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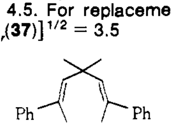

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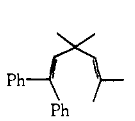

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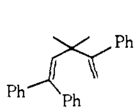

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(b) $k_{d_r}(\text{calcd})(\mathbf{8}) = k_{d_r}(\mathbf{36})/(K_{CH_3 \rightarrow Ph}\, K_{H \rightarrow CH_3})$.
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Propellanes. X. The Dimerization of 9,9-Dichlorotricyclo[4.2.1.$0^{1,6}$]non-3-ene[1]

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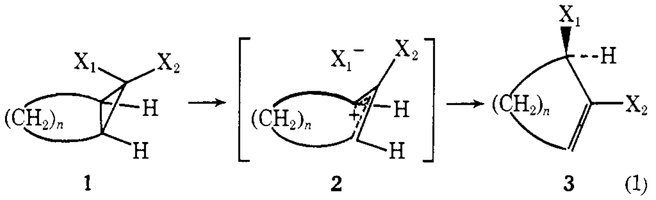
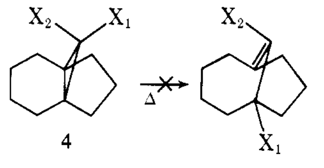
Abstract: The syntheses and subsequent dimerization of 9,9-dichlorotricyclo[4.2.1.$0^{1,6}$]non-3-ene and 9,9-dichlorotricyclo[4.2.1.$0^{1,6}$]nonane are reported. Both dimerizations occur via the intermediacy of a bridgehead olefin (comparable to a *trans*-cycloheptene). In the former case, this olefin has been trapped as a Diels–Alder adduct with furan. The double bond of the first above-mentioned dichloride exerts a retarding effect on the ring-opening (leading to dimerization) reaction, either via a rather large inductive effect, or a bishomoantiaromatic (electronic) effect.

It has long been known that bicyclic dihalocyclopropanes are subject to ring opening to give vinyl allylic dihalides (eq 1).[3] The rate of the reaction is a function of the strain relief inherent in the transformation and generally requires $n \leq 4$ in order to occur at moderate temperatures. The reaction meets all the criteria for ionicity (including Ag^+ promotion) and may be formulated as proceeding through an allylic ion (**2**). When this ring opening is monitored for its stereochemistry, it is found to follow the Woodward-Hoffmann-De Puy rules[4] (i.e., **1** gives **3** when n is small).



1 2 3 (1)

When the dihalocyclopropane unit is contained within a propellane structure (e.g., **4**), the ring-opening reaction is not expected to occur easily since the product would necessarily contain a bridgehead double bond[5] (in the case of **5**, comparable to a trans double bond in a seven-membered ring[5c]). Thus **4** ($X_1 = X_2 = Br$) is thermally stable, unless heated in polar solvents.[6] It was thus initially surprising when we found[7] that 9,9-dichlorotricyclo[4.2.1.$0^{1,6}$]non-3-ene (**6**) was thermally unstable with respect to ring opening.

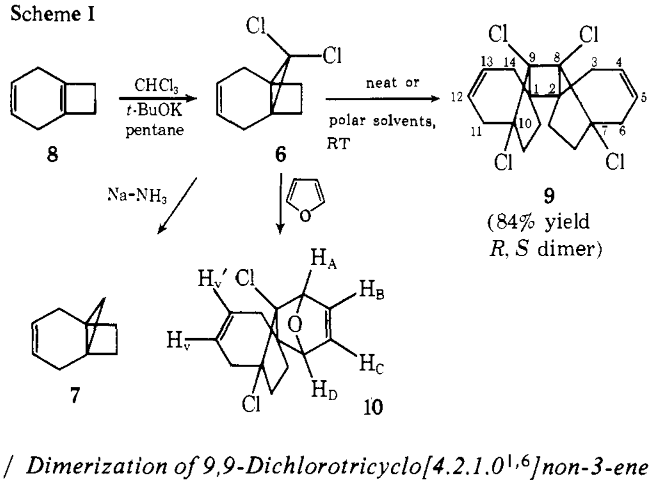


4 5 (2)

Results and Discussion

Our synthesis of **6** stemmed from our desire to study the chemistry of the corresponding [4.2.1]propell-3-ene[8] (**7**). Upon our first attempt to isolate **6** following dichlorocarbene addition to dihydrobenzocyclobutene (**8**), the oil obtained after rotoevaporation of the pentane solvent suddenly underwent an exothermic reaction upon warming to room temperature. A white, crystalline material (**9**) was simultaneously deposited (Scheme I). Subsequently, we found the

Scheme I



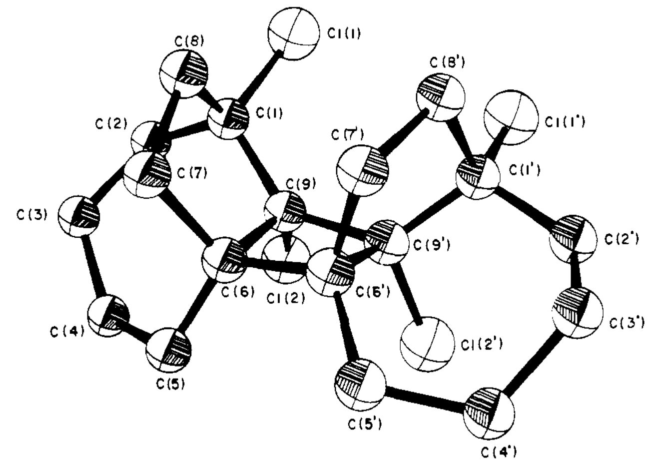


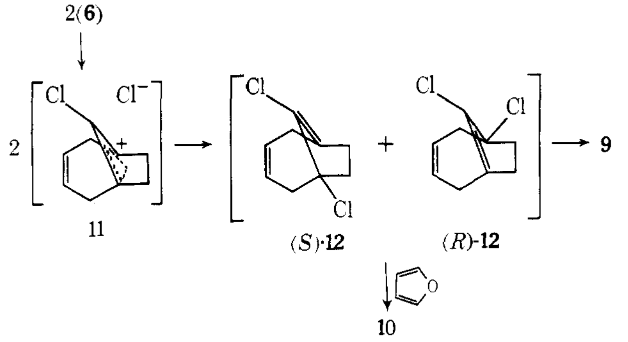
Figure 1. Computer-generated drawing of the final X-ray model of **9**.

yield of this dimer to be quite high (>80% isolated), and we could not identify any isomeric dimer (if any is formed, we estimate it constitutes <5% of the product). Since the usual spectral techniques (mass, NMR, ir) were uninformative with respect to the molecular structure of **9**, an X-ray analysis was performed.

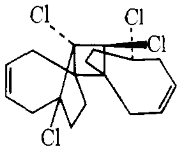
Figure 1 is a computer-generated drawing of the final X-ray model of **9**. Bond distances and angles generally agree with accepted values within the estimated standard deviations (0.01 Å and 1°, respectively). The dihedral angle between the five- and four-membered rings is 118°, while that between the five- and seven-membered rings is approximately 130°. The cyclobutane ring is folded with a dihedral angle of 170°.

Further examination of the dimerization reaction of **6** showed a rough dependence on solvent polarity. Thus in acetone, DMF, Me_2SO, CH_3CN, and methanol, dimer formation (**9** only) occurred within minutes. At comparable concentrations, dimerization in solvents such as pentane, benzene, and hexafluorobenzene took at least 1-2 days. These observations reinforced our supposition of an ionic reaction leading to a bridgehead olefin intermediate (**12**) which dimerizes (Scheme II). It would be particularly difficult to explain the dimerization in methanol without invoking **12** as an intermediate.[9] Cation **11** is represented as a "partially-opened" cyclopropyl cation, in accord with the effect of the double bond (vide infra) and other evidence in similar systems.[4c,11]

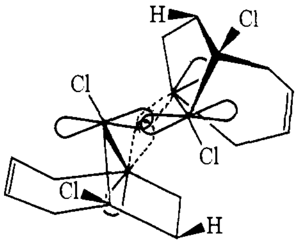
Scheme II



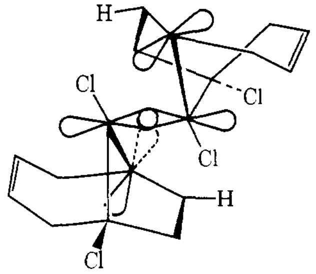
Inasmuch as there are 11 possible stereoisomeric structures for the dimer of **12**, it is interesting that only one is formed in consequential quantities. Examination of a molecular model of **12** indicates that the four-carbon bridge completely shields the bridgehead double bond from attack on that side. Hence attack must come from the side syn to the two-carbon bridge. If, as seems likely on steric grounds, dimerization begins via bridge-bridge bonding, only two dimers could result: meso dimer **9** and *S,S (R,R)* dimer **13** (note the chlorines on the cyclobutane ring of **13** are trans). Since (*S*)-**12** and (*R*)-**12** must be formed in equal amounts, statistically one would expect equal quantities of dimer **9** and **13**. However, further examination of models reveals that two molecules of **12** can approach each other in only one transoid manner if they are of the same chirality, and another way if they are enantiomeric; this is depicted below for the *S,S* combination (**14**) and *R,S* combination (**15**).



(*S,S*)-**13**
(*S, S* dimer)



14
S,S dimerization mode



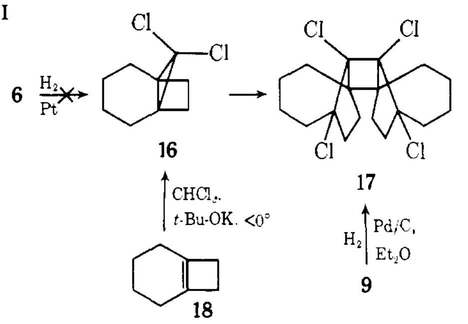
15
R,S dimerization mode

The *S,S* dimerization mode (**14**) apparently requires that both new bonds be made synchronously, thereby clearly violating the strong symmetry restriction against $\pi_{2s} + \pi_{2s}$ cycloadditions. On the other hand, the *R,S* dimerization mode (**15**) leads, initially, to a transoid 1,4 biradical, which can subsequently rotate and cyclize to **9**.

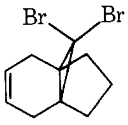
Further evidence for the intermediacy of bridgehead olefin **12** was obtained via trapping experiments. When **6** was mixed with ca. 3 equiv of furan and allowed to stand at room temperature, crystals of **9** were deposited slowly.[12a] After 12 hr, a 65% yield of furan adduct **10** could be isolated.[12b] The dissolution of **6** in acetic acid (room temp) led to a complex product mixture, which was not fully investigated. However, it could be determined that dimer formation was a minor mode of reaction, whereas trapping of intermediate **12** by HOAc led to an important percentage of the product mixture.[13] Irrespective of the exact product composition, it is noteworthy that acetic acid is able to trap **12** whereas methanol cannot.[14]

The effect of the double bond of **6** on the dimerization was next investigated. Initially we attempted to hydrogenate **6** (Pt/C, ether) under conditions where **7** was similarly reduced.[8] However, only a complex mixture was obtained, and this approach was abandoned.[15] Thus we resorted to the somewhat tedious synthesis[16] of **18**.[18] Base-generated dichlorocarbene addition to **18** below 0° led to **16** (Scheme III); however, **16** was extremely labile, darkening rapidly

Scheme III



(even in chloroform solution) with formation of dimer **17.** Evidence for **16** was attained mass spectrometrically; the parent ions observed for **16** at *m/e* 190, 192, and 194 were not present in the mass spectrum of dimer **17.** Thus **16** is clearly more reactive toward ionization and ring opening than is **6.** While we have no kinetic measurements on the relative reactivity of **6** and **16,** the higher lability of **16** is in line with the observed greater solvolytic reactivity of **4** over **19** (a factor of 26).[6a,11] The source of this reactivity difference is either an unusually high inductive effect, or bishomoantiaromaticity in the ion initially formed from **6** (or **19**).



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Experimental Section

All melting and boiling points are uncorrected; melting points were determined in open capillaries. Mass spectra were run on an Atlas CH-4 spectrometer. NMR spectra were obtained using a Perkin-Elmer R-20B or Varian A-60 spectrometer. Either $CDCl_3$ or CCl_4 was used as solvent (as specified); in the former, residual $CHCl_3$ (δ 7.27) or Me_4Si (δ 0.00) and, in the latter, Me_4Si used as internal standards. Analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany.

3,6-Dihydrobenzocyclobutene (8). Prior to Radlick's[21] report of the Birch reduction of benzocyclobutene, we had successfully applied the Birch reduction as described by Hückel[22] to benzocyclobutene (i.e., by merely substituting benzocyclobutene for indane in Hückel's procedure). Our isolated yields were about 90%; Radlick has described the physical properties of **8.**[21]

9,9-Dichlorotricyclo[4.2.1.0^{1,6}]non-3-ene (6). In a 3-l., three-necked round-bottomed flask, equipped with mechanical stirrer, addition funnel, and nitrogen inlet atop the addition funnel suitable for maintaining a static atmosphere of nitrogen, were placed 45 g (0.40 mol) of *t*-Bu-OK, 27.2 g (0.26 mol) of **8**, and 1.5 l. of pentane. After cooling to −40 to −50° (temperature of outside bath), 30.6 g (0.26 mol) of chloroform was slowly added dropwise.[23] The reaction mixture was stirred for another 1.5 hr after addition was complete. After allowing the flask to warm to ca. 0°, a saturated ammonium chloride solution was added to dissolve all solid material. The layers were separated, and the water layer was extracted three times with pentane. The original pentane layer was shaken with more ammonium chloride solution. The pentane layers were combined, dried for 15 min over potassium carbonate, and filtered through Celite. Evaporation of the pentane gave an oil which contained anywhere from 60 to 90% of **6** (NMR analysis). The yield of **6** was generally between 50 and 60% (as determined by weighing oil and immediately running NMR spectrum in CCl_4). It was best to store **6** in dilute pentane solution (about 500 ml of pentane for the above scale reaction).

The NMR of **6** (CCl_4) showed narrow multiplets (almost broad singlets) at δ 2.06 (4 H), 2.22 (4 H), and 5.55 (2 H). The mass spectrum showed important peaks at: *m/e* 188 (P^+ for two^{35} Cl's, rel intensity 39), 190 (intensity 28, calcd, 25), 192 (intensity 8, calcd, 4), 153 ($P^+ - Cl$, intensity 100), 155 ($P^+ - Cl$, intensity 38, calcd, 33), 125 ($P^+ - C_2H_4Cl$, intensity 25), 127 ($P^+ - C_2H_4Cl$, intensity 15, calcd, 16).

Tricyclo[4.2.1.0^{1,6}]non-3-ene (7). About 3.5 l. of ammonia was distilled into a 5-l., three-necked flask equipped with a Dry Ice condenser, mechanical stirrer, and addition funnel. Freshly cut sodium (14 g, 0.6 mol) was added to the ammonia. The above-attained crude pentane solution (500 ml) of **6**, together with 150 ml of methanol, was added rapidly through the addition funnel. After stirring for 1 hr, the ammonia was allowed to evaporate (over night). Next, 500 ml of pentane was added, followed by cooling to 0°, and addition of 250 ml of H_2O. The pentane layer was washed twice with H_2O and dried over potassium carbonate. The solvent was rotoevaporated at room temperature and the product distilled [51–53°, water aspirator, reported,[24] 61° (50 Torr)] to give 12 g (39% overall from **8**) of **7.**

The NMR spectrum has been described;[8] the mass spectrum gave the correct P^+ at *m/e* 120 (rel intensity 45) and the base peak at *m/e* 91. Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.82; H, 9.98.

(1*R,2*S**,7*S**,8*R**,9*S**,10*R**)-7,8,9,10-Tetrachloropentacyclo[8.4.2.2^{2,7}.0^{1,9}.0^{2,8}]octadeca-4,12-diene (9).** Evaporation of the solvent (pentane) from a solution of **6** led to precipitation of a solid, mp 228° dec. For purposes of determining the yield of **9**, a sample of **6** was analyzed by NMR. Solvent was then evaporated and the sample (oil) quickly weighed (this told how much **6** was initially present). The dimerization was then allowed to proceed and the product weighed after collection and washing (pentane). Three separate experiments of this type led to isolated yields of **9** of 56, 62, and 84%. The NMR ($CDCl_3$) showed peaks at δ 5.47 (4 H, olefinics) and 1.79–3.32 (mult, 16 H, aliphatics), while the mass spectrum gave a barely visible P^+ at *m/e* 376 (4^{35}Cl's) and the appropriate peaks for successive loss of the chlorine atoms. Anal. Calcd for $C_{18}H_{20}Cl_4$: C, 57.19; H, 5.33. Found: C, 57.09; H, 5.24.

The dimerization of **6** (to **9**) in solvents (acetone, DMF, Me_2SO, acetonitrile, methanol, benzene, etc.) was typically carried out by evaporating the pentane from a stock solution and adding enough of the appropriate solvent to form an approximately 0.25 *M* solution of **6.** The solutions were then watched (at room temperature) for precipitation of dimer **9**, and ultimately checked by NMR (precipitation did not always occur).

6,7-Dichloro-14-oxatetracyclo]5.4.2.1^{2,5}.0^{1,6}]tetradeca-3,9-diene (10). To approximately 1.8 g of crude **6** (ca. 60% pure) was added, at 0°, 2 g of freshly distilled furan. The mixture was left at room temperature for 12 hr, at which time some crystals of dimer **9** had precipitated. After evaporation of the excess furan, the material was chromatographed on silica gel. Dimer **9** was eluted with pentane (ca. 20% yield), while Diels–Alder adduct **10** was eluted with a 1:1 ether–pentane mixture (ca. 65% yield).

The NMR spectrum has been reported.[7] The mass spectrum shows the appropriate trio of parent ions at *m/e* 256, 258, and 260. Anal. Calcd for $C_{13}H_{14}OCl_2$: C, 60.72; H, 5.49; Cl, 27.57. Found: C, 60.64; H, 5.60; Cl, 27.54.

Attempted Hydrogenation of 6. Approximately 150 mg of **6**, dissolved in 50 ml of ether and containing a catalytic amount of platinum oxide, was placed in a room-pressure microhydrogenation apparatus. After hydrogen uptake was complete (0.5 hr, NMR showed no vinyl protons), the mixture was filtered and the solvent evaporated. Since the NMR was complex in the aliphatic region, the crude product was examined utilizing GLC (10% Carbowax 4000 on 80–100 Chromosorb W). The large number of peaks observed, along with the fact that $Na-NH_3$ reduction of the crude product did not lead to identifiable amounts of [4.2.1]propellane,[8] led us to abandon this approach.

9,9-Dichlorotricyclo[4.2.1.0^{1,6}]nonane (16). In a 25-ml round-bottomed flask, equipped with magnetic stirring bar, 60-ml addition funnel, and nitrogen inlet (static pressure) atop the funnel, were placed 70 mg (0.65 mmol) of **18**[19,20] (**18** showed $\nu_{C=C}$ = 1689.5 in the Raman spectrum), 80 mg of *t*-Bu-OK (0.7 mmol), and 10 ml of pentane. After cooling the flask below 0°, 100 mg (0.84 mmol) of chloroform dissolved in 5 ml of pentane was slowly added. After stirring the reaction for an additional hour, work-up was carried out as described for **6.**

Compound **16** proved to be a very labile oil. A mass spectrum could be obtained which showed the proper trio of weak parent ions at *m/e* 190, 192, and 194, as well as the doublet for loss of one chlorine atom at *m/e* 155, 157. Although dimerization clearly occurred during the process of obtaining an NMR spectrum ($CDCl_3$), one could identify two sets of multiplets [δ 2.8–2.2 (4 H) and δ 2.0–1.4 (8 H)] as belonging to **16.** Perhaps the best evidence for **16** is its rapid dimerization (with darkening) to **17.**

(1*R,2*S**,7*S**,8*S**,9*R**,10*R**)-7,8,9,10-Tetrachloropentacyclo[8.4.2.2^{2,7}.0^{1,9}.0^{2,8}]octadecane (17).** In a 50-ml round-bottomed flask, 50 mg of dimer **9** (0.13 mmol) was dissolved in 25 ml of Et_2O. After addition of a catalytic amount of Pd/C, hydrogenation (room pressure) was commenced. After 75 min, 6.8 ml of H_2 (theoretical 5.9 ml) had apparently been consumed. The reaction mixture was then filtered and solvent evaporated, leaving a virtually quantitative yield of **17**, mp 123–125° dec. The NMR spectrum (CCl_4) showed a continuous multiplet between δ 3.0 and 1.3. In the mass spectrum, the only visible parent ion was at *m/e* 380 (4

Table I. Final Atomic Positional and Thermal Parameters with Their Standard Deviations for 9[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	−0.0538 (5)	0.1284 (2)	0.5426 (2)	597 (11)	89 (2)	74 (2)	88 (3)	−78 (3)	2 (1)
Cl(2)	−0.5047 (3)	0.1753 (1)	0.5098 (1)	414 (7)	55 (1)	70 (1)	−11 (2)	82 (2)	0 (1)
Cl(1′)	0.0644 (3)	0.3312 (2)	0.5010 (1)	261 (5)	111 (2)	60 (1)	−26 (3)	−20 (2)	11 (1)
Cl(2′)	−0.3863 (3)	0.3338 (1)	0.5468 (1)	312 (5)	54 (1)	45 (1)	11 (2)	33 (2)	8 (1)
C(1)	−0.1917 (14)	0.1289 (5)	0.4288 (5)	429 (28)	52 (4)	51 (5)	46 (9)	−15 (9)	−9 (3)
C(2)	−0.2874 (20)	0.0487 (6)	0.4248 (8)	642 (53)	52 (5)	86 (8)	42 (14)	49 (18)	−17 (5)
C(3)	−0.4446 (18)	0.0331 (7)	0.3548 (8)	516 (43)	59 (6)	105 (9)	−31 (14)	70 (18)	−19 (6)
C(4)	−0.5545 (16)	0.0786 (7)	0.2985 (8)	389 (33)	78 (8)	116 (9)	−56 (15)	50 (15)	−40 (7)
C(5)	−0.5573 (13)	0.1673 (7)	0.2834 (7)	259 (22)	88 (6)	76 (6)	−36 (10)	7 (9)	−22 (5)
C(6)	−0.3816 (9)	0.2088 (5)	0.3155 (4)	186 (16)	68 (4)	36 (4)	−19 (7)	0 (6)	−4 (3)
C(7)	−0.2300 (11)	0.1686 (6)	0.2537 (5)	258 (18)	72 (5)	42 (4)	9 (9)	12 (7)	1 (4)
C(8)	−0.0844 (13)	0.1425 (6)	0.3325 (6)	320 (25)	62 (5)	78 (6)	29 (10)	25 (10)	−13 (4)
C(9)	−0.3201 (10)	0.1994 (4)	0.4281 (4)	245 (18)	55 (4)	38 (4)	5 (7)	14 (7)	2 (3)
C(1′)	−0.1219 (10)	0.3498 (5)	0.4158 (5)	219 (18)	80 (5)	52 (4)	−14 (8)	−3 (7)	4 (3)
C(2′)	−0.1851 (17)	0.4372 (6)	0.4295 (8)	453 (39)	55 (5)	94 (8)	−50 (13)	81 (14)	−15 (5)
C(3′)	−0.3647 (16)	0.4682 (7)	0.3935 (9)	375 (41)	59 (6)	129 (9)	18 (13)	70 (16)	7 (6)
C(4′)	−0.5098 (16)	0.4360 (7)	0.3561 (7)	378 (33)	67 (6)	96 (7)	54 (14)	54 (13)	26 (5)
C(5′)	−0.5485 (12)	0.3507 (6)	0.3270 (6)	270 (22)	73 (6)	60 (6)	40 (9)	11 (9)	13 (4)
C(6′)	−0.3775 (9)	0.3011 (4)	0.3237 (4)	182 (16)	56 (4)	44 (4)	12 (6)	14 (6)	9 (3)
C(7′)	−0.2477 (10)	0.3408 (6)	0.2485 (5)	215 (18)	74 (5)	51 (5)	3 (8)	7 (7)	12 (4)
C(8′)	−0.0640 (11)	0.3368 (7)	0.3040 (5)	258 (20)	69 (5)	47 (5)	−21 (10)	10 (7)	10 (4)
C(9′)	−0.2870 (9)	0.2946 (4)	0.4325 (4)	201 (16)	54 (3)	33 (4)	2 (6)	8 (6)	−8 (3)
H(2a)	−0.310 (15)	0.039 (7)	0.481 (9)	6.7 (3.8)					
H(2b)	−0.194 (10)	0.011 (45)	0.407 (5)	2.3 (1.6)					
H(3)	−0.501 (11)	−0.035 (5)	0.366 (6)	4.0 (4.7)					
H(4)	−0.652 (13)	0.032 (6)	0.272 (7)	5.6 (2,4)					
H(5a)	−0.660 (15)	0.193 (6)	0.324 (8)	5,5 (2.5)					
H(5b)	−0.576 (15)	0.182 (6)	0.207 (9)	6.1 (2.6)					
H(7a)	−0.165 (10)	0.207 (4)	0.203 (6)	2.7 (1.6)					
H(7b)	−0,285 (14)	0.111 (7)	0.216 (8)	6.0 (2.4)					
H(8a)	0.018 (14)	0.192 (6)	0.353 (7)	5.3 (2.5)					
H(8b)	−0.043 (10)	0.090 (5)	0,319 (5)	2.9 (1.8)					
H(2′a)	−0.105 (10)	0.463 (4)	0.405 (5)	2.1 (1.9)					
H(2′b)	−0.184 (13)	0.457 (6)	0.502 (7)	5.4 (2.4)					
H(3′)	−0.352 (15)	0.524 (7)	0.420 (8)	6.2 (3.0)					
H(4′)	−0.605 (15)	0.486 (6)	0.352 (7)	6.0 (2.7)					
H(5′a)	−0.588 (9)	0.343 (4)	0.260 (5)	2.0 (1.6)					
H(5′b)	−0.640 (14)	0.327 (6)	0.380 (8)	6.0 (2.5)					
H(7′a)	−0.278 (11)	0.404 (5)	0.237 (6)	4.0 (2.1)					
H(7′b)	−0.258 (10)	0,308 (4)	0.184 (6)	3.4 (1.9)					
H(8′a)	−0.024 (11)	0.384 (5)	0.286 (6)	3.3 (2.0)					
H(8′b)	0,002 (10)	0.278 (4)	0.298 (5)	2.5 (1.7)					

[a] The β_{ij}'s are ×10^4. The hydrogen β's are isotropic. The form of the anisotropic temperature factor is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$. Estimated standard deviations are given in parentheses for the least significant figure. [b] Numbering as in Figure 1 with hydrogens receiving the same number as the heavy atom to which they are attached.

^{35}Cl's); the appropriate sets of peaks for successive Cl loss were also present. Anal. Calcd for $C_{18}H_{24}Cl_4$: C, 56.57; H, 6.33. Found: C, 56.71; H, 6.40.

Crystallographic and X-Ray Data

Crystals in the form of colorless plates were grown by slow evaporation of a CH_2Cl_2–heptane solution. Weissenberg and precession photographs displayed $2/m$ Laue symmetry, indicating a monoclinic space group. Systematic extinctions of the reflection type $0k0$, $k = 2n + 1$ and $h0l$, $l = 2n + 1$ were consistent with the space group $P2_1/n$ ($C^5{}_{2h}$ alternate setting). The unit cell parameters and their standard deviations were obtained from a least-squares fit to 12 independent reflection angles, whose centers were determined by a left–right, top–bottom beam splitting technique, using a previously aligned Hilger-Watts four-circle diffractometer. The unit cell dimensions were a = 7.474 (2), b = 16.734 (3), c = 13.100 (3) Å, and β = 91.16 (2)°. The volume was 1638.1 (6) Å^3, and ρ_{obsd} was 1.50 g/cm^3 which agreed well with ρ_{calcd} of 1.5 g/cm^3 for $Z = 4$.

The crystals were observed to be air stable, and one with approximate dimensions 0.20 × 0.10 × 0.20 mm was mounted along a axis. Intensity data were collected at ca. 25°, utilizing a Hilger-Watts four-circle diffractometer equipped with a scintillation counter and interfaced to a SDS-910 computer in a real time mode, and using Zr-filtered Mo Kα radiation. Using a θ–2θ scan technique, two octants of data (hkl, $hk\bar{l}$) within a 2θ sphere of 57° were taken. Symmetric scan ranges of 1.00° in 2θ at low 2θ values to 2.0 at high 2θ limits were used. Background measurements were obtained using stationary crystal–stationary counter method for one-half the total scan time at each end of the scan. The intensities of three standard reflections were measured periodically during the data collection. Monitoring options based on these standard counts were used to maintain crystal alignment and to test for decomposition of the crystal. No decomposition was observed during data collection. A total of 2662 unique reflections were collected. The intensity data were corrected for Lorentz, polarization, and background effects. Because of the small linear absorption coefficient (7.10 cm^{-1}), no absorption correction was made. There were 1790 independent reflections having $|F_o|$ greater than or equal to three times the standard deviation of intensities ($\sigma(I)$), where

$$[\sigma(I)^2] = C_T + C_B + (0.05C_T)^2 + (0.05C_B)^2$$

C_T and C_B are the total count and the background count, respectively. The estimated standard deviation in each structure factor was calculated from the deviation in intensity by the method of finite differences.[25] The reciprocal of the structure factor variances were used as weights in the least-squares refinements.

Table II. Selected Bond Distances[a] for 9[b]

C(1)–Cl(1)	1.795 (8)	C(9')–C(9)	1.614 (10)
C(2)–C(1)	1.518 (15)	C(9')–C(1')	1.560 (11)
C(3)–C(2)	1.498 (18)	C(9')–C(6')	1.568 (9)
C(4)–C(3)	1.332 (16)	H(2a)–C(2)	0.77 (12)
C(5)–C(4)	1.499 (16)	H(2b)–C(2)	0.97 (8)
C(6)–C(5)	1.537 (12)	H(3)–C(3)	1.23 (8)
C(7)–C(6)	1.559 (11)	H(4)–C(4)	1.12 (10)
C(8)–C(1)	1.527 (12)	H(5a)–C(5)	1.03 (11)
C(8)–C(7)	1.548 (12)	H(5b)–C(5)	1.03 (11)
C(9)–Cl(2)	1.809 (7)	H(7a)–C(7)	1.06 (7)
C(9)–C(1)	1.522 (11)	H(7b)–C(7)	1.15 (11)
C(9)–C(6)	1.544 (8)	H(8a)–C(8)	1.16 (10)
C(1')–Cl(1')	1.794 (8)	H(8b)–C(8)	0.94 (9)
C(2')–C(1')	1.548 (13)	H(2'a)–C(2')	0.81 (7)
C(3')–C(2')	1.506 (17)	H(2'b)–C(2')	1.00 (10)
C(4')–C(3')	1.300 (15^+)	H(3')–C(3')	0.99 (11)
C(5')–C(4')	1.502 (15^-)	H(4')–C(4')	1.09 (11)
C(6')–C(6)	1.548 (11)	H(5'a)–C(5')	0.92 (7)
C(6')–C(5')	1.524 (11)	H(5'b)–C(5')	1.06 (11)
C(7')–C(6')	1.547 (10)	H(7'a)–C(7')	1.09 (9)
C(8')–C(1')	1.551 (10)	H(7'b)–C(7')	1.01 (8)
C(8')–C(7')	1.542 (12)	H(8'a)–C(8')	0.88 (7)
C(9')–Cl(2')	1.808 (6)	H(8'b)–C(8')	1.10 (7)

[a] The bond distances are in Å. Estimated standard deviations are given in parentheses for the least significant figure. [b] Numbering as in Figure 1.

Table III. Table of Selected Bond Angles for 9[a,b]

Angle	Degrees	Angle	Degrees
Cl(1)–C(1)–C(2)	106.8 (6)	Cl(1')–C(1')–C(2')	109.1 (6)
Cl(1)–C(1)–C(8)	112.6 (7)	Cl(1')–C(1')–C(8')	109.6 (5)
Cl(1)–C(1)–C(9)	111.1 (5)	Cl(1')–C(1')–C(9')	114.6 (5)
C(2)–C(1)–C(9)	112.8 (9)	C(2')–C(1')–C(9')	107.4 (7)
C(2)–C(1)–C(8)	111.0 (7)	C(2')–C(1')–C(8')	109.5 (7)
C(9)–C(1)–C(8)	102.7 (6)	C(8')–C(1')–C(9')	106.6 (6)
C(1)–C(2)–C(3)	122.7 (9)	C(1')–C(2')–C(3')	124.2 (9)
C(2)–C(3)–C(4)	134.7 (10)	C(2')–C(3')–C(4')	134.9 (11)
C(3)–C(4)–C(5)	130.4 (10)	C(3')–C(4')–C(5')	130.2 (10)
C(4)–C(5)–C(6)	113.6 (9)	C(4')–C(5')–C(6')	111.6 (8)
C(5)–C(6)–C(7)	106.8 (6)	C(5')–C(6')–C(6)	122.0 (7)
C(5)–C(6)–C(9)	116.8 (6)	C(5')–C(6')–C(7')	108.7 (6)
C(5)–C(6)–C(6')	119.0 (7)	C(5')–C(6')–C(9')	111.0 (5)
C(7)–C(6)–C(6')	117.0 (6)	C(6)–C(6')–C(9')	90.1 (5)
C(7)–C(6)–C(9)	104.3 (6)	C(6)–C(6')–C(7')	113.3 (6)
C(9)–C(6)–C(6')	91.7 (5)	C(7')–C(6')–C(9')	110.1 (6)
C(6)–C(7)–C(8)	106.5 (5)	C(C')–C(7')–C(8')	104.2 (6)
C(7)–C(8)–C(1)	102.7 (7)	C(7')–C(8')–C(1')	100.1 (6)
Cl(2)–C(9)–C(1)	108.1 (5)	Cl(2')–C(9')–C(1')	103.9 (4)
Cl(2)–C(9)–C(6)	111.9 (5)	Cl(2')–C(9')–C(9)	108.8 (4)
Cl(2)–C(9)–C(9')	108.5 (4)	Cl(2')–C(9')–C(6')	123.4 (5)
C(1)–C(9)–C(9')	132.1 (7)	C(1')–C(9')–C(6')	99.2 (5)
C(1)–C(9)–C(6)	105.1 (5)	C(1')–C(9')–C(9)	134.5 (6)
C(6)–C(9)–C(9)	88.6 (5)	C(6')–C(9')–C(9)	88.4 (5)

[a] Estimated standard deviations are given in parentheses for the least significant figure. [b] Numbering as in Figure 1.

Solution and Refinement. The Patterson map[26] showed extensive overlapping of peaks so that interpretation of the Patterson function was difficult even after sharpening to reduce the peak width. Consequently a solution based on iterative application of Sayre's equation was attempted.[27] The phased, three-dimensional E synthesis revealed all nonhydrogen atoms. Full-matrix least-squares refinements reduced the conventional discrepancy index to 0.082 for the observed reflections.[26] No hydrogens were included in the final model. A computer-generated drawing of the final model is given in Figure 1.[26] Table I lists fractional coordinates, thermal parameters, and their errors. Table II gives bond distances and errors, Table III bond angles and errors, and Table IV lists observed and calculated structure factors for the observed reflections (see paragraph concerning supplementary material at the end of this paper).

Acknowledgment. We thank Dr. Kurt Loening, Chemical Abstracts Service, for the correct names for dimers **9** and **17.**

Supplementary Material Available. Table IV—a listing of bond distances, bond angles, and structure factors—will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-5507.

References and Notes

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(2) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee, 1972–1977; Fellow of the Alfred P. Sloan Foundation, 1973–1975.

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(9) It is noteworthy that **12** is stable enough to not react with MeOH. This is in contrast to what has been found for the more strained 1-adamantene[10] (bridgehead olefin comparable to a *trans*-cyclohexene).

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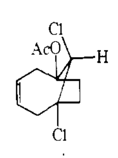
(11) P. Warner and S. Lu, submitted for publication.

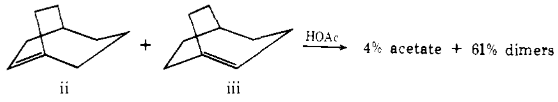
(12) (a) Furan is an inefficient trap for even more strained bridgehead olefins. For instance, 1-norbornene [R. Keese and E. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971)] gives 18–40% dimers and 55–62% Diels–Alder adducts in furan. These highly twisted olefins are apparently not all that well suited for 2 + 4 cycloadditions. (b) There are two stereoisomers of **10** formed in an approximately 9:1 ratio. Whereas we have not established the stereochemistry of these adducts, we believe, based on examination of models and the mode of dimerization, that both have the Cl syn to the four-carbon bridge (as in **9**).

(13) By NMR analogy to similar products in the [4.3.1]propell-3-ene case,[6] and with the observation of mass spectral parent ions at *m/e* 248, 250, 252, we tentatively propose structure i for one of the chief products in acetic acid.



i

(14) Interestingly, ii and iii are trapped to the extent of only 4% in acetic acid as solvent, whereas a 61% yield of dimers is isolated [J. R. Wiseman and J. Chong, *J. Am. Chem. Soc.*, **91**, 7775 (1969)].



(15) A certain amount of **16** was probably formed but dimerized to **17** under the hydrogenation conditions (room temperature); see text.

(16) An attempt to reduce benzocyclobutene directly to **18** with Li/*n*-$PrNH_2$ (a useful method in the indan system[17)] was unsuccessful, as were attempts to convert **8** to **18.**

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(18) We used both the carbene rearrangement method[19] and the diene photocyclization method.[20]

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(23) If more than 1 equiv of $CHCl_3$ is used, bis addition appears to occur. While the use of just 1 equiv results in incomplete conversion of starting material to product, we found it more convenient to have readily identifiable **8** as an impurity, rather than biscarbene adducts. A very small amount of carbene addition to the 4,5 double bond of **8** could also be detected, but this product was not investigated.

(24) After our synthesis was complete, we learned of the independent work of J. Garrett and C. Chang (C. C. Chang, Master's Thesis, Stephen F. Austin State University, 1971) who approached **7** via Simmons–Smith addition to **8**.

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The Continuous Diradical as Transition State. II. Internal Rotational Preference in the Cyclopentene Rearrangement of the Vinylcyclopropanes, (1*S*,2*R*)-(+)-*cis*- and (1*R*,2*R*)-(−)-*trans*-1-Cyano-2-isopropenylcyclopropane

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Abstract: Stereochemical dissection of the 4-cyano-1-methylcyclopentene obtained from thermal rearrangement of *cis*- and *trans*-1-cyano-2-isopropenylcyclopropane has revealed partial retention of optical activity (a freely rotating diradical as intermediate requires racemic product) owing to predominance of retention of configuration from cis and of inversion of configuration from trans (some factor(s) beyond control by orbital symmetry become important). Pending quadrisection of the rearrangement, a tentative description in terms of a not-obviously-concerted reaction involving rotational preference within the framework of the continuous diradical hypothesis is offered.

Study of an optically active vinylcyclopropane was undertaken to elucidate the chiral and configurational characteristics of a not obviously concerted thermal rearrangement. The first phase, which dealt with the enantiomerization and diastereomerization of the cyclopropane ring,[1] is now extended to include the ring enlargement to cyclopentene.[2]

The large enthalpy change in the vinylcyclopropane rearrangement ($\Delta H \sim -22$ kcal/mol)[5] generally makes the rearrangement irreversible, except in those instances in which strain in the cyclopentene matches exothermicity[3] or exceeds it.[8]

The experimental enthalpy of activation ($\Delta H^{\ddagger}$ 48.5 kcal/mol)[9] is close to that predicted ($\Delta H^{\ddagger}$ 46.7 kcal/mol)[10] by subtraction of the allylic stabilization energy expected on replacement of methyl by vinyl (12.5 kcal/mol)[11] from the enthalpy of activation of the diastereomerization of 1,2-dideuterio-3-methylcyclopropane ($\Delta H^{\ddagger}$ 59.2 kcal/mol).[12] In terms of the criterion of concert which is based on the observed enthalpy of activation being *lower* than the predicted (by at least 3 kcal/mol to make reasonable allowances for uncertainties in estimated and experimental values), the ring enlargement appears to be no more obviously concerted than the diastereomerization of cyclopropane.[12]

Experimental confirmation of this conclusion is given by the failure of *cis*-1,2-dideuterio-3-vinylcyclopropane to rearrange faster to cyclopentene than it undergoes diastereomerization.[13] Although this behavior, as that of 1-cyano-2-isopropenylcyclopropane,[1] may be no more than the reflection of the greater ease of generating a transoid allylic radical,[10a,14] from which, in the first instance, the thermochemically improbable *trans*-cyclopentene is to be expected, it nonetheless implies a potential concert too feeble to muster the 1-kcal/mol extra cost of the cisoid configuration required for the realization of the concert.

Configurational characterization of the vinylcyclopropane rearrangement has already been afforded by the investigation of Willcott and Cargle.[13] Their "experimental result is consistent only with a mechanism in which stereochemistry is lost at two centers". The absence of stereospecificity excludes the operation of a single, concerted path preferred by 3 kcal/mol or more over the model of a stereorandom, energetically nonconcerted path.

Theoretical predictions of stereochemistry are mixed. Analysis according to Woodward and Hoffmann[15] favors $\sigma^2{}_a + \pi^2{}_s$ or $\sigma^2{}_s + \pi^2{}_a$ (the is and ra processes of Figure 1, respectively), whereas control by subjacent orbitals[16] favors processes rs and ia, respectively.

A complete configurational specification of the rearrangement can be achieved if both carbon atoms of the newly formed, cyclopentene-generating bond be chiral. This condition can be realized either by a diastereomeric or an enantiomeric marker, either through the introduction of a third chiral atom (e.g., if R = H and P ≠ Q ≠ S ≠ H in Figure 1) or optical activity (e.g., if P = R = H and Q ≠ S). The former approach has been pursued by Mazzocchi and Tamburin[17] (P = -$COOC_2H_5$, Q = S = CH_3 and R = H) but has resisted a definitive experimental expression, presumably owing to the kinetic complexity of the system.[18] Of the two approaches, optical activity seems the less perturbing (even should P be deuterium) and the more conducive to reliable quantitative assessment.

In the present work, the stereochemical characterization of the nonallylic carbon atom, that is, the relative amount