

Homoallylic Rearrangement of Bicyclobutylcarbiny Radicals[†]

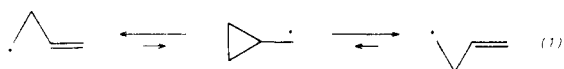
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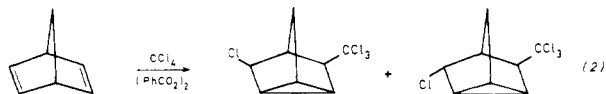
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The free-radical additions of tetrachloromethane and bromotrichloromethane to a bicyclobutane-bridged enone (1) and diene (2) are reported. These reactions give in high yield products formed as result of a homoallylic rearrangement of the initially generated bicyclobutylcarbiny radicals to vinylcyclopropyl radicals. The *endo*-halo-substituted cyclopropyl derivatives, obtained in the reaction of tetrachloromethane and diene (2) are thermally unstable and isomerize to benzyl derivatives, whereas the isomeric *exo* derivatives prove to be thermally stable. This difference in stability between *endo*- and *exo*-halo compounds is explained in terms of an electrocyclic, disrotatory opening of a cyclopropyl cation.

Whereas rearrangements of carbocationic species are phenomena which have been extensively studied in many systems, rearrangements of radicals are less common.^{1,2} For example, a 1,2-methyl shift, being a well-known process in carbocationic chemistry, has not been observed for radicals.³ A radical rearrangement that has been widely studied is the homoallylic rearrangement^{4,5} (eq 1).



The rate constant for isomerization of the cyclopropylcarbiny radical to the allylcarbiny radical was recently determined⁶ to be $1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The vicinal vinyl shift displayed by radicals is generally believed to involve such a homoallylic rearrangement. An example of the homoallylic rearrangement is found in the equilibrium of the norbornenyl radical with the nortricycyl radical:^{4b} the free-radical addition of tetrachloromethane to norbornadiene affords a mixture of isomeric nortricyclanes.⁷



Although much attention has been focused on cyclopropylcarbiny radicals, there have, to our knowledge, not been reports on bicyclobutylcarbiny radicals. It was of interest to us to examine in what way the highly strained bicyclobutane moiety would interact with a radical center, especially because of a comparison with the behavior of the corresponding bicyclobutylcarbocation^{8,9} and carbene,¹⁰ which are subjects of study in our laboratory. We chose to generate bicyclobutylcarbiny radicals by the free-radical additions of tetrachloromethane and bromotrichloromethane^{11,12} to bicyclobutane-bridged unsaturated substrates, e.g., the enone 1¹³ and diene 2¹⁴ that were recently prepared starting from hexamethyl(Dewar benzene).



Results

(a) **Addition of Polyhalomethanes to Enone 1.** When enone 1 was refluxed in tetrachloromethane solution for 6 h in the presence of catalytic amounts (10 mol %) of

benzoyl peroxide as initiator, a mixture of two isomeric products, 3 and 4, was obtained in 90% yield; they occur in a ratio of 85:15, respectively, and were separated by using high-pressure LC. The same mixture of compounds 3 and 4 was obtained in the initial stage of a reaction in which enone 1 was irradiated in tetrachloromethane solution; however, products 3 and 4 proved to be photolabile and preliminary results indicate that an isomeric phenol is produced.¹⁵

We have finally applied a third method for the addition of tetrachloromethane to enone 1, based on a procedure that we recently developed by using an iron-carbonyl complex (either (trimethylamino)iron tetracarbonyl or iron nonacarbonyl) as a catalyst at room temperature.¹⁶ The same mixture of compounds 3 and 4 was obtained (yield 90%). Although we believe that these reactions do also involve radicaloid intermediates, they differ fundamentally from the free-radical addition reactions initiated by benzoyl peroxide or UV irradiation and will therefore not be discussed here.

The irradiation of enone 1 in bromotrichloromethane solution provided a mixture of compounds 5 and 6 in a ratio of 78:22, respectively (yield 70%). Prolonged irradiation caused photodecomposition of 5 and 6 (see above), probably to afford a phenolic product.¹⁵ However, the addition of bromotrichloromethane is relatively fast, and therefore a good yield of a mixture of 5 and 6 can be

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(2) C. Walling in "Molecular Rearrangements", Vol. I, P. de Mayo, Ed., Interscience, New York, 1963, Chapter 7.

(3) Reference 1, p 340.

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(11) C. Walling, "Free Radicals in Solution", Wiley, New York, 1957, Chapter 6.2.

(12) G. Sosnovsky, "Free Radical Reactions in Preparative Organic Chemistry", Macmillan, New York, 1964, Chapter 2.

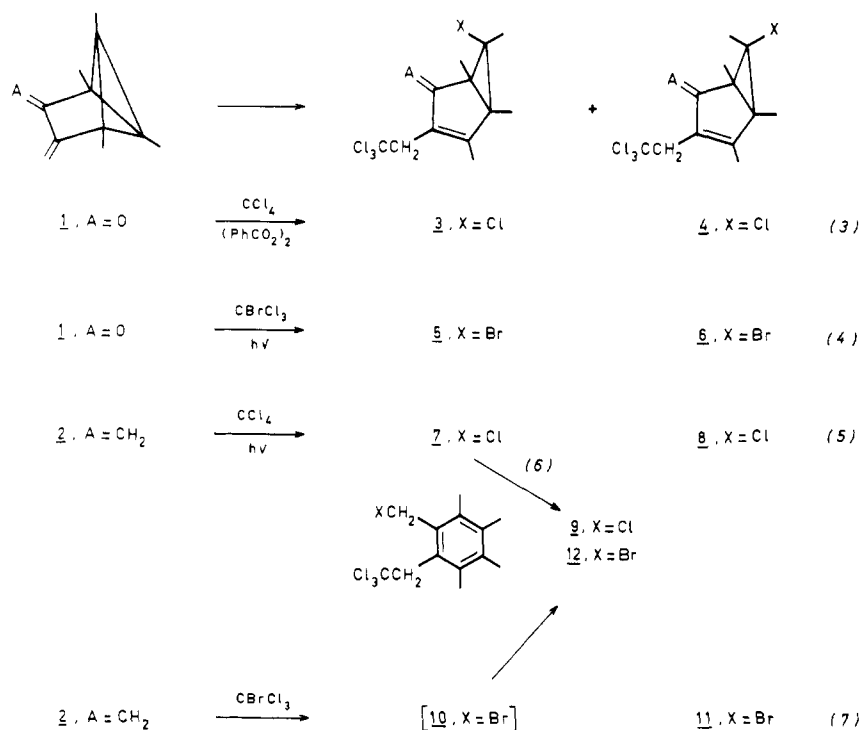
(13) R. F. Heldeweg and H. Hogeveen, *Tetrahedron Lett.*, 1517 (1975); R. F. Heldeweg, H. Hogeveen, and E. P. Schudde, *J. Org. Chem.*, **43**, 1912 (1978).

(14) H. Hogeveen and P. W. Kwant, *J. Org. Chem.*, **39**, 2624 (1974).

(15) Preliminary results indicate the product of photodecomposition of 3 and 4 to be a chloromethyl(2,2,2-trichloroethyl)trimethylphenol [IR 3610 (OH) cm^{-1} ; mass spectrum m/e 314, $\text{C}_{12}\text{H}_{14}^{35}\text{Cl}_4\text{O}$ (M^+); $^1\text{H NMR}$ (C_6H_6) δ 4.59 (s, 2 H), 4.07 (s, 2 H), 2.20 (s, 3 H), 2.05 (s, 6 H)] and the product of photodecomposition of 5 and 6 to be a bromomethyl(2,2,2-trichloroethyl)trimethylphenol [IR 3610, 3560 (OH) cm^{-1} ; mass spectrum m/e 358, $\text{C}_{12}\text{H}_{14}^{79}\text{Br}^{35}\text{Cl}_3\text{O}$ (M^+); $^1\text{H NMR}$ (CCl_3Br) δ 4.65 (s, 2 H), 4.20 (s, 2 H), 2.50 (s, 3 H), 2.37 (s, 3 H), 2.23 (s, 3 H)].

(16) J. Elzinga and H. Hogeveen, *J. Chem. Soc., Chem. Commun.*, 705 (1977). The full paper is in preparation.

[†] This paper is dedicated to Professor E. Havinga for his contributions to chemistry.



obtained by this method; separation of compounds 5 and 6 was accomplished by applying high-pressure LC.

(b) Addition of Polyhalomethanes to Diene 2. The irradiation of the bicyclobutane-bridged diene 2 in tetrachloromethane solution for 6 h at 0 °C afforded a mixture of two products to which structures 7 and 8 are assigned on the basis of spectroscopic evidence. Compounds 7 and 8 were formed in a ratio of 68:32, respectively (yield 90%). Attempts to separate the mixture of 7 and 8 by high-pressure LC were not successful, due to the instability of 7.

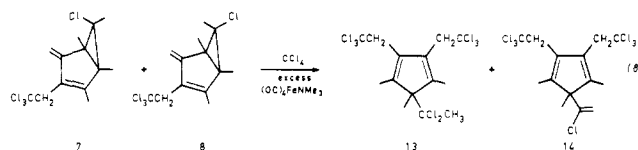
However, when the addition reaction was carried out by boiling 2 for 6 h in tetrachloromethane solution in the presence of 10 mol % of benzoyl peroxide, a mixture of 8 and 9 was obtained (ratio 32:68, yield 90%), with no 7 being observed. Aromatic compound 9 is formed from 7 by a thermal isomerization, because when a mixture of 7 and 8, obtained by photoinitiated addition of tetrachloromethane to 2, was boiled in tetrachloromethane solution during 1 h, complete conversion of 7 to 9 was observed, whereas 8 was unaffected under these conditions.¹⁵ The reaction mixture consisting of 8 and 9 was separated by preparative TLC.

When bromotrichloromethane was added at room temperature to diene 2 in a quartz NMR tube, a spontaneous, strongly exothermic reaction occurred. The NMR spectrum of the solution showed only absorptions due to products 11 and 12 (ratio 27:73, respectively; yield 70%).

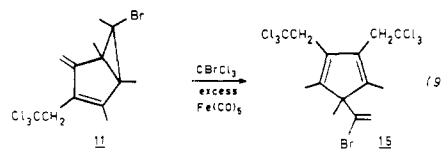
Larger scale preparations of 11 and 12 were carried out by adding bromotrichloromethane to diene 2 in pentane solution, subsequent irradiation being necessary to drive the reaction to completion (yield 70%). Although not observed, we assume in the formation of 12 the intermediacy of *endo*-bromo derivative 10, which is thermally even more unstable than *endo*-chloro derivative 7. On the other hand, *exo*-bromo derivative 11 is stable, just like 8. The mixture of 11 and 12 was separated into its components by applying preparative TLC.

Attempts to add a second mole of polyhalomethane to diene 2, either by treatment of 8 with tetrachloromethane in the presence of benzoyl peroxide or by irradiating 11

in bromotrichloromethane, were unsuccessful. However, treatment of 2, or alternatively a mixture of 7 and 8, in tetrachloromethane solution with excess (trimethylamino)iron tetracarbonyl overnight afforded a mixture of diadducts 13 and 14; the yield was 70%.¹⁶

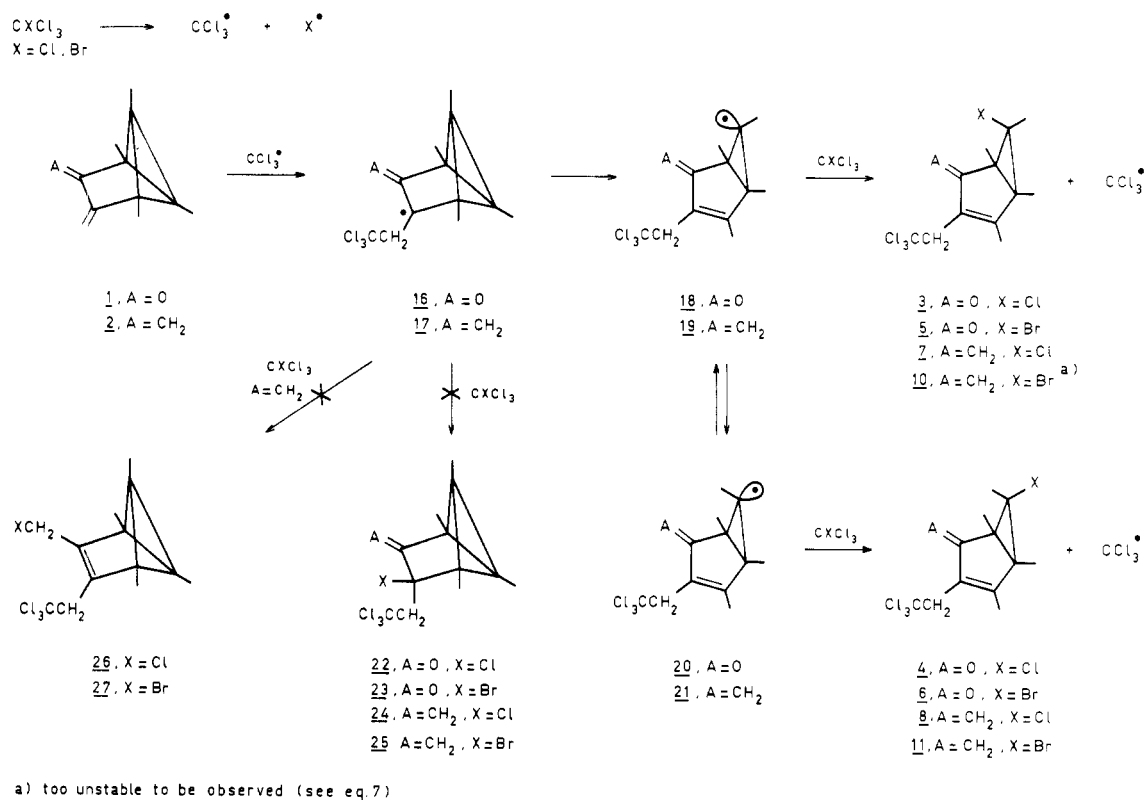
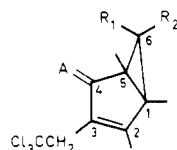


Treatment of 11 in bromotrichloromethane solution in the presence of excess iron pentacarbonyl gave diadduct 15 in about 80% yield.¹⁶



Structural Assignment. The assignment of the given structures is mainly based on IR, UV, NMR, and mass spectroscopic data. Whereas IR, UV, and mass spectral data are reported in the Experimental Section together with NMR data of aromatic compounds 9 and 12, the ¹H and ¹³C NMR spectra of the bicyclic products are discussed in this section, because especially the ¹H NMR spectra allow assignment of *exo*- and *endo*-halo stereochemistry. ¹H NMR data are compiled in Table I and ¹³C NMR data are listed in Table II. Compounds 3 and 4 differ significantly only in the chemical shift of the absorption due to the methyl substituent at C6: δ 1.61 and 1.71. For compound 4 this methyl substituent at C6 is located over the enone system, in the shielding region, which will cause an upfield shift compared with the case for 3. So we conclude that 4 is the compound having the absorption due to the C6 methyl group at δ 1.61. Distinction between 5 and 6 as well as between 7 and 8 was made on the basis of the same argument. In tetrachloromethane solution the absorptions due to CH₂(C3) show singlets for all compounds except for 5, in which an AB system is observed

Scheme I

Table I. ¹H NMR Data^a

	CH ₃ (C1/5) ^b	CH ₃ - (C6)	CH ₃ - (C2)	CH ₂ (C3)	CH ₂ (C4)
3	1.31, 1.41	1.71	2.20	3.57 ^c	
4	1.33, 1.42	1.61	2.20	3.55 ^c	
5	1.27, 1.37	1.86	2.17	3.45-3.60 ^c	
6	1.38, 1.48	1.79	2.19	3.55 ^c	
7	1.26, 1.26	1.62	1.92	3.55 ^c	4.93, 5.22
8	1.33, 1.33	1.49	1.96	3.54 ^c	4.97, 5.22
11	1.37, 1.37	1.58	1.95	3.53 ^c	5.01, 5.23

^a CCl₄, 35 °C; chemical shifts given in parts per million relative to Me₄Si. ^b No individual assignment to these methyl groups is given. ^c All absorptions due to CH₂(C₃) show singlets, except for 5, which shows an AB system, $J = 13$ Hz.

with a coupling constant of 13 Hz; the spectrum of compound 3, if taken in hexadeuteriobenzene solution, shows also an AB-type absorption ($J = 13$ Hz) for the CH₂(C₃) hydrogens. The dissymmetry of these compounds causes the CH₂(C₃) hydrogens to be diastereotopic. Although compounds 4, 6-8, and 11 are dissymmetric, the absorptions due to CH₂(C₃) hydrogens coincide and are observed as singlets in both tetrachloromethane and hexadeuteriobenzene. Finally, the assignment of exo and endo stereochemistry based on NMR spectroscopy is in accordance with the chemical reactivity of the various compounds (Discussion).

Discussion

Free-radical additions of polyhalomethanes to unsaturated substrates have been extensively studied.^{11,12} In the case of tetrachloromethane the first step involves

cleavage of a C-Cl bond either by an initiator radical or by UV light. The C-Br bond in bromotrichloromethane is weaker than the C-Cl bond, and cleavage occurs already by action of visible light, no initiator being necessary. In both cases trichloromethyl radicals are produced that are able to add to carbon-carbon double bonds with formation of a new radical that may abstract either a chlorine atom from tetrachloromethane or a bromine atom from bromotrichloromethane with generation of a new trichloromethyl radical (propagation step). The mechanism that we propose for the addition of tetrachloromethane and bromotrichloromethane to enone 1, initiated by benzoyl peroxide or UV irradiation, is depicted in Scheme I.

The highly reactive trichloromethyl radical adds to the carbon-carbon double bond of enone 1 to generate bicyclobutylcarbinyl radical 16. To establish the exact hybridization at the radical center of 16, an ESR investigation would be necessary. However, we expect the radical center to have pyramidal geometry analogous to related radicals.¹⁷⁻¹⁹ Instead of abstraction of a chlorine (bromine) atom from tetrachloromethane (bromotrichloromethane) by 16 to give a 1,2-addition product, e.g., 22 (23), ring opening of the bicyclobutane moiety occurs to afford cyclopropyl radical 18 via a homoallylic rearrangement. Because none of 22 (23) could be detected, the homoallylic rearrangement of 16 to 18 is probably irreversible and much faster (probably $k > 1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$)⁶ than the chain-transfer reaction of 16.

The driving force of the rearrangement is conceivably relief of ring strain as a result of opening of the highly strained bicyclobutane moiety to a vinylcyclopropane

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(18) J. Gloux, M. Guglielmi, and H. Le Maire, *Mol. Phys.*, **17**, 425 (1969).

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Table II. ^{13}C NMR Data^a

	C1/5 ^{b,e}	C4	C3	C2	C6	CH ₂ (C3)	CCl ₃	A	CH ₃ ^b	
3	41.0/42.0	202.2	130.8	174.7	70.8	47.5 ^c	98.5		7.3	8.3
									16.4	22.1
5	41.5/42.1	202.1	130.5	176.9	65.8	47.7 ^c	98.5		7.1	7.9
									16.2	24.3
6	40.3/41.1	202.7	132.7	175.0	62.6	47.7 ^c	98.5		11.8	12.5
									16.9	21.7
7	38.2/43.4	152.0/155.7 ^b		130.3	61.2	49.5 ^c	99.4	105.0 ^d	9.1	11.7
									15.1	21.4
8	37.4/42.6	152.4/155.3 ^b		131.2	61.1	49.7 ^c	99.4	105.1 ^d	10.5	13.2
									15.2	19.3
11	37.1/42.4	152.1/155.0 ^b		131.4	58.1	49.5 ^c	99.4	105.2 ^d	13.2	15.3
									16.1	21.5

^a CDCl₃, 35 °C, except for 11 (15 °C); chemical shifts given in parts per million relative to Me₄Si. Compound 4 was not measured due to lack of sufficient material. ^b C3/4; no individual assignment to these carbons is given. ^c $J_{\text{CH}} = 132$ Hz. ^d $J_{\text{CH}} = 160$ Hz. ^e See structure in Table I for atom labeling.

system, stabilized by conjugation with the ketone function. Moreover, the stereoelectronic conditions required for the occurrence of a homoallylic rearrangement, viz., maximum overlap between the orbital containing the odd electron and the orbital of the cyclopropane bond to be broken,²⁰⁻²² are favorable because the angle between these orbitals in 16 will be rather small.

It is of interest to note that, whereas a bicyclobutyl-carbinyl radical displays cleavage of a side bond to afford a vinylcyclopropyl radical, a bicyclobutyl radical displays ring opening of the central bond to afford a cyclobutenyl radical.²³

Cyclopropyl radicals are relatively stable species, although it was estimated that at least 30 kcal/mol of energy should be gained by ring opening to an allyl radical.²⁴ The activation energy for ring opening has been calculated²⁵ to be 19 kcal/mol at 186 °C.

Rapid inversion at the cyclopropyl radical center²⁶⁻²⁸ will lead to fast equilibration between 18 and 20. In the final step, chain transfer of 18¹ and 20 affords 3 and 4 (tetrachloromethane) or 5 and 6 (bromotrichloromethane), respectively, and a new trichloromethyl radical is formed. That the ratio of isomers is 85:15 for 3 and 4 (78:22 for 5 and 6) may be explained by different activation energies for chlorine (bromine) abstraction from tetrachloromethane (bromotrichloromethane) by 18 and 20, possibly due to different steric factors.³⁰

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(28) However, some examples are known of cyclopropyl radicals, being configurationally stable, viz., the bicyclobutyl²³ and *exo*-tricyclo-[3.2.1.0²⁴]octan-3-yl^{27b,28} radicals. Substitution of the α hydrogen by halogen leads to a decreased rate of inversion; e.g., the α -fluorocyclopropyl radical was found to be²⁷ configurationally stable at -108 °C.

(29) P. K. Freeman, L. L. Hutchinson, and J. N. Blazejevich, *J. Org. Chem.*, **39**, 3606 (1974).

(30) An alternative explanation for the observed product ratios of 3 and 4 and of 5 and 6 would be partial trapping of radical 17 by tetrachloromethane (bromotrichloromethane) prior to inversion. This explanation, however, can be ruled out because abstraction of chlorine from tetrachloromethane by alkyl radicals is known to be much slower than inversion: the rate constant for chlorine abstraction from tetrachloromethane by a methyl radical has been determined to be³¹ about 10^9 M⁻¹ s⁻¹ at 65 °C, whereas the rate constant for inversion of the cyclopropyl radical was calculated to be^{27b} $k > 8 \times 10^7$ s⁻¹ at -99 °C.

The mechanism for the addition of tetrachloromethane (and bromotrichloromethane) to diene 2 is also depicted in Scheme I. The addition of tetrachloromethane and bromotrichloromethane to diene 2 is faster than the addition to enone 1, which is likely due to the slightly electrophilic character of the trichloromethyl radical.³² Earlier studies also indicated a preference of tetrachloromethane to add to electron-rich double bonds.¹¹

The trichloromethyl radical adds to a double bond of the diene system to produce bicyclobutylcarbinyl radical 17, which shows a homoallylic rearrangement to cyclopropyl radical 19. Rapid inversion between configurationally isomeric radicals 19 and 21, followed by chlorine (bromine) abstraction from tetrachloromethane (bromotrichloromethane), affords both *endo*- and *exo*-halocyclopropyl derivatives 7 and 8 (10 and 11, 10 being too unstable to observe because of isomerization to 12). Free-radical additions of polyhalomethanes to planar, conjugated dienes usually afford 1,4- and 1,2-addition products,^{11,12} the former being produced in major yield. However, in the case of 2 neither a 1,2-addition product 24 (25) nor a 1,4-addition product 26 (27) could be detected, because ring opening of the initially formed bicyclobutylcarbinyl radical 17 to afford 19, is more favorable than the chain-transfer reaction of 17. The anomalous character of bicyclobutane-bridged unsaturated substrates was observed earlier in the SO₂ cycloaddition to diene 2³³ and transition-metal-promoted carbon monoxide insertion reactions³⁴ of enone 1 and diene 2.

Whereas *exo*-chloro derivative 8 proves to be thermally stable in solution, the corresponding *endo*-chloro derivative 7 isomerizes easily to give aromatic isomer 9. This rearrangement was monitored with ¹H NMR spectroscopy and proved to be first order in [7]. The first-order rate constant at 21 °C (benzene solution) was calculated to be 6.9×10^{-6} s⁻¹. *endo*-Bromo derivative 10 proves to be much less stable than 7, isomerization to give 12 occurring instantaneously at room temperature, whereas *exo*-bromo derivative 11 is stable. A conceivable mechanism for the rearrangement is shown in Scheme II.

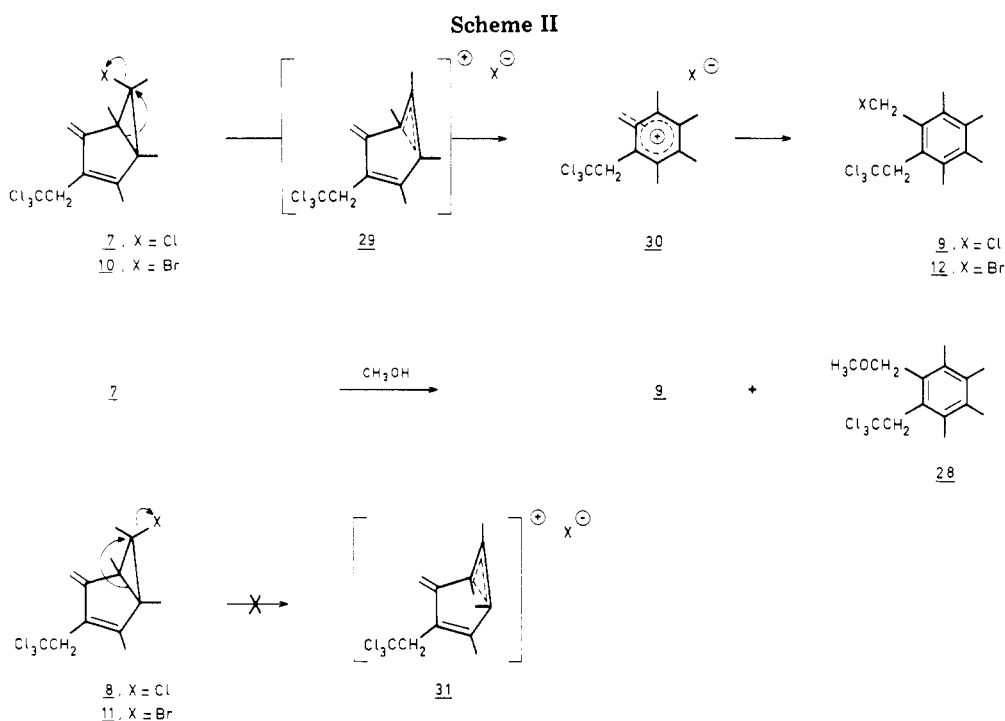
The thermal instability of 7 and 10 vs. the stability of 8 and 11 is understandable on the basis of Dupuy's suggestion^{35,36} upon the electrocyclic disrotatory opening

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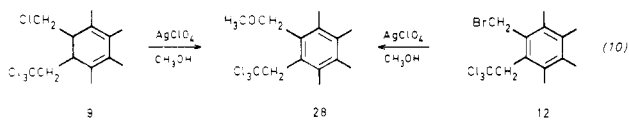
(32) I. Fleming, "Frontier Orbitals and Organic Chemical Reactions", Wiley, New York, 1976, Chapter 5.

(33) R. F. Heldeweg and H. Hogeveen, *J. Am. Chem. Soc.*, **98**, 2341 (1976).

(34) R. F. Heldeweg and H. Hogeveen, *J. Am. Chem. Soc.*, **98**, 6040 (1976); J. Elzinga and H. Hogeveen, *J. Org. Chem.*, **43**, 745 (1978).



of a cyclopropyl cation:³⁷ the departure of the chlorine (bromine) atom from C6 is accompanied by a concerted moving of the *cis*-methyl groups at C1 and C5—outward in the case of 7 and 10 and inward in the case of 8 and 11. For compounds 7 and 10 the resulting rotation causes these methyl substituents to move away from each other to give benzyl cation 30 via transition state 29, whereas for compounds 8 and 11 these methyl substituents move toward each other via transition state 31, to form a sterically impossible six-membered ring with *trans,trans*-substituted double bonds. Compound 10 is much less stable than 7, in agreement with the greater leaving ability of bromine as compared to that of chlorine. Evidence that the mechanism is ionic is provided by the following observations: (i) When a mixture of 7 and 8 is dissolved in the polar solvent perdeuteriomethane, the rate of conversion of 7 to 9 is greatly enhanced, if compared to that in benzene, and the reaction is complete within 10 min at room temperature, whereas compound 8 is stable under these conditions. (ii) When a mixture of 7 and 8 is dissolved in methanol and left overnight at room temperature, 7 is completely converted into a mixture of 9 and 28, whereas 8 is not affected. Compound 9 itself proves to be stable in methanol solution and no conversion to 28 is observed even in boiling methanol. However, treatment of 9 (and also of 12) in methanol solution in the presence of 1 equiv of silver perchlorate affords 28 in 70% yield.



The difference in thermal stability between *exo*- (8 and 11) and *endo*-halo compounds (7 and 10), derived from diene 2, is not observed with *exo*- (4 and 6) and *endo*-halo compounds (3 and 5), derived from enone 1, conceivably

because rearrangement via a stable benzyl cation is not possible. However, a remarkable difference between *endo*- (5) and *exo*-bromo compound 6 is observed toward the effect of silver perchlorate: treatment of a mixture of 5 and 6 with excess silver perchlorate in tetrahydrofuran solution leaves 6 unaffected, whereas 5 decomposes completely to unidentified products. The results presented in this paper agree with the difference observed for other *endo*- and *exo*-halo-substituted cyclopropanes.³⁸⁻⁴⁰ Whereas *endo*-halocyclopropyl derivatives readily undergo ring opening upon solvolysis,^{38,39} the corresponding *exo*-halo derivatives are either unreactive or prefer substitution reactions without ring opening.⁴⁰

Experimental Section

General Procedures. All reagents and solvents were purified when necessary by standard methods. Elemental analyses were performed in the microanalytical department of this laboratory by Mr. H. Draayer, Mr. J. Ebels, Mr. J. E. Vos, and Mr. A. F. Hamminga. Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. Mass spectra were measured on an AEI MS-902 apparatus by Mr. A. Kiewiet. ¹H NMR spectra were determined with a Hitachi Perkin-Elmer R24B with tetramethylsilane as internal standard. ¹³C NMR spectra were recorded by using a Varian XL-100 spectrometer operating at 25.2 MHz. UV spectra were obtained with a Beckman DB-G spectrophotometer. Analytical and preparative-scale separations by means of high-pressure liquid chromatography were carried out with a Waters high-pressure LC ALC/GPC apparatus equipped with a differential refractometer and a Schoeffel spectraflo SF 770 monitor. Irradiations were performed with a Hanau Q-81 high-pressure mercury arc, if not otherwise indicated. Experimental details concerning the iron carbonyl catalyzed addition of tetrachloromethane and bromotrifluoromethane are reported in a separate paper.¹⁶

Additions of Tetrachloromethane to Enone 1. Synthesis of 6-*endo*-Chloro-3-(2,2,2-trichloroethyl)-1,2,5,6-tetra-methylbicyclo[3.1.0]hex-2-en-4-one (3) and 6-*exo*-Chloro-

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3-(2,2,2-trichloroethyl)-1,2,5,6-tetramethylbicyclo[3.1.0]hex-2-en-4-one (4). Initiated by Benzoyl Peroxide. Enone 1 (440 mg (2.7 mmol)) and benzoyl peroxide (83 mg (0.27 mmol)) were dissolved in 25 mL of tetrachloromethane. The solution was refluxed for 5 h in a dry nitrogen atmosphere. The solvent was evaporated under reduced pressure, after which an oily residue was obtained. Extraction with pentane and removal of the solvent afforded 840 mg of a colorless viscous oil, which contained a mixture of 3 and 4 in a ratio of 85:15 (yield 90%, based on NMR spectroscopic integration with benzene as internal reference). The crude mixture was purified by preparative TLC (silica gel, dichloromethane), which yielded 660 mg (80%, based on intake of 1) of a mixture of pure 3 and 4 as a colorless viscous oil.

Anal. (for the mixture of 3 and 4). Calcd for $C_{12}H_{14}Cl_4O$: C, 45.61; H, 4.47; Cl, 44.86. Found: C, 45.85; H, 4.57; Cl, 44.10.

Separation of this mixture was achieved by using high-pressure LC (silica gel, dichloromethane/hexane, 23/74), which gave samples of 4 and 3, respectively, both contaminated with decomposition products formed on the high-pressure LC column; they were removed by using preparative TLC again (silica gel, dichloromethane). Compounds 3 and 4 are both colorless oils, stable at room temperature.

Spectroscopic data of 3: 1H NMR, see Table I; ^{13}C NMR, see Table II; IR (CCl_4 solution) 1710 (C=O), 1640 (C=C) cm^{-1} ; UV (hexane) λ_{max} 230 (ϵ 6000), λ_{max} 255 nm (ϵ 5500); mass spectrum m/e 313.977 (calcd 313.980) $C_{12}H_{14}^{35}Cl_4O$ (M^+), 279 ($M^+ - ^{35}Cl$), 243 ($M^+ - ^{35}Cl - H^{35}Cl$).

4: 1H NMR, see Table I; IR (CCl_4 solution) 1710 (C=O), 1640 (C=C) cm^{-1} ; UV (hexane) λ_{max} 233 (ϵ 6000), λ_{sh} 250–265 nm (ϵ ~5500); mass spectrum m/e 314 $C_{12}H_{14}^{35}Cl_4O$ (M^+), 279 ($M^+ - ^{35}Cl$), 243 ($M^+ - ^{35}Cl - H^{35}Cl$).

Initiated by UV Irradiation. Enone 1 (20 mg), dissolved in 2 mL of tetrachloromethane in an NMR tube, attached to a UV lamp, was irradiated for 0.5 h. Besides the excess of starting material, compounds 3 and 4 were shown to be present in a ratio of 85:15. Prolonged irradiation caused not only further conversion of 1 but mainly photochemical decomposition of 3 and 4 to an isomeric product, probably a phenol.¹⁵

Addition of Bromotrichloromethane to Enone 1. Synthesis of 6-endo-Bromo-3-(2,2,2-trichloroethyl)-1,2,5,6-tetramethylbicyclo[3.1.0]hex-2-en-4-one (5) and 6-exo-Bromo-3-(2,2,2-trichloroethyl)-1,2,5,6-tetramethylbicyclo[3.1.0]hex-2-en-4-one (6). Enone 1 (160 mg (1 mmol)), dissolved in a mixture of 40 mL of bromotrichloromethane and 80 mL of pentane, was irradiated for 0.5 h at room temperature. Without irradiation no reaction was observed. After removal of solvent in vacuo a slightly yellow viscous oil was obtained and was extracted with pentane. Evaporation of the pentane left 350 mg of a slightly yellow viscous oil, containing 5 and 6 (ratio 78:22, yield 70%, based on NMR spectroscopic integration with benzene as internal reference).

Repeated preparative TLC (silica gel, dichloromethane) afforded 197 mg (55% yield, based on intake of 1) of a mixture of 5 and 6 as a colorless viscous oil.

Anal. (for the mixture of 5 and 6). Calcd for $C_{12}H_{14}BrCl_3O$: C, 39.98; H, 3.92; Br, 22.17. Found: C, 39.93; H, 4.00; Br, 22.40.

Separation of this mixture was accomplished by applying high-pressure LC (silica gel, dichloromethane/hexane, 23/74), which gave samples of 6 and 5, respectively, both contaminated with decomposition products formed on the high-pressure LC column that were removed by applying preparative TLC (silica gel, dichloromethane). Compounds 5 and 6 were both obtained as colorless oils, moderately stable at room temperature, which were stored at 0 °C.

Spectroscopic data of 5: 1H NMR, see Table I; ^{13}C NMR, see Table II; IR (CCl_4 solution) 1705 (C=O), 1640 (C=C) cm^{-1} ; UV (hexane) λ_{max} 220 (ϵ 7000), λ_{max} 255 nm (ϵ 6500); mass spectrum m/e 357.926 (calcd 357.929) $C_{12}H_{14}^{79}Br^{35}Cl_3O$ (M^+), 279 ($M^+ - ^{79}Br$), 243 ($M^+ - ^{79}Br - H^{35}Cl$).

Anal. Calcd for $C_{12}H_{14}BrCl_3O$: C, 39.98; H, 3.92. Found: C, 40.42; H, 4.12.

6: 1H NMR, see Table I; ^{13}C NMR, see Table II; IR (CCl_4 solution) 1705 (C=O), 1640 (C=C) cm^{-1} ; UV (hexane) λ_{max} 215 (ϵ 9000), λ_{sh} 235 (ϵ 7000), λ_{sh} 258 nm (ϵ 6000); mass spectrum m/e 358 $C_{12}H_{14}^{79}Br^{35}Cl_3O$ (M^+), 279 ($M^+ - ^{79}Br$), 243 ($M^+ - ^{79}Br - H^{35}Cl$).

Addition of Tetrachloromethane to Diene 2. Initiated by UV Irradiation. Diene 2 (200 mg (1.25 mmol)), dissolved in 100 mL of tetrachloromethane, was irradiated for 3 h; the temperature of the solution was maintained between 0 and 5 °C by external cooling. The solvent was removed in vacuo, which left 390 mg of a mixture of 7 and 8 (ratio 68:32, 90% yield, based on NMR spectroscopic integration with benzene as internal reference).

All attempts to separate the mixture of 7 and 8 by chromatography (TLC, high-pressure LC) failed due to the instability of 7. (When kept at -40 °C, no decomposition of 7 was observed after several days.)

The spectra of 7 were obtained from the mixture of 7 and 8, by subtracting the data of pure 8; the latter is prepared by the benzoyl peroxide initiated addition of tetrachloromethane to diene 2.

Spectroscopic data of 7: 1H NMR, see Table I; ^{13}C NMR, see Table II; IR, a mixture of 7 and 8 shows the same IR spectrum as that obtained from pure 8; mass spectrum, similar spectrum to that obtained from pure 8.

Addition of Tetrachloromethane to Diene 2. Initiated by Benzoyl Peroxide. Synthesis of 6-exo-Chloro-4-methylene-3-(2,2,2-trichloroethyl)-1,2,5,6-tetramethylbicyclo[3.1.0]hex-2-ene (8) and 1-(2,2,2-Trichloroethyl)-2-chloromethyl-3,4,5,6-tetramethylbenzene (9). A solution of 600 mg (3.75 mmol) of diene 2 and 80 mg (0.3 mmol) of benzoyl peroxide in 100 mL of tetrachloromethane was boiled for 6 h in the presence of 100 mg of sodium carbonate (to prevent acid-catalyzed reactions). Hereafter the solvent was removed in vacuo, leaving 1170 mg of a viscous colorless oil, which contained a mixture of 8 and 9 (ratio 32:68, 90% yield, based on NMR spectroscopic integration by using benzene as internal reference). Separation of the mixture of 8 and 9 was achieved by preparative TLC (silica gel, pentane), affording 230 mg (yield 20%, based on intake of 2) of 8 as a colorless viscous oil and about 400 mg of crude 9. Partial decomposition of 9 occurred during chromatography (TLC, high-pressure LC) to unidentified products. Whereas 8 is stable in solution even at elevated temperatures (boiling tetrachloromethane), slow decomposition takes place in the pure state at room temperature.

Crude 9 was further purified by repeated crystallization from methanol at -40 °C, affording 9 as white crystals, mp 63–68 °C, in an overall yield of 20% (based on intake of 2).

Spectroscopic data of 8: 1H NMR, see Table I; ^{13}C NMR, see Table II; IR (CCl_4 solution) 1625 (C=C) cm^{-1} ; mass spectrum m/e 311.997, (calcd 312.001) $C_{13}H_{16}^{35}Cl_4$ (M^+), 277 ($M^+ - ^{35}Cl$), 241 ($M^+ - ^{35}Cl - H^{35}Cl$).

9: 1H NMR (C_6D_6 , 35 °C) δ 4.87 (s, 2 H, CH_2Cl), 4.20 (s, 2 H, CH_2CCl_3), 2.15 (s, 3 H), 2.06 (s, 3 H), 1.90 (s, 6 H); ^{13}C NMR ($CDCl_3$, 35 °C) δ 136.8, 136.4, 135.0, 134.1, 133.6, 128.0, 100.4 (CCl_3), 52.2 (t, $J_{CH} = 132$ Hz, CH_2CCl_3), 43.2 (t, $J_{CH} = 145$ Hz, CH_2Cl), 19.8, 17.4, 17.1, 16.4; IR (CCl_4 solution) 1610 (C=C) cm^{-1} ; UV (hexane) λ_{max} 221 (ϵ 20000), λ_{max} 278 (ϵ 2000) nm; mass spectrum m/e 312.002 (calcd 312.001) $C_{13}H_{16}^{35}Cl_4$ (M^+), 277 ($M^+ - ^{35}Cl$), 241 ($M^+ - ^{35}Cl - H^{35}Cl$).

The same mixture of 8 and 9 was obtained when a mixture of 7 and 8, obtained from the photochemically initiated addition of tetrachloromethane to diene 2, was boiled in tetrachloromethane or benzene solution for 1 h.

Addition of Bromotrichloromethane to Diene 2. Synthesis of 1-(2,2,2-Trichloroethyl)-2-bromomethyl-3,4,5,6-tetramethylbenzene (12) and 6-exo-Bromo-4-methylene-3-(2,2,2-trichloroethyl)-1,2,5,6-tetramethylbicyclo[3.1.0]hex-2-ene (11). When 2 mL of bromotrichloromethane was added to 20 mg of diene 2 in a quartz NMR tube, a spontaneous strongly exothermic reaction occurred. The NMR spectrum recorded just after mixing revealed only absorptions due to 11 and 12 (ratio 27:73, yield 60%, determined by NMR with benzene as internal reference). No indications of 10 were obtained.

For preparative-scale reaction: to 320 mg (2 mmol) of diene 2, dissolved in 10 mL of pentane, was added a mixture of 30 mL of bromotrichloromethane and 20 mL of pentane. Under these conditions only partial conversion into products 11 and 12 occurred. The reaction was driven to completion by irradiation of the solution in a Pyrex flask with a Philips 500-W lamp for 10 min, while the flask was kept at about 10 °C by external cooling. Then pentane and bromotrichloromethane were removed in vacuo,

leaving 620 mg of a slightly yellow oil, containing 11 and 12 (ratio 27:73, yield 70%, based on NMR integration with benzene as internal reference).

Separation of the mixture of 11 and 12 was accomplished by preparative TLC (silica gel, pentane) affording 105 mg (0.3 mmol, 10% yield based on intake of 2) of 11 as a colorless oil. In the pure state at room temperature 11 proved to be quite unstable, decomposing completely within 2 h to unidentified products, in tetrachloromethane solution at 0 °C, 11 could be kept for weeks without decomposition.

Crude 12 was obtained as a colorless, very viscous oil after preparative TLC (silica gel, dichloromethane) in about 50% yield (determined by NMR integration, with benzene as internal reference). Although stable at room temperature a complete purification could not be achieved, due to decomposition during chromatography. All efforts to crystallize 12 at lower temperatures were in vain.

Spectroscopic data of 11: ¹H NMR, see Table I; ¹³C NMR, see Table II; IR (CCl₄ solution) 1625 (C=C) cm⁻¹; mass spectrum *m/e* 356 C₁₃H₁₆³⁵Cl₃⁷⁹Br (M⁺), 41 277 (M⁺ - ⁷⁹Br), 241 (M⁺ - ⁷⁹Br - H³⁵Cl).

12: ¹H NMR (C₆D₆, 35 °C) δ 4.78 (s, 2 H, CH₂Br), 4.20 (s, 2 H, CH₂CCl₃), 2.10 (s, 3 H), 2.03 (s, 3 H), 1.87 (s, 6 H); ¹³C NMR (CDCl₃, 35 °C) δ 137.3, 136.6, 135.2, 134.2, 133.5, 128.0, 100.1 (CCl₃), 52.3 (t, *J*_{CH} = 130 Hz, CH₂CCl₃), 32.5 (t, *J*_{CH} = 150 Hz, CH₂Br), 19.8, 17.4, 17.1, 16.4; mass spectrum *m/e* 355.947 (calcd 355.950) C₁₃H₁₆³⁵Cl₃⁷⁹Br (M⁺), 277 (M⁺ - ⁷⁹Br), 241 (M⁺ - ⁷⁹Br - H³⁵Cl).

Kinetic Measurements of the Conversion of 7 into 9. To 30 mg (0.1 mmol) of a mixture of 7 and 8 was added 1 mL of hexadeuteriobenzene. The solution, kept at 21 °C, was measured every 6 h by ¹H NMR spectroscopy. When the logarithm of the concentration of 7 was plotted vs. time, a straight line (to 85% conversion) was obtained from which the rate constant was calculated to be 6.9 × 10⁻⁶ s⁻¹. No decomposition of 8 was observed.

Behavior of 7 and 8 in Nitromethane and Methanol

(41) The intensity of the parent peak was too low to be used for an exact mass determination.

Solution. When a mixture of 7 and 8 was dissolved in perdeuterionitromethane, the ¹H NMR spectrum taken after mixing displayed only peaks due to 8 and 9, showing that the conversion of 7 into 9 was complete within 10 min, whereas 8 was unaffected.

A mixture of 7 and 8, left overnight in methanol solution, afforded, after removal of the solvent in vacuo, a (1:1) mixture of 28 and 9 (90% yield, determined by ¹H NMR with benzene as internal reference); 8 had remained unchanged.

Synthesis of 1-(2,2,2-Trichloroethyl)-2-methoxymethyl-3,4,5,6-tetramethylbenzene (28). A total of 160 mg (0.5 mmol) of 9 was treated with 200 mg (1 mmol) of silver perchlorate in 20 mL of methanol overnight. Soon a white precipitate (silver chloride) was formed. After filtration and evaporation of the solvent, the residue was extracted with pentane and the pentane solution was filtered and dried over sodium sulfate. Removal of the solvent gave a colorless oil, containing 28 in 70% yield (based on NMR integration, with benzene as internal reference). Further purification was achieved by preparative TLC (silica gel, dichloromethane), affording 80 mg of 28 as a colorless oil (50% yield, based on intake of 9). Compound 28 was prepared in the same way from 12, also in 50% yield (silver bromide being precipitated).

Spectroscopic data of 28: ¹H NMR (CCl₄, 35 °C) δ 4.59 (s, 2 H, CH₂OCH₃), 4.31 (s, 2 H, CH₂CCl₃), 3.28 (s, 3 H, OCH₃), 2.40 (s, 3 H), 2.24 (s, 6 H), 2.22 (s, 3 H); IR 1610 (C=C) cm⁻¹; mass spectrum *m/e* 308.051 (calcd 308.050) C₁₄H₁₈³⁵Cl₃O (M⁺), 276 (M⁺ - CH₃OH), 272 (M⁺ - H³⁵Cl).

Treatment of a Mixture of 5 and 6 with Sodium Perchlorate. A mixture of 5 and 6 was stirred overnight in tetrahydrofuran in the presence of a small excess (1.2 equiv) of silver perchlorate at room temperature, silver bromide being precipitated. Excess silver perchlorate was then removed by adding an aqueous solution of sodium chloride, followed by filtration of the precipitate. The resulting solution was extracted with pentane, and the latter was dried over sodium sulfate. Evaporation of the solvent afforded, according to NMR, a mixture of 6 and unidentified products, no 5 being present anymore.

Registry No. 1, 56745-77-8; 2, 50590-86-8; 3, 70130-71-1; 4, 70190-91-9; 5, 70130-72-2; 6, 70190-92-0; 7, 70130-73-3; 8, 70190-93-1; 9, 70130-74-4; 11, 70130-75-5; 12, 70130-76-6; 28, 70130-77-7; tetrachloromethane, 56-23-5; bromotrichloromethane, 75-62-7.

Bicyclo[4.2.0]oct-3-ene-7,8-dione and Its Monoenol Silyl Ether

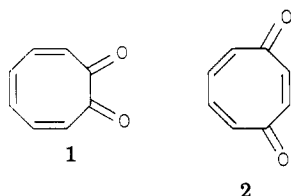
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The readily available enediol bis(trimethylsilyl) ether 7 has been demonstrated to be a useful intermediate in the synthesis of free bicyclo[4.2.0]oct-3-ene-7,8-dione (3) as well as a protected form, the monoenol silyl ether 6. Bromination of 7 gave small amounts of both 3 and 6. If bromination was followed by addition of triethyl amine, 6 could be obtained in 41% yield. Other products isolated from the bromination of 7, depending on the conditions, were the cyclobutene-1,2-dione 13, the benzocyclobutene-1,2-dione 15, and the benzocyclobutenol silyl ether 16. The best route to 3 involved the oxidative desilylation of 7 by means of DDQ in dioxane.

Rather unexpectedly, the theoretically interesting molecule 3,5,7-cyclooctatriene-1,2-dione 1 proved to be an



elusive synthetic target. Much effort has been expended on this problem, by a number of groups,¹ which only saw

fruition in early 1977 with the successful generation of 1 in solution by Oda, Oda, Miyakoshi, and Kitahara.^{1e} The corresponding 1,4-isomer 2 had been prepared earlier by

(1) Complete surveys of the early work on the attempted syntheses of 1 are found in the following: (a) P. Gund, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1967; *Diss. Abstr. B*, 28, 3642 (1968); *Chem. Abstr.*, 69, 35531 (1968); (b) J.-H. Tsao, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1974; *Diss. Abstr. B*, 35, 4401 (1975); *Chem. Abstr.*, 83, 42891 (1975). For collected references to the more recent work, see: (c) P. A. Chaloner and A. B. Holmes, *J. Chem. Soc., Perkin Trans. 1*, 1838 (1976); (d) T. R. Kowar and E. LeGoff, *J. Org. Chem.*, 41, 3760 (1976); (e) M. Oda, M. Oda, S. Miyakoshi, and Y. Kitahara, *Chem. Lett.*, 293 (1977).