5 H), 2.7–2.2 (overlapping m, 4 H), 1.9–1.5 (m, 4 H); exact mass 162.1043 (calcd for $C_{11}H_{14}O$, 162.1045). **2-Benzylcyclobutanone (14):** IR (CCl_4) 1788 cm^{-1}; 100-MHz NMR (CCl_4) δ 7.13 (m, 5 H), 3.7–3.3 (m, 1 H), 3.2–2.5 (m, 4 H), 2.4–1.5 (m, 2 H); exact mass 160.0884 (calcd for $C_{11}H_{12}O$, 160.0888).

Pyrolysis of α-Phenylfurfuryl-α-*d*$_1$ Acetate (4-*d*$_1$). A quantity of 500 mg of 4-d_1 was pyrolyzed at 600 °C in the normal manner. The products were collected in 10 mL of ethyl acetate, catalytically hydrogenated as described above, and the reduction products were collected by GLC as described above. **5-Phenylpentanal (13):** IR (CCl_4) 1734 cm^{-1}; exact mass 162.1038 (calcd for $C_{11}H_{14}O$, 162.1045); 37% d_0; exact mass 163.1085 (calcd for $C_{11}H_{13}OD$, 163.1108); 59% d_1 (remaining, 4% d_2). Comparison of the integration of signals in the 100-MHz NMR (CCl_4) spectrum of this product showed a relative decrease in intensity at δ 9.65 (t, J = 1.5 Hz) for the aldehydic proton. **2-Benzylcyclobutanone (14):** IR (CCl_4) 1788 cm^{-1}; exact mass 160.0875 (calcd for $C_{11}H_{12}O$, 160.0888); 22% d_0; exact mass 161.0928 (calcd for $C_{11}H_{11}OD$, 161.0951); 75% d_1 (remaining, 3% d_2). Comparison of the integration of signals in the 100-MHz NMR (CCl_4) spectrum of this product showed a relative decrease in the intensity at δ 3.2–2.5 (multiplet) for the benzylic protons.

In another run 300 mg of **4**-d_1 was pyrolyzed at 600 °C in the normal manner and collected in 10 mL of ethyl acetate. The solution was treated with a 10% sodium hydroxide solution and 7 and **8** were collected by GLC as previously described. Relative integration of resonances in the 100-MHz NMR (CCl_4) spectrum indicated 51% deuterium incorporation in this product mixture. Analysis by high-resolution mass spectrometry showed 44% d_0, 53% d_1, 3.0% d_2.

Pyrolysis of (*E*)- and (*Z*)-5-Phenylpent-2-en-4-ynals 7, 8. Approximately 50 mg of a mixture of **7** and **8** was pyrolyzed at 600 °C in the normal manner. The products were collected in ca. 10 mL of acetone and the solution was concentrated: IR (CCl_4) 2200, 1789, 1774, 1694 cm^{-1}; 100-MHz NMR ($CDCl_3$) δ 10.02 (d, J = 8.0 Hz), 9.37 (d, J = 6.0 Hz), 8.84 (d, J = 3.0 Hz), 8.47 (d, J = 3.0 Hz). (Only the low-field region of the NMR spectrum was recorded).

Deuterium–Hydrogen Exchange in α-Phenylfurfuryl-α-*d*$_1$ Acetate (4-*d*$_1$). A quantity of **4**-d_1 was pyrolyzed at 500 °C in the normal manner. The products were collected in 10 mL of carbon tetrachloride. The solution was concentrated and the 100-MHz NMR spectrum recorded. The production of **5–8** was evidenced by the appearance of the previously described low-field doublets. Multiplets at δ 6.15 and 6.03 indicated the presence of **4**-d_1. The twofold expansion of the region from δ 7.15 to 5.93 gave no signal at δ 6.73 for the methine proton of α-phenylfurfuryl acetate (**4**). Upon addition of **4** a singlet appeared at δ 6.73.

Pyrolysis of Naphthalene. A quantity of 200 mg of naphthalene was pyrolyzed at 600 °C. The IR and NMR spectra of the material in the trap were identical with those of naphthalene.

Acknowledgment. We thank Professor Charles P. Casey for the suggestion that scrambling of the deuterium atom of **4**-d_1 by 1,5-hydrogen shifts might be significant under our pyrolysis conditions.

References and Notes

(1) (a) We thank the Mobil Foundation for partial support of this work. (b) Based on work by D.L.A. in partial fulfillment of the requirements for the M.S. degree at I.S.U.
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Syntheses of Trans Doubly Bridged Ethylenes.[1] (±)-C_2-Bicyclo[10.8.0]eicos-1(12)-ene and (±)-D_2-Bicyclo[8.8.0]octadec-1(10)-ene

Masao Nakazaki,* Koji Yamamoto, and Junichiro Yanagi

Contribution from the Department of Chemistry, Facility of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan. *Received June 16, 1978*

Abstract: Ultraviolet irradiation converted C_{2v}-bicyclo[10.8.0]eicos-1(12)-ene (**18**) and D_{2h}-bicyclo[8.8.0]octadec-1(10)-ene (**16**) into (±)-C_2-bicyclo[10.8.0]eicos-1(12)-ene (**23**) and (±)-D_2-bicyclo[8.8.0]octadec-1(10)-ene (**21**), respectively. Their chemistry was found to reflect the unusually buried and strained nature of their double bonds sandwiched between two polymethylene bridges.

On replacing two of its equivalent hydrogen atoms by a polymethylene bridge, D_{2h} symmetry inherent to ethylene molecule **1** permits the formation of three types of monocyclic compounds, **2**, **3**, and **4**, each possessing approximately C_{2v}, C_{2v}, and C_s symmetry, respectively.

When the spanning carbon chain becomes smaller, the trans cycloalkene **4**[2] cannot have the achiral planar conformation **4** and is forced to have the nonplanar chiral conformations **5** or **8**, both with C_2 symmetry.[3,4] In *trans*-cyclooctene (**7**) the energy barrier between two enantiomeric conformers **7** and **10** is high enough to make its optical resolution[5,6] feasible at room temperature. Further replacing the remaining equivalent two hydrogen atoms in **2**, **3**, and **6** by the second carbon chain affords the bicyclic olefins **11**, **14**, and **19** illustrated in Chart III; each exhibits characteristic symmetry depending upon the relationship between *n* and *m*. Among them, the "trans"

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Chart I

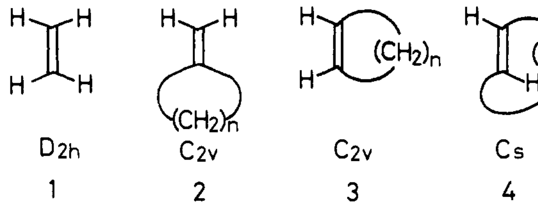


Chart II

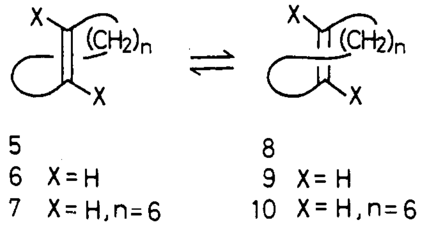
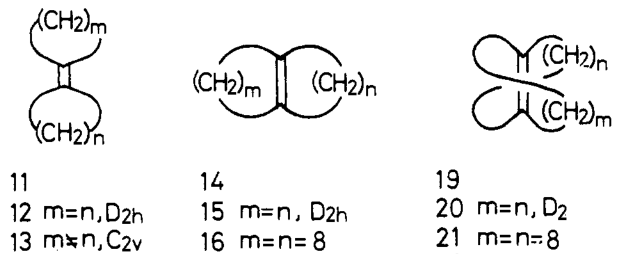


Chart III



doubly bridged ethylene **19**[7] is conspicuous in several structural aspects: (1) chirality, (2) chemical topology (vide infra), and (3) unusual buried nature of the double bond sandwiched between two polymethylene bridges.

We have been interested in the preparation and chiroptical properties of high-symmetry chiral (gyrochiral)[8] molecules having twisted and strained π-electron systems, and the syntheses of (−)-(*R*)-[3]chochin (**24**)[9] and (+)-(*S*)-[8][8]paracyclophane (**25**)[10] have been reported from our laboratory.

We report here the syntheses of (±)-C_2-bicyclo[10.8.0]eicos-1(12)-ene (**23**)[7] and (±)-D_2-bicyclo[8.8.0]octadec-1(10)-ene (**21**)[7] which can be regarded as ethylene analogues **26** of [*m*][*n*]paracyclophanes.[10]

Results and Discussion

In principle, the practical synthetic strategy to build up "trans" doubly bridged ethylene **19** from precursors with the double bond can be roughly classified into the following three routes:[11] (a) synthesis of monocyclic trans-cycloalkene derivative **5** with suitable substituents (X), followed by modification and ring closure of the substituents to afford the second ring; (b) synthesis of more easily accessible monocyclic cis-cycloalkene derivatives with suitable substituents, followed by modification and ring closure of the substituents to give the second ring, with cis-trans configurational inversion somewhere before the ring closure; (c) synthesis of the "cis" doubly bridged ethylene **14**, followed by cis-trans configurational inversion to yield the "trans" doubly bridged ethylene **19.**

While the first was eventually Marshall's synthetic approach to his "[10.10]betweenanene" (**20,** *m* = *n* = 10),[12] the third was our choice to secure "trans"-[10][8] (**23**) and "trans"-[8][8] (**21**) doubly bridged ethylenes from their precursors **18** and **16,** respectively.

Synthesis of (±)-C_2-Bicyclo[10.8.0]eicos-1(12)-ene (23) (Chart V). A modification of Heimbach's procedure[13] for the

Chart IV

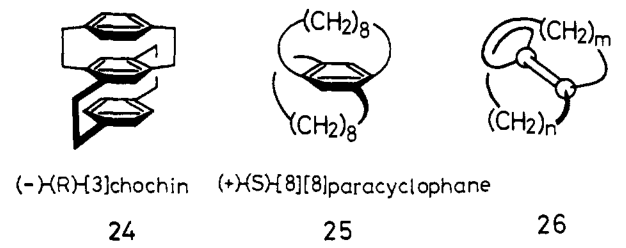
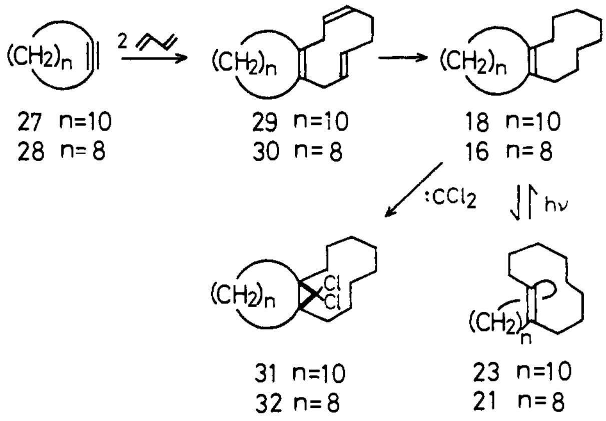


Chart V



cooligomerization of cyclododecyne (**27**)[14] with 2 mol of 1,3-butadiene afforded a 70% yield of the "cis" bicyclic triene **29,** mp 90–91 °C, whose partial catalytic hydrogenation with Raney nickel catalyst gave the "cis"-[10][8] doubly bridged ethylene **18,** mp 63–64 °C, in 86% yield.

Stereochemical considerations predicted that when applied on the "cis" doubly bridged ethylene **14** the cis–trans isomerization process based on the addition–elimination principle[15] should fail in the elimination stage because of the expected steric crowdedness around the reaction center, and this prompted us to invoke photochemical cis–trans isomerization[16] to effect this final and critical step in our synthetic sequence.

A cyclohexane solution of "cis"-[10][8] doubly bridged ethylene **18** with xylene as sensitizer was irradiated with a medium-pressure mercury lamp (Toshiba, SHL-100UV) in a photolysis tube through which a slow and fine stream of nitrogen was passed. Monitoring the reaction by GLC indicated that irradiation for 12 h yielded a 2.4:1 mixture of "cis" and "trans" isomers and this ratio remained unchanged after further irradiation. After several trials to improve the conversion ratio, 3-h irradiation with a low-pressure mercury lamp[17] (HALOS, PIL-30, Eikosha Co., Osaka) was found to be enough to afford a 1:2 mixture of "cis" and "trans" isomers without sensitizer.

Attempts to separate these isomers in quantity by several methods including silica gel-$AgNO_3$ chromatography were found unsatisfactory, and our final success was achieved by a chemical method which made use of the expected inertness of the "trans" isomer toward dichlorocarbene because of the buried nature of the double bond.

The isomeric mixture was stirred with 50% sodium hydroxide, chloroform, and cetyltrimethylammonium chloride (phase transfer catalyst)[18] at 50 °C to yield a mixture of unchanged "trans" isomer **23** and the dichlorocarbene adduct **31** of the "cis" isomer. On preparative silica gel chromatography, elution with hexane afforded the "trans"-[10][8] doubly bridged ethylene **23,** mp 37–38 °C, in the fast-moving zone, and the dichlorocarbene adduct **31,** mp 120–121 °C, in the slow-moving zone, yielding the "trans" isomer **23** in 26 and

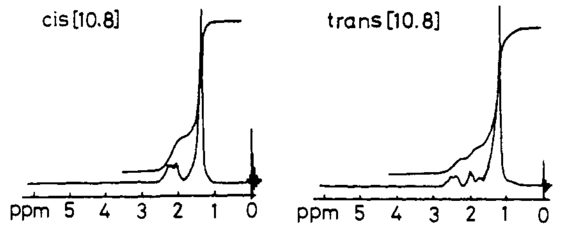


Figure 1. NMR spectra of "cis"-[10][8] (**18**) and "trans"-[10][8] (**23**) doubly bridged ethylenes (60 MHz, in CCl_4).

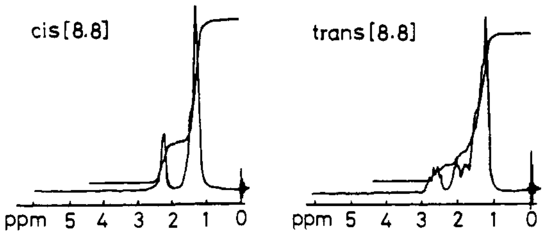


Figure 2. NMR spectra of "cis"-[8][8] (**16**) and "trans"-[8][8] (**21**) doubly bridged ethylenes (60 MHz, in CCl_4).

Table 1. Ultraviolet Spectral Data of Doubly Bridged Ethylenes in Hexane

compd	λ_{max}, nm (ϵ)
"cis"-[8][8] (**16**)	201.5 (10 500), 206 sh (9900), 213 sh (5600)
"cis"-[10][8] (**18**)	202 (9000), 206 sh (8800), 213 sh (5000)
"trans"-[8][8] (**21**)	201 sh (3300), 222.5 (5400)
"trans"-[10][8] (**23**)	200 sh (3900), 217.5 (6600)

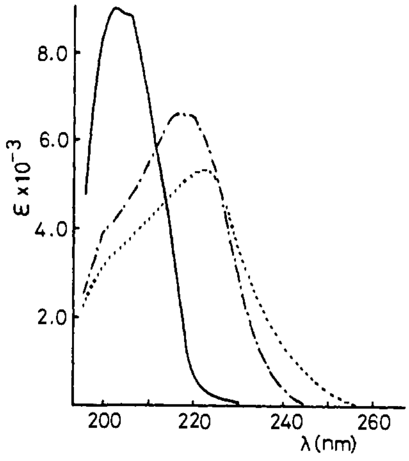


Figure 3. Ultraviolet spectra of "cis"-[8][8] (**16**) (—), "trans"-[10][8] (**23**) (— — —), and "trans"-[8][8] (**21**) (- - - - - - -) doubly bridged ethylenes in hexane.

46% yields, respectively, from the reaction mixtures irradiated with medium- and low-pressure mercury lamps.

Synthesis of (±)-D_2-Bicyclo[8.8.0]octadec-1(10)-ene (21) (Chart V). Starting from cyclodecyne (**28**),[14] Heimbach's cooligomerization[13] with 2 mol of 1,3-butadien afforded a 75% yield of the cis,cis,trans bicyclic triene **30**, mp 72.5–73.5 °C, which was partially hydrogenated with Raney nickel catalyst to give "cis"-[8][8] doubly bridged ethylene **16**, mp 105–106 °C.

Since experiences in photochemical cis–trans isomerization of monocyclic olefins with smaller ring members had told us that much reluctant conversion must be expected, we were not surprised to find no "trans" isomer **21** formed after 48-h irradiation of "cis"-[8][8] doubly bridged ethylene **16** with the medium-pressure mercury lamp in a cyclohexane solution containing xylene as the sensitizer. Irradiation with the low-pressure mercury lamp, however, saved the situation, yielding a 9:1 mixture of "cis" and "trans" isomers after 4-h irradiation. Extraction with cold pentane enriched the "trans" isomer to give a 1:1 mixture which was treated with dichlorocarbene as described in the [10][8] series of compounds. Preparative silica gel TLC gave a 4% yield of "trans"-[8][8] doubly bridged ethylene **21**, bp 125–127 °C (0.1 mm), but attempts to isolate the dichlorocarbene adduct **32** of the "cis" isomer **16** in pure form was unsuccessful at this time.

NMR Spectra. Figures 1 and 2 illustrate the NMR spectra of the "cis" and "trans" doubly bridged ethylenes whose preparations are reported in this communication.

The most conspicuous features are the peaks corresponding to allylic protons which characteristically reflect their molecular symmetries. The "cis"-[10][8] isomer **18** with C_{2v} symmetry exhibits the allylic peaks at δ 1.87–2.50, while the allylic protons of the "trans"-[10][8] isomer **23** with C_2 symmetry shows a rather complex pattern consisting of three separate groups at δ 1.58–1.82 (2 H), 1.85–2.10 (2 H), and 2.22–2.76 (4 H) (Figure 1). These characteristic differences between the pair of "cis" and "trans" doubly bridged ethylenes are demonstrated more markedly in the [8][8] homologues with higher symmetries. The allylic protons of the "cis"-[8][8] isomer **16** with D_{2h} symmetry appear at δ 1.92–2.60 as a fairly sharp symmetrical peak, while the "trans" isomer **21** with D_2 symmetry shows three separate peaks with chemical shifts of δ 1.60–1.83 (2 H), 1.83–2.20 (2 H), and 2.25–2.90 (4 H).

Ultraviolet Spectra. The ultraviolet spectra of the "cis" and "trans" pair of [10][8] and [8][8] doubly bridged ethylenes are reproduced in Figure 3 and summarized in Table I.

Dramatic changes in ultraviolet spectra were observed on going from the "cis" to the "trans" series doubly bridged ethylenes, and this can most clearly be seen among the pair of stereoisomers in [8][8] doubly bridged ethylenes where a bathochromic shift as large as 21 nm accompanied with marked decrease in extinction coefficient plainly reflects an unusual nature of double bond in the "trans" isomer **21** caused by out of plane bending and rehybridization of the strained π bond.[19]

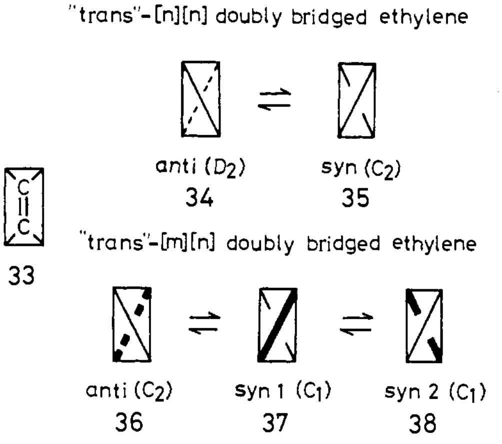
Comparative Reactivities between the "Cis" and "Trans" Doubly Bridged Ethylenes. Inspecting the molecular models, one could not fail to notice the most interesting feature about the "trans"-[10][8] and [8][8] doubly bridged ethylenes: the double bonds which are deeply buried in cavities formed by two polymethylene bridges. Undoubtedly, this steric hindrance explains the inertness of the "trans" isomers toward dichlorocarbene, the fact we made use of for isolating the "trans" isomers from the photochemical isomerization mixtures.

Additional information on the buried and hindered nature of the double bonds came from their catalytic hydrogenation (60–65 °C, in ethyl acetate with acetic acid) with PtO_2 at 1 atm pressure of hydrogen, where both "trans" isomers **21** and **23** resisted hydrogenation while their "cis" counterparts **16** and **18** under the same condition were found to be saturated to give the dihydro derivatives within 32 and 10 h, respectively.

It seems pertinent to note here the fact that competing with the "cis" isomers, the "trans" isomers are always the ones to be detected in the fast-moving zone in chromatography (GLC, TLC, and column chromatography) which also reflects the unexposed and protected nature of the double bond in the "trans" isomers as well as their impact and somewhat spherical molecular shapes.

Finally the reversible nature of the photochemical cis–trans isomerization in the doubly bridged ethylenes has been demonstrated when gas chromatography of the irradiation products of "trans"-[10][8] and [8][8] isomers indicated that both

Chart VI



isomers converted into a 1:1 mixture of "cis" and "trans" isomers by 48-h irradiation with a medium-pressure mercury lamp and 2-h irradiation with a low-pressure mercury lamp, respectively.

Chemical Topology. Inspection of the molecular models of "trans"-[10][8] (**23**) and [8][8] (**21**) doubly bridged ethylene reveals that their polymethylene bridges should be on the opposite side of the double bond (anti conformer **34**), and this is supported by the buried nature of the double bond demonstrated by their observed inertness toward catalytic hydrogenation and dichlorocarbene.

However, when the polymethylene chains become long enough, we can expect to have anti (D_2 symmetry) and syn (C_2 symmetry) geometrical conformers for "trans"-[*n*][*n*] doubly bridged ethylene as can be seen from the schematic illustration in Chart VI, where the rectangle **33** symbolizes the central double bond and diagonal lines represent the polymethylene bridges.

A little complication appears in "trans"-[*m*][*n*] doubly bridged ethylenes with different polymethylene bridges where we can expect one anti (C_2 symmetry), **36**, and two syn forms (C_1 symmetry), **37** and **38**, depending upon which chain comes nearer to the double bond. These situations are completely parallel to those observed in [*n*][*n*]- and [*m*][*n*]paracyclophanes.[10]

Experimental Section

Melting and boiling points are uncorrected. Infrared spectral data and nuclear magnetic resonance spectra were obtained from a Hitachi EPI-S2 spectrophotometer and a JNM-MH-60 spectrometer, respectively. Ultraviolet spectra were recorded on a Hitachi EPS-3T spectrometer. Mass spectral data were measured on a Hitachi RMS-4 spectrometer. Gas-liquid chromatography (GLC) was carried out using a JEOL JGC-20K gas chromatograph equipped with a 2-m stainless steel column packed with 5% SE-30 (200 °C) on Chromosorb W. Elemental analyses were performed with a Yanagimoto CHN-Corder type 11.

***cis,cis,trans*-Bicyclo[10.8.0]eicos-1(12),14,18-triene (29).** Cooligomerization of cyclododecyne (**27**)[14] with 1,3-butadiene was carried out by the method reported by Heimbach and Brenner.[13] To a stirred solution of cyclododecyne (**27**, 14.5 g, 8.8 mmol), nickel acetylacetonate (1.2 g, 4.7 mmol), triphenylphosphine (1.2 g, 4.6 mmol), and 1,3-butadiene (3 mL), in dry toluene (50 mL) was added dropwise triethylaluminum (1 mL, 8.8 mmol) at 0 °C. A slow stream of 1,3-butadiene (90 mL) was introduced into the stirred mixture at 40 °C for 8 h. After evaporation of excess 1,3-butadiene and toluene at 5 °C under reduced pressure, the residue was mixed with ether (100 mL) and 20% hydrochloric acid (50 mL). The resulting mixture was bubbled with oxygen at room temperature for 0.5 h and the separated organic layer was washed with 3% sodium bicarbonate solution and water and then dried over Na_2SO_4. Evaporation of the ether gave a solid, which was recrystallized from pentane to give **29** (16.8 g, 70% yield), mp 90–91 °C (lit.[13] mp 89–93 °C).

***cis,cis,trans*-Bicyclo[8.8.0]octadec-1(10),12,16-triene (30).** Preparation of the bicyclotriene **30** was carried out by the same method described for the preparation of **29**, utilizing cyclodecyne (**28**,[14] 18.5 g, 13.6 mmol), nickel acetylacetonate (1.4 g, 5.5 mmol), triphenylphosphine (1.4 g, 5.4 mmol), dry toluene (60 mL), triethylaluminum (1.7 mL, 14.9 mmol), and 1,3-butadiene (90 mL). Recrystallization of the product gave **30** (24.9 g, 75% yield): mp 72.5–73.5 °C (from pentane); IR (KBr) 3010, 2925, 2850, 1665, 1645, 1470, 1440, 1200, 968, 810, 790, 720, 709, 690 cm^{-1}; NMR ($CDCl_3$) δ 1.38 (m, 12 H), 1.98 (m, 8 H), 2.73 (m, 4 H), 4.90–5.60 (m, 4 H). Anal. ($C_{18}H_{28}$) C, H.

C_{2v}-Bicyclo[10.8.0]eicos-1(12)-ene (18). A solution of the bicyclotriene **29** (14 g, 51.5 mmol) in 200 mL of hexane, to which 5 g of Raney nickel (W-5) had been added, was hydrogenated in a 1-L steel bomb at 100 atm of hydrogen for 5 h at room temperature. After removal of the catalyst, the filtrate was concentrated to give crystals. Recrystallization from acetone yielded **18** (12 g, 85% yield), mp 63–64 °C (lit.[13] mp 63.5–64 °C).

D_{2h}-Bicyclo[8.8.0]octadec-1(10)-ene (16). The bicyclotriene **30** (21 g, 86 mmol) was partially hydrogenated by the procedure described for the preparation of **18**. The crude product was recrystallized from acetone to give **16** (18.7 g, 88% yield): mp 105–106 °C; IR (KBr) 2920, 2850, 1480, 1458, 1444, 1240, 1170, 1114, 800, 790, 765, 697 cm^{-1}; NMR (CCl_4) δ 0.90–1.72 (24 H), 1.92–2.60 (8 H); UV and NMR spectra are tabulated in Table I and Figures 2 and 3; mass spectrum *m/e* 248 (M^+). Anal. ($C_{18}H_{32}$) C, H.

(±)-C_2-Bicyclo[10.8.0]eicos-1(12)-ene (23). A. Photoisomerization with a Medium-Pressure Mercury Lamp. A solution of **18** (1 g) in cyclohexane (10 mL) containing 2 mL of xylene was placed in a photolysis tube, and a slow, fine stream of nitrogen was passed through the solution during the reaction. After 12-h irradiation with a medium-pressure mercury lamp (Toshiba, SHL-100 UV), the solvent was removed in vacuo, leaving an oil whose GLC analysis (retention times: cis isomer **18** > trans isomer **23**) revealed a 2.4:1 ratio of *cis*-**18** and *trans*-**23** isomers. After the mixture was stirred with 50% aqueous NaOH (8 mL), chloroform (10 mL), and cetyltrimethylammonium chloride (30 mg) at 50 °C for 1 h, the chloroform layer was separated and washed with water, then dried over $MgSO_4$. After evaporation of the solvent, the residue was PTL chromatographed on silicic acid. Elution with hexane gave two bands which contained the following compounds. (±)-C_2-Bicyclo[10.8.0]eicos-1(12)-ene (**23**) was isolated from the fast-moving zone, and recrystallization from acetone yielded colorless crystals: mp 37–38 °C (260 mg, 26% yield); IR (KBr) 2925, 2850, 1465, 1450, 1265, 733, 704 cm^{-1}; NMR (CCl_4) δ 0.92–1.58 (m, 28 H), 1.58–1.82 (m, 2 H), 1.85–2.10 (m, 2 H), 2.22–2.76 (m, 4 H); UV and NMR spectra are tabulated in Table I and Figures 1 and 3; mass spectrum *m/e* 276 (M^+). Anal. ($C_{20}H_{36}$) C, H.

The dichlorocarbene adduct **31** was isolated from the slow-moving zone, and was recrystallized from hexane to melt at 120-121 °C (600 mg, 46% yield): IR (KBr) 2930, 2850, 1480, 1446, 865, 842, 735 cm^{-1}; NMR (CCl_4) δ 1.12-1.95 (m, 36 H); mass spectrum *m/e* 359 (M^+). Anal. ($C_{21}H_{36}Cl_2$) C, H, Cl.

B. Direct Photoisomerization with a Low-Pressure Mercury Lamp. A solution of **18** (1 g) in hexane (100 mL) was irradiated with a 30-W low-pressure mercury lamp (HALOS, PIL-30, Eikosha Co., Osaka) for 4 h to give a 1:2 mixture of *cis*-**18** and *trans*-**23** isomers. Isolation of the trans isomer **23** was carried out following the procedure described above affording **23**, mp 37–38 °C (460 mg, 46% yield), and the dichlorocarbene adduct, mp 120–121 °C (300 mg, 23% yield).

(±)-D_2-Bicyclo[8.8.0]octadec-1(10)-ene (21). The cis bicyclooctadecene **16** (3 g) was dissolved in 300 mL of cyclohexane, and three 100-mL aliquots were irradiated with the 30-W low-pressure mercury lamp for 4 h as described for the photoisomerization of **18**. A GLC analysis of the reaction mixture revealed the pressure of *cis*-**16** and *trans*-**21** isomers in a ratio of 9:1. The combined hexane solutions were concentrated to yield a semisolid which was extracted with two 10-mL portions of cold pentane. Concentration of the combined pentane extracts afforded 0.5 g of an oil whose GLC analysis indicated that the trans isomer **21** was enriched to a ratio of 1:1 against the cis isomer **16**. Isolation of the trans isomer **21** was carried out by the procedure described for the preparation of **23**. To the mixture of the isomers dissolved in 4 mL of chloroform was added 50% aqueous NaOH (3 mL) and cetyltrimethylammonium chloride (12 mg), and the reaction mixture was stirred at 50 °C for 1.5 h. After cooling to room temperature, the chloroform solution was separated, washed with water, and then dried over $MgSO_4$. Evaporation of the solvent gave an oily material which was PTL chromatographed over silicic acid. Elution of hexane yielded (±)-D_2-bicyclo[8.8.0]octadec-1(10)-ene (**21**, 120 mg, 4% yield): bp 125–127 °C (0.1 mm); $n^{21}{}_{D}$ 1.5279; IR (film) 2925, 2850, 1460, 1450, 1264, 731, 705 cm^{-1}; NMR (CCl_4) δ 0.76–1.60 (m, 24 H), 1.60–1.83 (m, 2 H), 1.83–2.20 (m, 2 H), 2.25–2.90 (m, 4 H); UV and NMR spectra are tabulated in Table I and Figures 2 and 3; mass spectrum *m/e* 248 (M^+). Anal. ($C_{18}H_{32}$) C, H.

References and Notes

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Effect of Pressure on the [2 + 2 → 4] Cycloaddition Reaction of Tetracyanoethylene to Enol Ethers

Jörn von Jouanne,* Hartwig Kelm,* and Rolf Huisgen

Contribution from the Institute for Physical Chemistry of the University, D-6000 Frankfurt(Main), West Germany, and the Institute for Organic Chemistry of the University, D-8000 München 2, West Germany.

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Abstract: The general volume profile of the cycloaddition reaction of tetracyanoethylene to different enol ethers was determined. It consists at 25 °C in CH_2Cl_2 solutions of a reaction volume of −30 mL/mol for the formation of the cycloadducts, a reaction volume of −4 mL/mol for the charge transfer complex formed between the educts, and a volume of activation of −36 mL/mol. A variation of the enol ether has no major effect on these volume data. This is in agreement with a mechanism which includes a zwitterionic intermediate and a "dead-end" charge transfer complex.

Introduction

Since their discovery[1] the thermal cycloaddition reactions between enol ethers and tetracyanoethylene (TCNE) have attracted much attention.[2-14] The mechanism of this type of ring formation, which in principle can proceed by three different pathways, was the subject of recent investigations. Several criteria like the steric course of the cycloadditions to cis-trans isomeric enol ethers,[4] the reversibility of the first step,[5] the solvent effect on the rate,[6] and the structure-rate relationship of the enol ether reactant[7] present strong evidence for an at least two-step mechanism involving a zwitterionic intermediate. The proposed intermediate could, in fact, be trapped with alcohols[8] and was amenable to 1,4-dipolar cycloadditions[9] to various heteromultiple bond systems to give six-membered rings.

A study of the pressure dependence of the reaction rate between TCNE and *n*-butyl vinyl ether[10] in different solvents showed that the experimentally observed volume of activation, $\Delta V^{\neq}_{\text{exp}}$, can be split into a part due to bond formation, $\Delta V^{\neq}_{\text{intr}}$, and a solvation term, $\Delta V^{\neq}_{\text{solv}}$. The latter proved to depend strongly on the electrostriction parameter

$$q_P = \frac{3}{(2D+1)^2}\frac{dD}{dP} \quad (D = \text{dielectric constant})$$

of the solvent. Within the Kirkwood formalism this agrees exactly with what one would expect for a highly polar transition state. The calculated dipole moment for the transition state, 15 ± 3 D, points to a zwitterionic structure in which, as opposed to the postulated intermediate, the charges are not yet fully developed.

The present study was undertaken to examine whether $\Delta V^{\neq}_{\text{intr}}$ depends on the structure of the enol ether reactant, while the solvent, and thus to a first approximation $\Delta \bar{V}^{\ddagger}_{\text{solv}}$, is

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*The University, D-6000 Frankfurt(Main), West Germany.

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