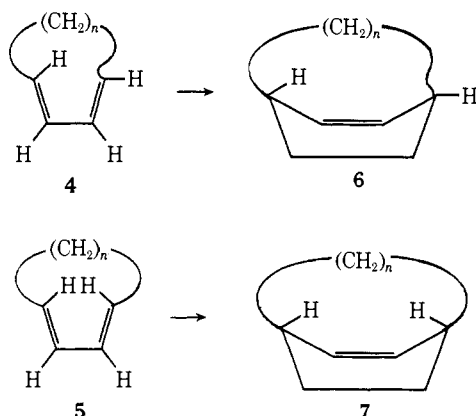
(5) For a discussion of the concept of bicyclic molecules with inverted bridgeheads, see H. E. Simmons, C. H. Park, R. T. Uyeda, and M. F. Habibi, *Trans. N. Y. Acad. Sci.*, **32**, 521 (1970).

(6) H. E. Simmons and C. H. Park, *J. Amer. Chem. Soc.*, **90**, 2428, 2429, 2431 (1968); *Chem. Eng. News*, **46** (July 3, 1967); C. H. Park and H. E. Simmons, U. S. Patent 3,531,468 (1970); *Chem. Abstr.*, **74**, 13189w (1971); J. M. Lehn, J. P. Sauvage, and B. Dietrich, *J. Amer. Chem. Soc.*, **92**, 2916 (1970); *Tetrahedron Lett.*, 2885, 2889 (1969); B. Dietrich, J. M. Lehn, J. P. Sauvage, and J. Blanzet, *Tetrahedron*, **29**, 1629 (1973); B. Dietrich, J. M. Lehn, and J. P. Sauvage, *ibid.*, **29**, 1647 (1973); see also B. Metz, D. Moras, and R. Weiss, *Chem. Commun.*, 217 (1970).

(7) For exceptions see ref 5.

isomeric forms. Since bridgehead stereochemistry has been achieved in these systems *via* reversible protonation, their method of synthesis does not lend itself to the preparation of the corresponding carbocyclic systems. Thus, an alternate approach to inside-outside and inside-inside bicyclics was desired.

An obvious approach to such molecules appeared to be the concerted  $[2\pi + 4\pi]$  Diels-Alder addition of dienophiles to cyclic conjugated *cis,trans* and *trans,trans* dienes, such as **4** and **5**. This might be expected to produce (i,o) and (i,i) bicyclics of the general formulas **6** and **7**, respectively.<sup>8,9</sup> Our early studies of



this route indicated that small, cyclic 1,3-dienes, which have at least one *trans* double bond, undergo  $[2\pi + 2\pi]$  addition of compounds normally considered to be good dienophiles.<sup>10,11</sup> This major complication was encountered due to the ability of many dienophile activating groups to stabilize neighboring radical species. Hence, the incursion of  $[2\pi + 2\pi]$  cycloaddition *via* the formation of diradical intermediates was often observed. In order to circumvent this problem we chose to use as our dienophile, perfluoro-2-butyne, a material noted for its tenacity as a dienophile,<sup>12</sup> but one which is a relatively poor participator in free-radical cycloadditions.<sup>13</sup> We selected as our diene systems the various isomers of 1,3-cyclododecadiene, since the presence of a *trans* double bond in these systems should be readily accomplished with a minimum incorporation of strain.

### Synthesis of the Isomeric 1,3-Cyclododecadienes

Although isomers of 1,3-cyclododecadiene had previously been described in the literature,<sup>14</sup> these materials had not been well characterized and some confusion existed concerning the stereochemistry about

(8) For a preliminary report of part of this study, see P. G. Gassman and R. P. Thummel, *J. Amer. Chem. Soc.*, **94**, 7183 (1972).

(9) For an alternate route to such carbocyclic systems, see C. H. Park and H. E. Simmons, *J. Amer. Chem. Soc.*, **94**, 7184 (1972).

(10) P. G. Gassman, H. P. Benecke, and T. J. Murphy, *Tetrahedron Lett.*, 1649 (1969).

(11) P. G. Gassman and H. P. Benecke, *Tetrahedron Lett.*, 1089 (1969).

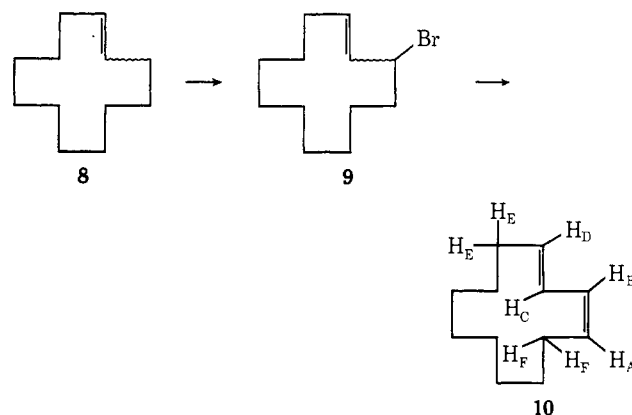
(12) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, **83**, 3428 (1961); C. D. Weis, *J. Org. Chem.*, **27**, 3693 (1962).

(13) P. G. Gassman and K. T. Mansfield, *J. Amer. Chem. Soc.*, **90**, 1517 (1968).

(14) (a) M. F. Bartlett, S. K. Figdor, and K. Wiesner, *Can. J. Chem.*, **30**, 291 (1952); (b) *Chem. Abstr.*, **59**, P11293b (1963); R. H. Perry, Jr., U. S. Patent 3,093,693; (c) A. J. Hubert and J. Dale, *J. Chem. Soc.*, 6674 (1965); (d) W. Ziegenbein and W. M. Schneider, *Chem. Ber.*, **98**, 824 (1965); (e) *Chem. Abstr.*, **64**, 19447g (1966); British Patent 1,023,540 (1966); (f) *Chem. Abstr.*, **69**, P35569r (1968); French Patent 1,493,858;

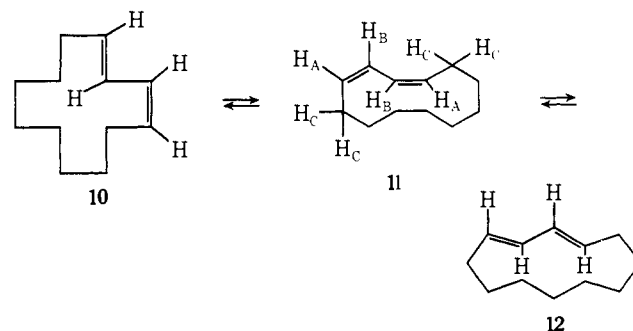
(g) for added discussion see A. W. Fawcett and J. Harris, *J. Chem. Soc.*, 2673 (1954).

the double bonds.<sup>14b,c</sup> In our hands, allylic bromination of a commercial mixture of *cis*- and *trans*-cyclododecene<sup>15</sup> (**8**) gave the previously described bromide,<sup>14b</sup> **9** (presumably as a mixture of isomers) in 86% yield. This very unstable bromide was dehydrohalogenated on passage through a column of activity I basic alumina to yield 93% of a single conjugated diene, **10**. The *cis,trans*-1,3-cyclododecadiene struc-



ture was assigned to **10** on the basis of its ir spectrum, which showed a strong absorption at  $10.2 \mu$  attributable to the *trans* double bond, and on the detailed analysis of its nmr spectrum. Four distinct olefinic C-H resonances were observed in the nmr spectrum at  $\tau$  3.58 (d of d,  $H_C$ ,  $J_{CD} = 15.3$  Hz,  $J_{CB} = 10.2$  Hz), 3.82 (t,  $H_B$ ,  $J_{BC} = 10.2$  Hz,  $J_{BA} = 10.2$  Hz), 4.32 (d of t,  $H_D$ ,  $J_{DC} = 15.3$  Hz,  $J_{DE} = 4.5$  Hz), and 4.58 (d of t,  $H_A$ ,  $J_{AB} = 10.2$  Hz,  $J_{AF} = 8.5$  Hz). In addition, the four allylic protons appeared as a broad multiplet centered at  $\tau$  7.85, while the remaining 12 protons appeared as a broad multiplet centered at  $\tau$  8.6. The *cis* and *trans* olefinic proton coupling constants can be compared with the values of 10.8 and 15.1 Hz for *cis*- and *trans*-cyclododecene, respectively.<sup>16</sup> The conjugated nature of the diene system was confirmed by the ultraviolet spectrum of **10** which showed  $\lambda_{max}$  (hexane) 236 nm ( $\epsilon$  17,300). Overall, the spectral data strongly supported the assignment of the *cis,trans* stereochemistry to **10**.

In order to obtain the other possible isomers of 1,3-cyclododecadiene, we studied the photoisomerization<sup>17</sup> of **10**. Irradiation of a pentane solution of **10**, utilizing



a 450-W Hanovia light source with a Pyrex filter and acetophenone as photosensitizer, gave, after 10 hr, a

(15) Depending on the source and batch, commercial cyclododecene can vary from an approximately 50:50 mixture of *cis* and *trans* to a 60% *trans*-cyclododecene, 35% *cis*-cyclododecene, 5% cyclododecene mixture [cf. *Chem. Abstr.*, **63**, P514g (1965); French Patent 1,389,362].

(16) G. V. Smith and H. Krloff, *J. Amer. Chem. Soc.*, **85**, 2016 (1963).

(17) For a leading reference to photochemical diene isomerization in cyclic systems see R. S. H. Liu, *J. Amer. Chem. Soc.*, **89**, 112 (1967).

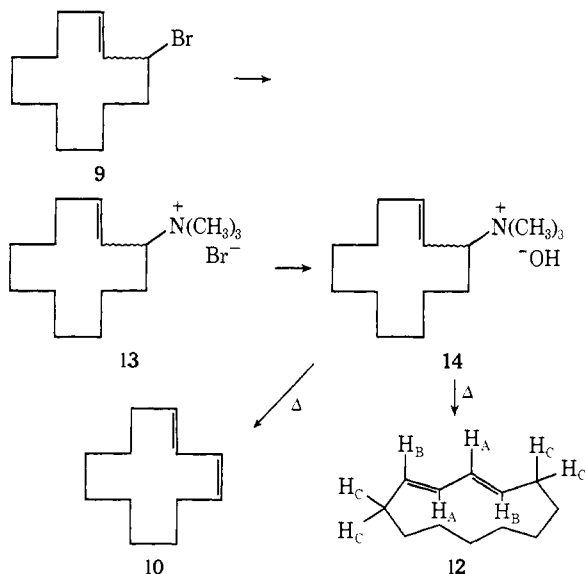
Table I. Ultraviolet Spectral Properties of Selected Conjugated Dienes of Known Stereochemistry

Compd	Solvent	$\lambda_{\max}$ , nm	$\epsilon$	Reference
<i>cis,cis</i> -1,3-Cyclohexadiene	Hexane	256	7,940	21
<i>cis,cis</i> -1,3-Cycloheptadiene	Isooctane	248	7,410	22
<i>cis,cis</i> -1,3-Cyclooctadiene	Cyclohexane	228	5,620	23
<i>cis,cis</i> -1,3-Cyclononadiene	Ether	<210		a
<i>cis,cis</i> -1,3-Cyclodecadiene	Ether	<210		a, b
<i>cis,cis</i> -1,3-Cyclododecadiene (11)	Hexane	226	9,610	c
<i>cis,trans</i> -1,3-Cyclooctadiene	Cyclohexane	230.5	2,630	23
<i>cis,trans</i> -1,3-Cyclononadiene	Isooctane	230	2,890	d, e
<i>cis,trans</i> -1,3-Cyclodecadiene	Isooctane	221	7,350	d, f
<i>cis,trans</i> -1,3-Cyclododecadiene (10)	Hexane	236	17,300	c
<i>trans,trans</i> -1,3-Cyclododecadiene (12)	Isooctane	235	19,900	c

<sup>a</sup> Unpublished work of G. J. Fonken, as reported by L. A. Paquette and R. W. Begland, *J. Amer. Chem. Soc.*, **88**, 4685 (1966). <sup>b</sup> A. T. Blomquist and A. Goldstein, *ibid.*, **77**, 998 (1955). <sup>c</sup> This study. <sup>d</sup> P. G. Gassman and R. P. Thummel, unpublished work. <sup>e</sup> For a different value ( $\lambda_{\max}^{\text{ether}}$  218–220) see footnote a. <sup>f</sup> A value of  $\lambda_{\max}$  222 ( $\epsilon$  7240) has been reported (see footnote b). However, no solvent was specified.

photostationary state consisting of *ca.* 44% of **10**, 44% of **11**, and 12% of **12**.<sup>18</sup> Careful spinning band distillation allowed the separation of pure **11** (19%) from the photostationary state mixture. This conjugated diene [ $\lambda_{\max}^{\text{hexane}}$  226 nm ( $\epsilon$  9610)] showed no trans double bond absorption in the infrared. The nmr spectrum of **11** showed peaks at  $\tau$  3.96 (d, H<sub>B</sub>,  $J_{AB}$  = 9 Hz), 4.54 (d of t, H<sub>A</sub>,  $J_{AB}$  = 9 Hz,  $J_{AC}$  = 8 Hz), 7.86 (m, 4 allylic H<sub>C</sub>), and 8.28–8.78 (broad m, 12 H). The presence of only the 9-Hz coupling constant between the olefinic protons tended to confirm the *cis* stereochemical assignment.

Unfortunately, the *trans-trans* isomer could not be isolated pure from the photostationary state mixture. Thus, an alternate method of synthesis was developed. The allylic bromide **9** was heated for 12 hr with trimethylamine at 55° to yield 82% of **13**. Reaction of **13** with silver oxide in water followed by filtration and evaporation gave **14** which was pyrolyzed at 180–200°



to give 64% of a 57:43 mixture of **10** and **12**. The infrared spectrum of pure **12** showed a very strong absorption at 10.05  $\mu$  characteristic of a *trans* disubstituted double bond. The ultraviolet spectrum [ $\lambda_{\max}^{\text{isooctane}}$  235 nm ( $\epsilon$  19,500)] indicated the presence of a con-

(18) In contrast to the studies of Liu,<sup>17</sup> cyclobutene formation did not appear to be a serious complication in our photolomerization. This was apparently due to the overwhelmingly *transoid* nature of the diene system in **10**, **11**, and **12** (*vide post*).

jugated diene system. The nmr spectrum of **12** was extremely complex in the olefinic proton region. A six-line multiplet centered at  $\tau$  4.00<sup>19</sup> was assigned to the two internal olefinic protons, H<sub>A</sub>, of **12**. The two olefinic protons on the end of the diene system appeared as a 14-line multiplet centered at  $\tau$  4.67. In addition, the four allylic protons were found as a doublet of triplets at  $\tau$  7.91 and the 12 remaining protons appeared as a broad multiplet at  $\tau$  8.4–9.0. The spectral properties of **12**, including the remarkable resemblance of the nmr spectrum of its olefinic protons to that of *trans,trans*-2,4-hexadiene, clearly established **12** as *trans,trans*-1,3-cyclododecadiene. In comparison to **10** and **11**, **12** was relatively unstable. At 100°, it was thermally converted into high-molecular-weight, intractable material.

In order to achieve a Diels–Alder reaction with **10**, **11**, or **12**, a *cisoid* conformation of the diene system would be required. Thus, the conformation of the diene portion of these systems was of importance. Examination of space-filling models (Fisher–Hirshfelder–Taylor) indicated the following conformational aspects for the isomers of 1,3-cyclododecadiene: *cis,cis*, slightly twisted *transoid* and extremely twisted *cisoid*; *cis,trans*, planar *transoid* and slightly twisted *cisoid*; and *trans,trans*, planar “bent” *transoid* and planar “bent” *cisoid*.<sup>20</sup> The ultraviolet spectra of **10**, **11**, and **12** tended to support the insight gained from the examination of molecular models. Table I lists the ultraviolet spectra of a series of conjugated dienes.<sup>21–23</sup> As can be seen from Table I, for the series of *cis,cis* dienes, there is a decrease in both the wavelength of absorption and in the extinction coefficient in going from the six-membered to the ten-membered ring.<sup>24</sup> For the 12-membered system there is an increase in both the

(19) This six-line multiplet was virtually identical with the six-line multiplet observed for the internal olefinic protons of *trans,trans*-2,4-hexadiene (obtained from Chemical Samples Co., Columbus, Ohio).

(20) In the case of the *trans,trans* isomer **12**, the models could not be completely closed. A slight “bending” (10–15°) of the C<sub>2</sub>–C<sub>3</sub> bond would have permitted completion of the model. When this “bending” was allowed for, both the *cisoid* and *transoid* conformations preferred to be planar. Models indicated that interconversion of the *cisoid* and *transoid* conformers of **12** would involve a high degree of transannular nonbonded interaction.

(21) V. Henri and L. W. Pickett, *J. Chem. Phys.*, **7**, 439 (1939).

(22) E. Pesch and S. L. Friess, *J. Amer. Chem. Soc.*, **72**, 5756 (1950).

(23) A. C. Cope and C. L. Bumgardner, *J. Amer. Chem. Soc.*, **78**, 2812 (1956).

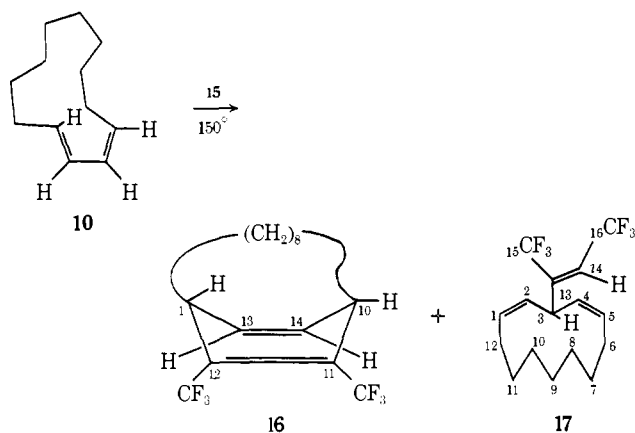
(24) The *cis,cis*-1,3-cycloundecadiene and *cis,trans*-1,3-cycloundecadiene systems could not be included in this tabulation since pure samples of these compounds have not been reported.

wavelength of the absorption and the extinction coefficient. We interpret this trend to be the result of a change from a rigidly cisoid diene (*cis,cis*-1,3-cyclohexadiene), through a series of relatively rigid and nonplanar diene systems, to a somewhat rigid, slightly twisted transoid diene (*cis,cis*-1,3-cyclododecadiene). The suggestion that **11** is a slightly twisted transoid diene is based on the wavelength of the absorption, which is somewhat short for a planar cisoid diene, and the extinction coefficient, which is near the maximum that one might expect for a cyclic cisoid diene if it were planar.<sup>14c, 25</sup>

Comparison of the ultraviolet spectrum of **10** with those of the eight-membered through ten-membered *cis,trans*-1,3-cycloalkadienes indicates that, whereas both the absorption maxima and extinction coefficients of these three smaller *cis,trans* dienes indicate a very nonplanar conformation, the ultraviolet properties of **10** are consistent with an almost planar transoid conformation. The large extinction coefficient (17,300) was particularly diagnostic. Comparison of the ultraviolet spectral data of **10** and **12** indicated that **12** also existed primarily in an almost planar transoid conformation.<sup>26</sup>

#### Cycloaddition Reactions of the 1-3-Cyclododecadienes

Having well characterized the three isomeric 1,3-cyclododecadienes, we investigated their cyclo addition reactions with perfluoro-2-butyne. Heating of a 2.5:1 mixture of perfluoro-2-butyne (**15**) and **10** in a sealed tube at 150° for 42 hr gave 78% of **16** and 16% of **17**,<sup>27</sup>



in addition to 2% of an unidentified component. Exact mass molecular weights indicated that **16** and **17** were 1:1 adducts of **10** and **15**.

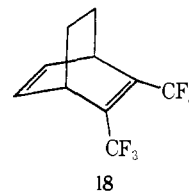
The structure of **16** was established on the basis of both spectroscopic and chemical evidence. This major product showed no trans double bond absorption in

(25) For an empirical relationship of dihedral angle (twist) of a diene system to its extinction coefficient, see E. A. Braude, *Chem. Ind. (London)*, 1557 (1954). For additional discussions, see ref 22 and 23, and L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 21.

(26) To our knowledge **12** is the smallest conjugated *trans,trans* cyclic diene to be characterized. Previous workers<sup>14c</sup> have implied that such conjugated *trans,trans* diene systems might be restricted to much larger rings.

(27) The structure originally assigned to this minor product on a tentative basis<sup>8</sup> was shown to be incorrect on the basis of more detailed spectral studies (*vide post*). This indicates that the tentative structural assignment of a  $[2\pi + 2\pi]$  adduct to the product obtained from *cis,cis*-1,3-cyclododecadiene and perfluoro-2-butyne also requires reassignment. The identification of this related product is currently under study.

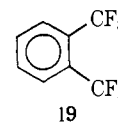
the infrared, while exhibiting a strong *cis* double bond absorption at 14.02  $\mu$ . A suitable model system was found to be 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octadiene (**18**),<sup>28</sup> which showed a similar absorption at 14.20



$\mu$ . The nmr spectrum of **16** showed vinylic C-H resonances at  $\tau$  3.98 (multiplet) and 4.01 (br s). The bridgehead protons appeared as complex multiplets centered at  $\tau$  6.49 and 6.97. The peak at  $\tau$  6.97 has tentatively been assigned to the interior bridgehead proton, which should feel the deshielding effects of the double bonds less than the external bridgehead proton. The remaining 16 protons appeared as part of a complex pattern extending from  $\tau$  7.72 to 8.80. The proton decoupled C-13 nmr spectrum showed two distinct olefinic carbons at 135.8 and 132.1 ppm downfield from TMS, while the bridgehead carbons appeared at 41.0 and 28.4 ppm downfield from TMS. The bridgehead carbons were identified through their coupling with the trifluoromethyl groups which resulted in the appearance of quartets with  $J_{13C-F}$  of approximately 2.5 Hz. The remaining eight aliphatic carbons appeared at 36.7, 29.8, 27.4, 27.0, 26.1, 24.5, 24.4, and 24.2 ppm downfield from TMS. The fluorine decoupled <sup>13</sup>C nmr spectrum showed the two trifluoromethyl groups at 123.1 and 122.4 ppm downfield from TMS. The carbon of the lowfield trifluoromethyl group appeared as a doublet ( $J_{13C-H} = 2.2$  Hz) presumably due to coupling with the neighboring bridgehead hydrogen. From the fluorine decoupled <sup>13</sup>C nmr spectrum, the <sup>13</sup>C-H coupling constants of the proton-bearing olefinic carbons was determined to be 167 Hz. In a similar manner the proton decoupled <sup>13</sup>C nmr spectrum gave the <sup>13</sup>C-F coupling constant of the trifluoromethyl groups at 277 Hz.<sup>29</sup>

The uv spectrum of **16** showed strong end absorption with a shoulder appearing at  $\lambda_{max}^{isooctane}$  233 nm ( $\epsilon$  1370) consistent with a nonconjugated interaction between adjacent double bonds. The diene **18** showed  $\lambda_{max}^{acetone/tri}$  234 nm ( $\epsilon$  950)<sup>28</sup> in excellent agreement with our observation for **16**.

The mass spectral cracking pattern provided strong support for the assigned structure. The cleavage of the eight-membered bridge could be clearly detected through the observation of major peaks, which corresponded to stepwise loss of each of the eight methylene units. The loss of this eight-carbon fragment gave *o*-bis(trifluoromethyl)benzene (**19**) as a major fragment



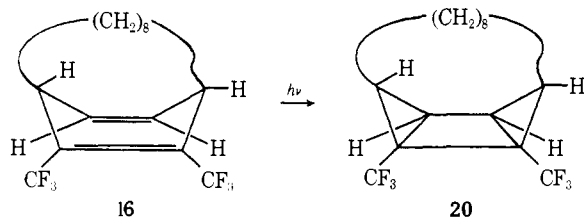
with *m/e* 214. The subsequent fragmentation of this portion of **16** corresponded to that of an authentic

(28) R. S. H. Liu, *Tetrahedron Lett.*, 1409 (1969).

(29) The <sup>13</sup>C-F coupling constant for the trifluoromethyl group of trifluoromethylbenzene was reported to be 272 Hz (L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," Wiley, New York, N. Y., 1972, p 225).

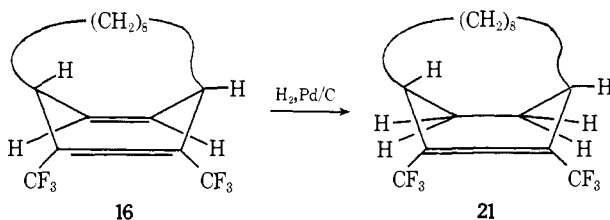
sample of **19** and to that observed below  $m/e$  214 for **18**. In addition to the cracking pattern which appeared below  $m/e$  214 due to **19**, the base peak for the fragmentation of **16** appeared at  $m/e$  159.0419 consistent with an ion formula of  $C_8H_6F_3^+$  (calcd  $m/e$  159.0422). This corresponds to the trifluoromethyltropylium ion, whose formation requires ring expansion and loss of one trifluoromethyl group.

Chemical evidence for the proximity of the two double bonds in **16** was obtained through the facile photochemical conversion of this diene into a saturated isomer. By analogy to the well-established photochemical conversion of bicyclo[2.2.1]heptadiene into quadricyclane<sup>30</sup> and of **18** into 1,6-bis(trifluoromethyl)tetracyclo[4.2.0.0<sup>2,8</sup>.0<sup>5,7</sup>]octane,<sup>28</sup> the photoisomer of **16** was assigned structure **20**. The nmr spectrum of



**20** indicated the absence of olefinic protons, while the ir spectrum demonstrated the absence of olefinic linkages. The mass spectral cracking pattern for **20** differed considerably from that of **16**. In particular, the formation of **19** as a major fragmentation product was no longer observed.

Lastly, catalytic reduction of **16** resulted in saturation of the disubstituted double bond with essentially no reduction of the tetrasubstituted double bond. The ir spectrum of **21** showed retention of the olefinic



stretching absorption of the tetrasubstituted double bond at  $6.16 \mu$ , but disappearance of the strong *cis* disubstituted double bond C-H vibrations at  $14.02$  and  $14.30 \mu$ , which was present in the spectrum of **16**. In addition, the nmr spectrum of **21** showed no absorptions assignable to olefinic protons.

The structural assignment for the minor product **17** was based on a combination of ir, uv, nmr, and mass spectral methods. The ir spectrum showed only *cis* double bond absorption, while the uv spectrum showed no long-wavelength maximum similar to those observed for **16** and **18**. The nmr spectrum, which was quite complex, integrated for six protons in the region  $\tau$  3.90–5.50, two 2-proton multiplets at 7.50 and 8.01, and a broad multiplet from 8.2 to 9.1 which integrated for ten protons. The absence of any indication of conjugation and the large number of apparently olefinic protons presented a rather perplexing situation. The proton decoupled  $^{13}C$  nmr spectrum showed two sharp absorptions at 132.7 and 127.4 ppm downfield from

(30) F. I. Sonntag and R. Srinivasan, *Org. Photochem. Syn.*, **1**, 97 (1971), and references contained therein.

TMS, which were assigned to olefinic carbons. In addition, five signals appeared at 37.5 (quartet,  $J_{^{13}C-F} = 2.2$  Hz, assigned to  $C_3$  of **17** coupled to fluorines of  $C_{16}$ ), 26.1, 25.6, 24.5, and 22.5 ppm downfield from TMS. The deceptively simple  $^{13}C$  nmr spectrum indicated a high degree of symmetry in the product. Closer examination of the proton decoupled  $^{13}C$  nmr spectrum (Fourier transform mode, 25,000 scans) indicated the presence of an additional low-field set of signals (quartet of quartets) centered at 123.5 ppm downfield from TMS. This 16-peak multiplet was assigned to  $C_{14}$  of **17** with  $J_{^{13}C_{14}-C_{16}F} = 38.5$  and  $J_{^{13}C_{14}-C_{16}H} = 3.0$  Hz. The fluorine decoupled  $^{13}C$  nmr spectrum of **17** showed  $C_{15}$  as a singlet at 121.4 ppm downfield from TMS;  $C_{16}$  appeared as a doublet of doublets, being coupled with  $H_{14}$  ( $J = 13.6$  Hz) and  $H_3$  ( $J = 2.6$  Hz), centered at 121.9 ppm. Having the detailed  $^{13}C$  data in hand, the proton spectrum became comprehensible. The downfield proton  $H_{14}$  appeared as a quartet of doublets at  $\tau$  4.04 ( $J_{H_{14}-C_{16}F} = 8.8$ ,  $J_{H_{14}-H_3} = 1.8$  Hz). Fluorine decoupling of the fluorines on  $C_{16}$  collapsed this eight-peak multiplet to a doublet ( $J = 1.8$  Hz). The triply allylic proton  $H_3$  appeared as a broad triplet centered at  $\tau$  5.41.<sup>31</sup> Saturation of this signal collapsed the eight-peak multiplet assigned to  $H_{14}$  to a quartet ( $J = 8.5$  Hz). Added support for these assignments was obtained from the fluorine spectrum of **17**, which showed a quartet ( $J_{FF} = 11.2$  Hz,  $C_{15}$  trifluoromethyl group) centered 3.24 ppm upfield from a 16-peak overlapping multiplet centered at 104.3 ppm downfield from hexafluorobenzene ( $J_{FF} = 11.2$ ,  $J_{F-H_{14}} = 8.8$ , and  $J_{F-H_3} = 2.3$  Hz,  $C_{16}$  trifluoromethyl group). Irradiation of the upfield trifluoromethyl signal collapsed the downfield signal to a doublet of doublets.

The mass spectrum of **17** showed the systematic loss of seven methylene units. This was consistent with the presence of a seven methylene unit chain in **17**. The combined ir, uv, mass spectral, and nmr data for **17** were only consistent with the assigned structure. The rather unique nature of this product raises many questions about its origin. Whether **17** arises from a direct abnormal "ene" reaction or from an initial  $[2\pi + 2\pi]$  cycloaddition followed by abnormal bond cleavage and hydrogen transfer cannot be determined on the basis of the presently available information.

Examination of molecular models of *cis,cis*-1,3-cyclododecadiene (**11**) indicated that formation of a planar cisoid conformation of the butadiene moiety of **11** would require a significantly strained distortion of the whole molecule. Thus, **11** would not be expected to form a  $[2\pi + 4\pi]$  adduct with **15**. Experimentally, the *cis,cis* diene **11** was found to be considerably less reactive than the *cis,trans* diene **10**. After 7 days heating at  $150^\circ$  with a twofold excess of hexafluoro-2-butyne, **11** gave 57% of a 1:1 adduct, **22**, which was accompanied by small amounts of several impurities. Isolation of this single major product by preparative vpc gave a material, whose ir, uv, and nmr spectra were substantially different from those of **16**. The mass spectrum of this product was identical with that of **17**. Both the ir and proton nmr spectra of this 1:1 adduct

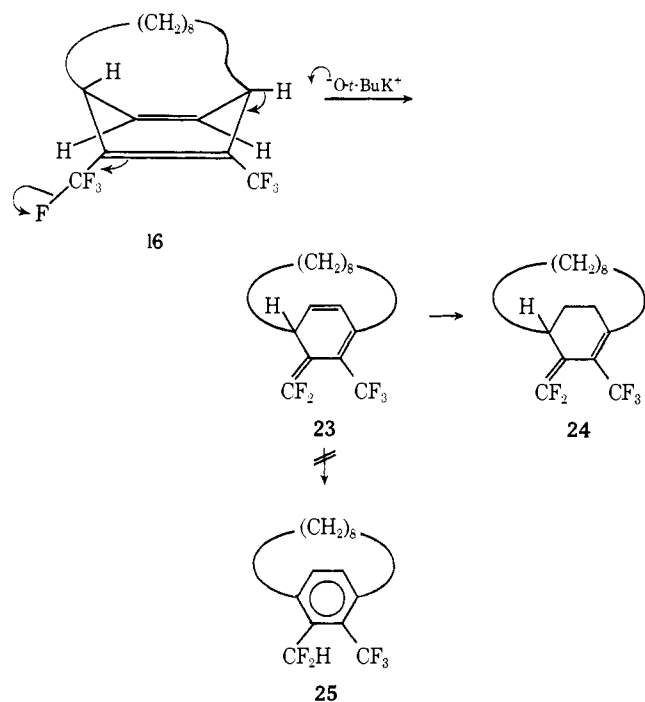
(31) This very low-field absorption for a nonolefinic proton has ample precedent in the bridgehead protons of 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octatriene which appears at  $\tau$  4.96 [R. S. H. Liu, *J. Amer. Chem. Soc.*, **90**, 215 (1968)], and in the tertiary proton of triphenylmethane which appears at  $\tau$  4.5 [Sadtler NMR Spectrum No. 220].

were different from those of **17**, although many similarities existed.<sup>32,33</sup>

Attempts to prepare  $[2\pi + 4\pi]$  adducts of *trans,trans*-1,3-cyclododecadiene (**12**) have thus far proved futile. As shown by our uv spectral studies, **12** exists in a transoid conformation. Since only the cisoid conformations can undergo the desired Diels–Alder addition, elevated temperatures would appear to be necessary in order to convert **12** into the required cisoid form in sufficient concentration for reaction to occur. Unfortunately, **12** was much less thermally stable than **10** or **11**. As noted above, at temperatures in the vicinity of 100°, **12** was rapidly converted into high-molecular-weight, intractable material. Thus, no  $[2\pi + 4\pi]$  cycloadduct could be obtained from **12**.

### Reactions of an Inside–Outside Bicyclic (**16**)

One of the more interesting reactions of the inside–outside bicyclic **16** was its facile loss of hydrogen fluoride on treatment with base. When **16** was heated with 1.5 equiv of potassium *tert*-butoxide in refluxing *tert*-butyl alcohol for 1 hr, we obtained **23** in 80% yield.



The structure of **23** was assigned primarily on the basis of its spectral properties. The ir spectrum of **23** showed strong absorptions at  $5.75 \mu$ , characteristic of a difluoromethylene–carbon double bond stretching vibration,<sup>34</sup> and at  $12.91$  and  $13.90 \mu$  characteristic of a *cis* disubstituted olefin. The uv spectrum of **23** showed  $\lambda_{\text{max}}^{\text{isooctane}}$   $260 \text{ nm}$  ( $\epsilon$  5760) indicating the presence of a conjugated  $\pi$  system. The nmr spectrum showed the presence of two olefinic protons at  $\tau$  3.75 (d of d, 1 H,  $J = 3.6$  and  $9.0 \text{ Hz}$ ), and 4.08 (d, 1 H,  $J = 9 \text{ Hz}$ ). The 9-Hz coupling constant supported the concept that

(32) A detailed study of the structure of **22** is currently in progress in our laboratories. This detailed study of the structure of **22** and of the mechanisms of formation of **17** and **22** will be the topic of a future report.

(33) Since **17** and **22** have virtually identical chromatographic properties, we were unable to establish whether **22** was contaminated by small amounts of **17** and *vice versa*. However, spectral evidence would require that any such contamination be considerably less than 10%.

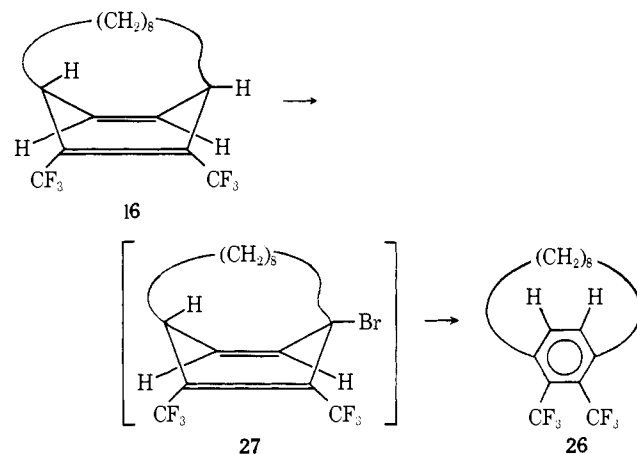
(34) W. H. Knoth and D. D. Coffman, *J. Amer. Chem. Soc.*, **82**, 3873 (1960).

the olefinic protons were *cis*. In addition, the nmr spectrum showed absorptions at  $\tau$  6.88 (m, 1 H), 7.22 (m, 1 H), and 7.7–9.1 (m, 15 H).

Catalytic reduction of **23** over 5% palladium on carbon gave **24**. Although **24** retained the strong ir absorption at  $5.75 \mu$ , the absorptions due to the *cis* double bond were not present. The nmr spectrum showed no olefinic protons and the exact mass molecular weight indicated the addition of 1 mol of hydrogen. The uv absorption at  $\lambda_{\text{max}}^{\text{isooctane}}$   $233 \text{ nm}$  ( $\epsilon$  7200) indicated that the reduction product still contained a conjugated  $\pi$  system. The 27-nm shift to shorter wavelength in going from **23** to **24** indicated that the double bond, which was reductively removed, had been linearly conjugated with the rest of the  $\pi$  system. These data are only consistent with **23** and **24** having the structures shown.

Mechanistically, it would appear that **16** was well set up for elimination of hydrogen fluoride as illustrated above. Removal of the exposed bridgehead proton by base could lead to a concerted elimination. It is of interest that **23** failed to aromatize during the base treatment to give **25**. Formation of **25** would not only provide for a gain in energy due to aromatization, but should also result in the relief of considerable strain energy. We wish to suggest that the failure to form **25** is a result of the encapsulated nature of the bridgehead proton of **23**. The mode of formation of **23** would require that the remaining bridgehead proton be “inside” the shell formed by the six-membered ring and the eight-carbon bridge. In this position it should be sterically inaccessible to removal by base.<sup>35</sup>

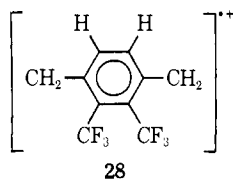
Lastly, the conversion of **16** into the paracyclophane **26**, albeit in very low yield, merits reporting. Refluxing of a carbon tetrachloride solution of **16** with 1.1 equiv of *N*-bromosuccinimide in the presence of benzoyl peroxide for 0.5 hr gave 23% of a 78:22 mixture of **16** and a new product. Partial purification of this mixture by chromatography on silica gel gave a very unstable bromide, which was tentatively assigned structure **27**.



The very unstable nature of this intermediate precluded its further purification and characterization. On heating, the intermediate readily lost hydrogen bromide and gave **26**. The structure of **26** was assigned on the basis of its spectral properties. The nmr spectrum of **26**

(35) The conversion of **23** to **25** also failed to occur in the presence of *p*-toluenesulfonic acid. Whether this was a result of the relatively electron-deficient triene system, **23**, resisting protonation, or whether it was due to the inaccessibility of the bridgehead hydrogen to proton acceptors was not determined.

was quite characteristic, showing a two-proton singlet at  $\tau$  2.76 for the aromatic hydrogens. Two of the benzylic protons appeared as a doublet of triplets ( $J = 13.5$  and  $4.5$  Hz) at  $\tau$  6.63. These signals were assigned to the two benzylic protons syn to the two trifluoromethyl groups, since the trifluoromethyl groups should have a deshielding effect. The other two benzylic protons appeared as a multiplet at  $\tau$  7.49. In addition, there appeared absorptions at  $\tau$  8.33 (m, 2 H), 8.56–9.30 (br m, 6 H), and 10.26 (m, 2 H). The two high-field protons were assigned to hydrogens on C-4 and C-5 which should be held over the center of the aromatic ring and, as a result, should be subject to the shielding effect of the aromatic ring current. The  $^{19}\text{F}$  nmr spectrum of **26** showed a single absorption of the two trifluoromethyl groups at 52.41 ppm upfield from trichlorofluoromethane. The uv spectrum of **26** showed  $\lambda_{\text{max}}^{\text{isoctane}}$  232 ( $\epsilon$  5420) and 292 nm ( $\epsilon$  1320).<sup>36</sup> The mass spectrum of **26** gave  $m/e$  324.1315 (calcd for  $\text{C}_{16}\text{H}_{12}\text{F}_6$  324.1313). The base peak appeared at  $m/e$  240, which would correspond to the cation radical **28**. The conversion of **16** into **26** provided



added support for the  $[2\pi + 4\pi]$  nature of the initial Diels–Alder adduct **16**.

### Experimental Section<sup>37</sup>

**Cyclododecene (8).** Commercial samples of cyclododecene were obtained from Columbia Carbon Co. or from Chemical Samples Co.

**3-Bromocyclododecene (9).** A solution of 200 g (1.2 mol) of **8** (50:50 *cis/trans* mixture) in 1 l. of carbon tetrachloride was heated to reflux under nitrogen in a 3-l. flask equipped with a mechanical stirrer and a reflux condenser. *N*-Bromosuccinimide (NBS) (214 g, 1.2 mol) was added in small portions together with 0.20 g of benzoyl peroxide. Intermittent cooling of the reaction mixture was necessary in order to control the very exothermic allylic bromination. When all the NBS had been added and the exothermic reaction had subsided, the reaction mixture was refluxed for 4 hr and cooled and the succinimide removed by filtration. The carbon tetrachloride was stripped off on a rotary evaporator, and the residual allylic bromide, **9**, was used without further purification.

***cis,trans*-1,3-Cyclododecadiene (10).** Crude **9** (30 g) was chromatographed on 550 g of activity I basic alumina eluting with hexane. This provided *cis,trans*-1,3-cyclododecadiene which was 93% pure by vpc analysis in ca. 60% yield.

The spectral properties of *cis,trans*-1,3-cyclododecadiene were: ir (neat) 3.31, 3.42, 6.85, 10.2, 10.55, 11.89, 12.33, 12.85, 13.16, 13.88, and 14.28  $\mu$ ;  $\lambda_{\text{max}}^{\text{hexane}}$  236 nm ( $\epsilon$  17,300); nmr  $\tau$  3.58 (d of d,  $\text{H}_C$ ,  $J_{CB} = 10.2$ ,  $J_{CD} = 15.3$  Hz), 3.82 (d of d,  $\text{H}_B$ ,  $J_{BC} = 10.2$ ,  $J_{BA} = 10.2$  Hz), 4.32 (d of t,  $\text{H}_D$ ,  $J_{DC} = 15.3$ ,  $J_{DE} = 4.5$  Hz), 4.58 (d of t,  $\text{H}_A$ ,  $J_{AB} = 10.2$ ,  $J_{AF} = 8.5$  Hz), 7.85 (br m, 4 H), and 8.6 (br m, 12 H);  $\eta^{25}\text{D}$  1.5170. Anal. Calcd for  $\text{C}_{12}\text{H}_{20}$ : C, 87.73; H, 12.27. Found: C, 88.05; H, 12.36. Exact  $m/e$  calcd for  $\text{C}_{12}\text{H}_{20}$ : 164.1565. Found 164.1566.

(36) For uv spectral data on related paracyclophanes, see D. J. Cram and G. R. Knox, *J. Amer. Chem. Soc.*, **83**, 2204 (1961); N. L. Allinger and T. J. Walter, *ibid.*, **94**, 9267 (1972).

(37) Melting points and boiling points are uncorrected. Ultraviolet spectra were obtained on either a Cary Model 15 or a Cary Model 14 recording spectrophotometer. Nmr spectra were obtained on a Varian A60A or HA-100 nuclear magnetic resonance spectrometer or on a Bruker HX90 nuclear magnetic resonance spectrometer. Mass spectra were measured on an AEI-MS-9 spectrometer. We wish to acknowledge the very able assistance of Mr. R. Weisenberger in obtaining the mass spectral data and of Mr. Michael Geckle in obtaining the Fourier transform  $^{13}\text{C}$  nmr spectra.

***cis-cis*-1,3-Cyclododecadiene (11).** Photoequilibration of the 1,3-Cyclododecadienes. In 2.6 l. of olefin-free pentane, 20.0 g of **10** and 0.5 g of acetophenone were irradiated for 10 hr in a Pyrex apparatus with a 450-W Hanovia medium pressure lamp. Vpc analysis of this solution on a 10% Carbowax 20M on Chromosorb W column showed a three-component mixture of dienes in the ratio of 44:12:44. Further irradiation of this mixture did not change the ratio of these peaks. The peak with the longest retention time was shown to be **10** through comparison with an authentic sample. Careful spinning band distillation of the photostationary state mixture afforded 3.71 g (19% yield) of the first component, bp 53.5–54.0° (0.5 mm), which was identified as *cis,cis*-1,3-cyclododecadiene (**11**) through its spectral properties: ir (neat) 3.31, 3.42, 3.50, 6.85, 6.94, 13.95, and 14.66  $\mu$ ;  $\lambda_{\text{max}}^{\text{hexane}}$  226 nm ( $\epsilon$  9610); nmr  $\tau$  3.96 (d,  $\text{H}_B$ ,  $J_{AB} = 9$  Hz), 4.54 (d of t,  $\text{H}_A$ ,  $J_{AB} = 9$ ,  $J_{AC} = 8$  Hz), 7.86 (m, 4 allylic  $\text{H}_C$ ), and 8.28–8.78 (br m, 12 H);  $\eta^{25}\text{D}$  1.5052. Exact  $m/e$  calcd for  $\text{C}_{12}\text{H}_{20}$ : 164.1565. Found: 164.1567.

The minor component, which was later shown to be *trans,trans*-1,3-cyclododecadiene, could not be isolated pure from the photostationary state mixture.

***trans,trans*-1,3-Cyclododecadiene (12).** The crude 3-bromocyclododecene, obtained from 200 g of cyclododecene as described above, was combined with 250 ml of methanol and 200 ml of trimethylamine in a 1-l. glass bomb which was sealed and heated to 55° for 12 hr. After cooling, the bomb was opened and the solvent was removed from the dark reaction mixture *via* evaporation on a rotary evaporator. The solid residue which remained was washed thoroughly with ether and dried to give 258 g (70% from cyclododecene) of 3-cyclododecenytrimethylammonium bromide (**13**).

Freshly prepared silver oxide (from 22.1 g of silver nitrate and 7.3 g of potassium hydroxide) was added to a stirred solution of 30.2 g of crude **13** in 120 ml of water. The thick brownish tan precipitate which formed was removed by filtration, and the filtrate was concentrated on a rotary evaporator. The residual oil was heated to 180–200° at atmospheric pressure and the pressure was then quickly reduced to 2 mm to facilitate distillation of the pyrolysis products. The two-phase distillate was extracted thoroughly with ether. The ethereal extracts were dried over anhydrous potassium carbonate and filtered, and the solvent was removed by distillation. Short-path distillation of the residue gave 9.5 g (64% yield based on **13**; 45% yield based on cyclododecene) of a mixture of dienes, bp 53–59° (0.25 mm). Analysis by vpc on a 10% Carbowax 20M on Chromosorb W column showed two peaks in the ratio of 43:57. This mixture was separated by preparative vpc on a 10% Carbowax 20M on Chromosorb W column. The major (57%) component was shown to be identical to *cis,trans*-1,3-cyclododecadiene (**10**). The minor (43%) component was identified as *trans,trans*-1,3-cyclododecadiene on the basis of its spectral data: ir (neat) 3.29, 3.39, 3.48, 6.84, 6.94, 10.02, 10.54, 11.26, 11.96, and 14.35  $\mu$ ; uv  $\lambda_{\text{max}}^{\text{isoctane}}$  235 nm ( $\epsilon$  19,900); nmr  $\tau$  4.00 (m,  $\text{H}_A$ ), 4.67 (m,  $\text{H}_B$ ), 7.93 (d of t, 4 allylic H), 8.4–9.0 (2 br s, 12 H);  $\eta^{25}\text{D}$  1.5132. Exact  $m/e$  calcd for  $\text{C}_{12}\text{H}_{20}$ : 164.1565. Found: 164.1566.

**Addition of Hexafluoro-2-butyne to *cis,trans*-1,3-Cyclododecadiene (10).** A. In a small Carius tube were placed 0.643 g of **10** and 1.72 g of hexafluoro-2-butyne (**15**).<sup>38</sup> The tube was sealed and heated to 150° for 42 hr in a steel bomb. The tube was cooled and then opened, and the excess **15** was allowed to evaporate. The residue (1.254 g, 98%) consisted of an impurity and two 1:1 adducts of **10** and **15** in the ratio of 2:17:81. The two 1:1 adducts were purified by preparative vpc on a Nester-Faust Prepkromatic gas chromatograph equipped with a  $(4 \times 2.5 \text{ ft}) \times \frac{3}{4}$  in. 10% XF-1150 on 60/80 Chromosorb W column at 130°.

The first product to elute was the 17% 1:1 adduct which was assigned the structure of the "ene" type adduct **17** on basis of the following spectral evidence: ir (neat) 3.31, 3.42, 3.50, 5.96, 6.85, 6.94, 7.28, 7.80, 8.7, 12.39, 12.99, 13.53, and 14.29  $\mu$  (no absorption assignable to a trans disubstituted olefin); uv, only weak end absorption; nmr (see main text);  $\eta^{25}\text{D}$  1.4442; mass spectral peaks at  $m/e$  326, 312, 298, 284, 270, 256, 242, 228, 216, 201, 195, 173, 159, 147, 127, 110, 95, 81, 67, 55, and 41 (base peak). Exact  $m/e$  calcd for  $\text{C}_{16}\text{H}_{20}\text{F}_6$ : 326.1469. Found: 326.1474.

The major 1:1 adduct eluted second. The spectral properties of this adduct (**16**) were: ir (neat) 3.26, 3.39, 3.46, 6.16, 6.79, 6.93, 7.25, 7.8, 8.7, 10.06, and 14.02  $\mu$ ; uv,  $\lambda_{\text{max}}^{\text{isoctane}}$  233 nm ( $\epsilon$  1370); nmr ( $\text{CCl}_4$ )  $\tau$  3.98 (m, 1 H), 4.01 (br s, 1 H), 6.49 (m, 1 H), 6.97 (m, 1 H), 7.72–8.80 (br m, 16 H) (see text for additional nmr data); mass spectrum  $m/e$  326, 256, 242, 228, 214, 195, 164, 159 (base peak),

(38) Hexafluoro-2-butyne was obtained from the Pierce Chemical Co. and used without further purification.

145, 95, 69, 57, 55, 43, and 41. Exact  $m/e$  calcd for  $C_{16}H_{20}F_6$ : 326.1469. Found: 326.1466.

**B.** Addition of 57.3 g of **15** to 42.0 g of **10** in the manner described above gave 72.9 g (87%) of a crude mixture of the two 1:1 adducts **16** and **17**. Careful distillation of this mixture on a Nester-Faust Auto Annular Teflon spinning band distillation column gave 36.2 g of **16**, bp 80–81° (0.03 mm), which was shown to be greater than 97% pure by vpc analysis;  $\eta^{21,4D}$  1.4508. Several fractions boiling lower were found to contain mixtures of **16** and **17**. The pure fraction of **16** was analyzed. *Anal.* Calcd for  $C_{16}H_{20}F_6$ : C, 58.89; H, 6.18. Found: C, 58.91; H, 6.25.

**Photochemical Isomerization of 16 into 20.** A solution of 211.5 mg of **16** in 400 ml of olefin-free pentane was purged with nitrogen for 30 min and irradiated for 2 hr with a 450-W Hanovia lamp in a quartz apparatus. At this time vpc analysis showed the complete absence of **16**. The solution was filtered to remove a small amount of polymeric material, and the pentane was removed from the filtrate by evaporation on a rotary evaporator. The residue was chromatographed on silica gel to give 181 mg (85%) of **20**: ir (neat) 3.42, 6.86, 7.9, and 8.8  $\mu$ ; nmr ( $CCl_4$  soln)  $\tau$  8.70 (br m). Exact  $m/e$  calcd for  $C_{16}H_{20}F_6$ : 326.1469. Found: 326.1466.

**Catalytic Reduction of 16 to 21.** In a high-pressure Parr bottle was placed 1.0 g of **16**, ca. 20 mg of 5% Pd/C, and 75 ml of absolute ethanol. The solution was hydrogenated at 60 psi for 6 hr. The solution was then filtered through a celite pad and the solvent was removed from the filtrate to yield 0.97 g (97%) of a single product: ir (neat) 3.46, 3.55, 6.85, 7.9, 8.8, and 10.09 (w)  $\mu$ ; nmr  $\tau$  6.74 (br s, 1 H), and 7.4–8.9 (br m, 21 H). *Anal.* Calcd for  $C_{16}H_{22}F_6$ : C, 58.52; H, 6.75. Found C, 58.38; H, 6.69.

**Treatment of 16 with Potassium *tert*-Butoxide.** In a 100-ml, round-bottomed flask was placed 5.00 g of **16**, 3.53 g of potassium *tert*-butoxide, and 30 ml of dry *tert*-butyl alcohol. The reaction mixture was refluxed for 1 hr, cooled, and poured into 300 ml of water. The solution was extracted with ether, and the ethereal extracts were washed with 5% aqueous hydrochloric acid and saturated sodium chloride solution and dried over anhydrous potassium carbonate. After filtration, the solvent was evaporated and the residue was distilled to give 3.77 g (80%) of **23**: bp 89–100° (0.15

mm); ir (neat) 3.37, 3.46, 5.75, 7.85, 8.92, 11.51, 12.91, and 13.90  $\mu$ ; uv  $\lambda_{max}^{isoctane}$  260 nm ( $\epsilon$  5760); nmr  $\tau$  3.75 (d of d, 1 H,  $J = 3.6$  and 9.0 Hz), 4.08 (d, 1 H,  $J = 9.0$  Hz), 6.88 (m, 1 H), 7.22 (m, 1 H), and 7.7–9.1 (br m, 15 H). *Anal.* Calcd for  $C_{16}H_{18}F_6$ : C, 62.73; H, 6.25. Found: C, 62.60; H, 6.30.

**Catalytic Reduction of 23 to 24.** In a Parr hydrogenation bottle were placed 148 mg of **23**, 35 ml of methanol, and 12 mg of 5% palladium on carbon. This solution was shaken for 2 hr under 60 psi hydrogen pressure at 40°. The catalyst was removed by filtration through celite and the solvent was removed from the filtrate to give 141 mg (95%) of **24**: ir (neat) 3.41, 3.50, 5.75, 6.85, 7.95, and 9.05  $\mu$ ; uv  $\lambda_{max}^{isoctane}$  233 ( $\epsilon$  7200); nmr  $\tau$  7.2–9.1 (br complex m). Exact  $m/e$  calcd for  $C_{16}H_{21}F_6$ : 308.1563. Found: 308.1558.

**1,4-Octamethylene-2,3-bis(trifluoromethyl)benzene (26).** In a three-necked, 100-ml, round-bottomed flask were placed 2.0 g of **16**, 40 ml of carbon tetrachloride, 1.20 g of *N*-bromosuccinimide, and 20 mg of benzoyl peroxide. The mixture was refluxed vigorously and irradiated with a sun lamp. After 0.5 hr, the succinimide floated on the surface of the solution; the reaction was cooled to room temperature and filtered and the solvent removed under vacuum. The residue yielded 23% of volatile material which was 78% starting **16** and 22% of an unstable bromide which was tentatively assigned structure **27**. Chromatography on silica gel permitted isolation of **27** in greater than 90% purity. Attempts to preparatively purify **27** by vpc resulted in the loss of hydrogen bromide and the formation of **26** which was collected: ir (neat) 3.40, 3.49, 6.84, 7.78, 8.78, and 12.14  $\mu$ ; uv  $\lambda_{max}^{isoctane}$  232 nm ( $\epsilon$  5420) and 292 (1320); nmr  $\tau$  2.76 (s, 2 H), 6.63 (d of t, 2 H,  $J = 13.5$  and 4.5 Hz), 7.49 (m, 2 H), 8.33 (m, 2 H), 8.56–9.30 (br m, 6 H), and 10.26 (m, 2 H);  $^{19}F$  nmr singlet at 52.41 ppm upfield from trichlorofluoromethane; mass spectra  $m/e$  240 (base peak). Exact  $m/e$  calcd for  $C_{16}H_{18}F_6$ : 324.1313. Found: 324.1315.

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## Carbanions. Electron Transfer *vs.* Proton Capture. I. Base-Catalyzed Hydrogen-Deuterium Exchange of Triphenylmethane in the Presence and Absence of Electron Acceptors

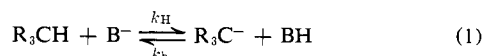
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**Abstract:** Triphenylmethide ions from the reaction of triphenylmethane with alkoxide ions in alcohol can be trapped by aromatic nitro compounds and by oxygen. The trapping is believed to be an electron-transfer process. The efficiency of trapping relative to protonation is a function of the nature of the reaction medium. Conditions favoring tight ion pairing increase the efficiency of trapping by nitrobenzene but have the opposite effect on oxygen trapping.

This paper and those to follow will describe the trapping of carbanions by one-electron oxidation. The rates of electron-transfer reactions are often nearly diffusion controlled, making the method uniquely suited for study of the short-lived carbanions characteristically observed during ionization rate measurements.

Exothermic protonation reactions are inherently fast. To permit the convenient measurement of  $k_H$  in eq 1,



$B^-$  must be selected such that  $K_{eq} = k_H/k_h \ll 1$ . In most carbanion studies,<sup>1</sup>  $k_H = 10^{-4}$  to  $10^{-6} M^{-1} sec^{-1}$ , and the estimated<sup>2</sup> value of  $k_h$  is  $10^5$  to  $10^8$ . This places carbanion concentrations well below the limits

(1) Examples of carbanion formation by slow ionization of carbon acids may be found in D. J. Cram, "Fundamentals of Carbanion Chemistry," A. T. Bloomquist, Ed., Academic Press, New York, N.Y., 1965.

(2) C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 2960 (1967).