Studies on the Stereochemistry of Polar 1,4 Addition of Bromine to Dienes. Structure Assignments for Dibromocyclohexenes and Dibromohexenes

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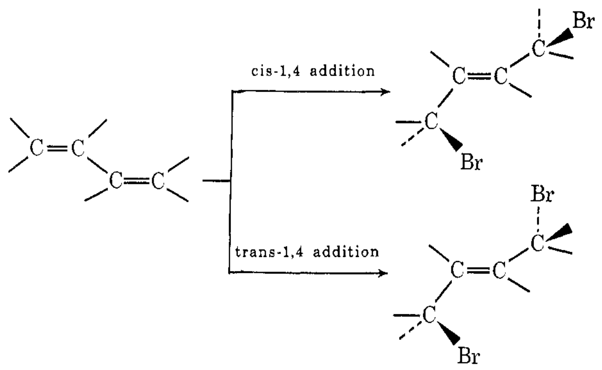
The compositions of dibromide mixtures obtained from the polar bromination of cyclopentadiene, 1,3-cyclohexadiene, and (*Z*,*Z*)-, (*E*,*Z*)-, and (*E*,*E*)-2,4-hexadiene under conditions of kinetic control have been determined. Compositions of equilibrated products were also determined. The stereochemistry of 1,4 addition is found to be primarily cis. The extent of 1,4 addition, which occurs cis, is highest with 1,3-cyclohexadiene and lowest with cyclopentadiene (96 and 52%, respectively, in carbon tetrachloride). The extent of cis 1,4 addition to the 2,4-hexadienes varies from 62 to 92% depending on diene and solvent. Structures of the 1,4-dibromides obtained from the 2,4-hexadienes, *rac*- and *meso*-2,5-dibromo-(*E*)-3-hexene, were proved by conversion *via* glycols to 2,3,4,5-diepoxyhexanes. The 1,2 addition to the 2,4-hexadienes was found to be nonstereospecific (91–69% trans addition), suggesting extensive charge dispersal in the intermediate vinylic bromonium ions of this system. Assignment of the structures of the three cyclohexadiene dibromides are established from their proton nmr spectra, physical properties, infrared spectra, and equilibrations. The proton nmr spectra of the three cyclopentadiene dibromides are shown to be completely consistent with previous structural assignments based on dipole moment measurements.

An important mechanistic problem which remains to be fully investigated is that of the stereochemistry of the 1,4 addition to 1,3-dienes. For example, the bromine molecule can add either cis or trans to the 1,4 carbon atoms of a diene, as illustrated by the following equations.

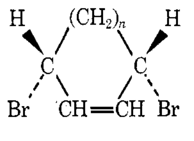


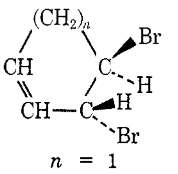
Previous studies on the polar bromination of certain acyclic conjugated dienes have shown that the 1,4-dibromide product consists predominantly of the trans isomer,[2-5] that the positive charge of the intermediate vinylic bromonium ion perturbs the neighboring vinyl group very little,[3,6,7] and that in many cases the kinetically controlled dibromide product (1,2 and 1,4 isomers) can be analyzed without rearrangement.[2-4,8]

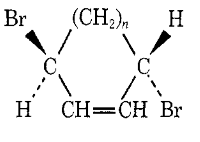
In this paper we present results of further investigations into the mechanism of 1,4 addition of halogen to dienes. Reported here are quantitative studies of the polar addition of bromine to cyclopentadiene, 1,3-cyclohexadiene, and the three 2,4-hexadienes (*E*,*E*, *Z*,*Z*, and *E*,*Z*)[9] in solvents of widely different polarity. The bromination of these dienes has been reported previously[10] but the compositions of the kinetically controlled product mixtures were not determined, and in the cases of the dibromides from 1,3-cyclohexadiene and the 2,4-hexadienes the structures of the products were not established. In the case of the cyclohexadiene dibromides, nmr, infrared, and equilibration evidence are presented here which for the first time establish their structures. How the structures of the 2,4-hexadiene dibromides were established by chemical means is also described. Also discussed in detail are the previously unreported proton nmr spectra of the three cyclopentadiene dibromides; these data are useful in discussing the nmr spectra of the cyclohexadiene dibromides and confirm the previous structure assignments for these five-membered ring derivatives which were based on chemical[10a] and dipole moment results.[11]

Results

Products from the Bromination of the Dienes.—The structures of the probable products from the bromination of cyclopentadiene and 1,3-cyclohexadiene are shown below.







$n = 1$

cis-3,5-dibromocyclopentene (3) *trans*-3,4-dibromocyclopentene (1) *trans*-3,5-dibromocyclopentene (2)

$n = 2$

cis-3,6-dibromocyclohexene (6) *trans*-3,4-dibromocyclohexene (4) *trans*-3,6-dibromocyclohexene (5)

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(1) (a) Bethany Nazarene College; (b) Pasadena College; (c) California Institute of Technology.

(2) V. L. Heasley, C. L. Frye, R. T. Gore, Jr., and P. S. Wilday, *J. Org. Chem.*, **33**, 2342 (1968).

(3) V. L. Heasley, G. E. Heasley, S. K. Taylor, and C. L. Frye, *ibid.*, **35**, 2967 (1970).

(4) L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Amer. Chem. Soc.*, **81**, 5943 (1959).

(5) K. Mislow, *J. Amer. Chem. Soc.*, **75**, 2512 (1953).

(6) V. L. Heasley and P. H. Chamberlain, *J. Org. Chem.*, **35**, 539 (1970).

(7) V. L. Heasley, G. E. Heasley, R. A. Loghry, and M. R. McConnell, *J. Org. Chem.*, **37**, 2228 (1972).

(8) V. L. Heasley and S. K. Taylor, *J. Org. Chem.*, **34**, 2779 (1969).

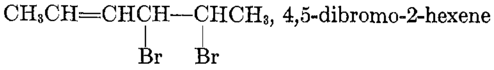
(9) For a discussion of alkene nomenclature see *J. Org. Chem.*, **35**, 2849 (1970).

(10) (a) Cyclopentadiene: W. G. Young, H. K. Hall, Jr., and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 4338 (1956). (b) Cyclohexadiene: E. H. Farmer and W. D. Scott, *J. Chem. Soc.*, 172 (1929). (c) 2,4-Hexadienes: A. V. Dombrovskii, *Zh. Obshch. Khim.*, **24**, 610 (1954).

(11) W. D. Kumler, A. C. Huitric, and H. K. Hall, Jr., *J. Amer. Chem. Soc.*, **78**, 4345 (1956).

Structures of the probable dibromide products from the bromination of the isomeric 2,4-hexadienes are shown below.

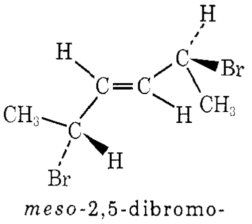
1,2 Addition



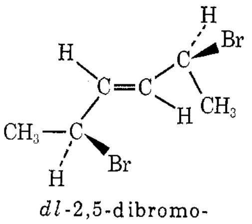
$$\mathrm{CH_3CH{=}CH\underset{\substack{|\\ Br}}{C}H{-}\underset{\substack{|\\ Br}}{C}HCH_3}$$, 4,5-dibromo-2-hexene

erythro, (*Z*), **7**; *threo*, (*Z*), **8**
erythro, (*E*), **9**; *threo*, (*E*), **10**

1,4 Addition



meso-2,5-dibromo-(*E*)-3-hexene (**11**)



dl-2,5-dibromo-(*E*)-3-hexene (**12**)

A stereospecific cis-1,4 addition of the bromine atoms to (*E*,*Z*)-2,4-hexadiene would yield the meso dibromide **11**, whereas trans-1,4 addition would give **12**, the racemic dibromide. Stereospecific cis-1,4 addition to (*Z*,*Z*)- and (*E*,*E*)-2,4-hexadiene should give **12**, and **11** would result from a stereospecific trans-1,4 addition.

The five dienes were brominated under carefully controlled conditions which should only result in polar addition[3,8] of halogen. The following dibromides were obtained: cyclopentadiene, **1**, **2**, and **3**; 1,3-cyclohexadiene, **4**, **5**, and **6**; (*Z*,*Z*)-2,4-hexadiene, **7**, **8**, **11**, and **12**; (*E*,*E*)- and (*E*,*Z*)-2,4-hexadiene,[12] **9**, **10**, **11**, and **12**. The kinetic yields of these dibromides are presented in Tables I (cyclic dienes) and II (acyclic dienes) as the percentages of cis-1,4 addition (per cent cis-1,4 addition = 100 × cis-1,4 addition/1,4 addition), the ratios of 1,4/1,2 addition, and the percentages of trans-1,2 addition (for the 2,4-hexadienes).

TABLE I

BROMINATION OF CYCLOHEXADIENE AND CYCLOPENTADIENE

Diene	Solvent	Dibromides, %[a] I	II	III	cis-1,4[b] addn, %	1,4/1,2 addn
C_5H_6	C_5H_{12}	48	24	28	54	1.1
C_5H_6	CCl_4	39	29	32	52	1.6
C_5H_6	CH_2Cl_2	26	21	53	72	2.8
C_5H_6	CH_3NO_2	31	29	40	58	2.2
C_6H_8	C_5H_{12}	25	13	62	83	3.0
C_6H_8	CCl_4	18	3	79	96	4.6
C_6H_8	CH_2Cl_2	19	2	79	98	4.3

[a] I, II, and III are **1**, **2**, and **3**, respectively, for cyclopentadiene and **4**, **5**, and **6**, respectively, for cyclohexadiene. [b] Computed as follows: **3**/**3** + **2** × 100 for cyclopentadiene, and **6**/**5** + **6** × 100 for cyclohexadiene.

Equilibrium Mixtures of the Dibromides.—Table III contains data on the mixtures of dibromides that are present at equilibrium. These data show that in general the mixtures of products formed under kinetic conditions (Tables I and II) show little resemblance to the thermodynamic mixtures. This is particularly evident in the case of the 1,3-cyclohexadiene dibromides, where the trans 3,6-dibromide is considerably more stable than the cis 3,6 isomer. For all dienes the percentages of cis 1,4 dibromide is higher under kinetic conditions than under thermodynamic conditions.

TABLE II

BROMINATION OF THE 2,4-HEXADIENES

Diene	Solvent	Dibromides, %[b] I	II	III	IV	trans-1,2,[c] %	cis-1,4 addn,[d] %	1,4/1,2 addn
(*Z*,*Z*)	C_5H_{12}	4	44	14	38	92	73	1.1
(*Z*,*Z*)	CCl_4	7	27	7	59	79	89	1.9
(*Z*,*Z*)	CH_2Cl_2	4	15	6	75	79	93	4.3
(*Z*,*Z*)	CH_3NO_2	5	39	17	39	89	70	1.3
(*E*,*Z*)[a]	C_5H_{12}	5	39	38	15	89	72	1.2
(*E*,*Z*)[a]	CCl_4	7	24	54	15	77	78	2.2
(*E*,*Z*)[a]	CH_2Cl_2	4	22	58	16	85	78	2.8
(*E*,*Z*)[a]	CH_3NO_2	9	32	39	20	78	66	1.4
(*E*,*E*)	C_5H_{12}	37	5	17	41	88	71	1.4
(*E*,*E*)	CCl_4	23	6	15	56	79	79	2.4
(*E*,*E*)	CH_2Cl_2	23	4	15	58	85	79	2.7
(*E*,*E*)	CH_3NO_2	24	10	25	41	71	62	1.9

[a] See footnote 12. [b] I = **7** from (*Z*,*Z*)-; **9** from (*E*,*Z*)- and (*E*,*E*)-; II = **8** from (*Z*,*Z*)-; **10** from (*E*,*Z*)- and (*E*,*E*)-; III = **11**; IV = **12**. [c] Computed as follows: (*Z*,*Z*)-, **8**/**8** + **7** × 100; (*E*,*E*)-, **9**/**9** + **10** × 100; (*E*,*Z*)-, **10**/**10** × **9** × 100. [d] Computed as follows: (*E*,*Z*)-, **11**/**11** + **12** × 100; (*Z*,*Z*)- and (*E*,*E*)-, **12**/**11** + **12** × 100.

TABLE III

EQUILIBRIUM MIXTURES OF THE DIBROMIDES[a]

Dibromide system	Solvent	Temp, °C	Dibromides, % I	II	III	IV	cis 1,4, %	1,4/1,2
$C_5H_6Br_2$	CCl_4	25	26	45	29		39	2.8
$C_5H_6Br_2$	CCl_4	78	22	47	31		40	3.5
$C_5H_6Br_2$	C_5H_{12}	25	29	43	28		39	2.4
$C_6H_8Br_2$	CCl_4	25	25	59	16		24	3.0
$C_6H_8Br_2$	CCl_4	78	26	57	17		23	2.9
$C_6H_{10}Br_2$	CCl_4	80	20	16	33	31	52[b]	1.8
$C_6H_{10}Br_2$	CH_3NO_2	25	12	9	40	39	51[b]	3.8

[a] Percentages and ratios were computed as described in Tables I and II. [b] Value refers to percentage of **11**.

Structural Assignments for Cyclic Dibromides.—The correct assignment of the structure of the cyclic dibromides under study here is very crucial to discussion below of the mechanisms of the polar bromine addition reaction. Thus, we felt compelled to treat this aspect of the problem in considerable detail, especially since no previous assignment existed for the three dibromides isolated from bromination of 1,3-cyclohexadiene. The structural assignments of the cyclopentadiene dibromides have been previously made based primarily on dipole moment measurements.[10a,11] We now describe 60-MHz proton nmr results which completely confirm these earlier assignments.

The trans 3,4 isomer (**1**) exhibits five types of protons at 60 MHz in the ratio of 1:1:1:1:2 and would be expected to give rise to a ABCDEF spin system.[13]

The methylene protons are expected to be at highest field.[14] Thus, the sets of signals centered about 2.72 and 3.31 ppm from TMS are assigned to these protons. These nuclei grossly exhibit a four-line AB spin system

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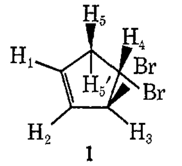
[12] In (*E*,*Z*)-2,4-hexadiene 1,2 addition of bromine occurs almost entirely at the cis bond. Small amounts (per cent of 1,2 addition) of **7** were formed (attack at the trans bond): pentane, 6.1; CCl_4, 1.3; CH_2Cl_2, 1.2; and CH_3NO_2, 1.2. A trace of **8** could have been formed but would not have been detected because it has the same retention time as **10**.

[13] J. W. Emsley, J. Feeney, and L. H. Satcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Elmsford, N. Y., 1965, Chapter 8.

[14] See, for example, (a) D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962); (b) D. D. Elleman, S. L. Manatt, and C. D. Pearce, *ibid.*, **42**, 650 (1965); (c) M. A. Cooper, D. D. Elleman, C. D. Pearce, and S. L. Manatt, *ibid.*, **53**, 2343 (1970).



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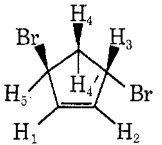

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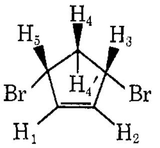

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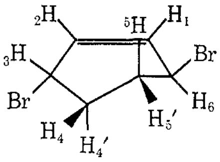

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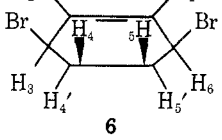

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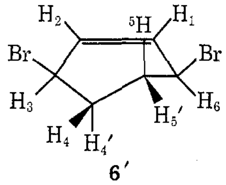

6′

pattern with a geminal coupling ($J_{55'}$) of −20.3 Hz.[15] Both members of the AB pattern possess much fine structure due to many other smaller couplings, but that at 3.31 ppm shows a well-resolved 5.4-Hz splitting which is characteristic of the vicinal coupling between two protons on the same side of a five-member ring.[16] This identifies these latter signals as due to proton H_5 so that $H_{5'}$ on the same side as the vicinal bromine is deshielded by 0.61 ppm. Then proton H_4 can be assigned to the signals at 4.72 ppm which also exhibit a well-resolved 5.4-Hz splitting. Indeed methine proton H_3 is expected to be less shielded than proton H_4 because of its adjacency to the vinyl group;[14b,c] so it is assigned to the signals centered at 5.22 ppm. The vinyl protons, as expected, give rise to a complex region centered at 6.05 ppm.[14a,c]

The trans 3,5 isomer (**2**) shows, as expected, only three kinds of protons in the intensity ratio of 1:1:1 and the signals are characteristic of a AA′BB′CC′ spin system,[13] whose nature is such that no spacing in any region would give any of the spin–spin couplings directly. However, for our purposes of structure assignment, it is enough to ascertain that there are three types of protons in the ratio of 1:1:1 and that the three chemical shifts correspond to those in molecules possessing similar chemical types, *i.e.*, comparisons with the proton chemical shifts for the 3,4-dibromo isomer **1**. Thus for **2** the methylene group is assigned to the triplet at 2.96 ppm. The triplet spacing of 5.5 Hz represents the sum of the couplings $J_{4'5}$ and J_{45} for the AA′BB′ system[17] of the 3,5,4,4′ protons. Since $J_{4'5}$ is probably very small[14b] (1 Hz or less), the observed splitting gives a reasonable approximation of J_{45}. The signals at 5.12 ppm are assigned to the H_3 and H_5 protons. Again a 5.5-Hz splitting is evident along with a 1.1-Hz splitting which arises from coupling of the methine protons with the vinyl protons. This 1.1-Hz splitting is the result of a positive vicinal coupling of one methine to the adjacent vinyl proton and a negative long-range coupling, $J_{HC{=}CCH'}$, to the distant vinyl proton.[14a] The vinyl protons' signal occurs as a deceptively simple doublet (1.1-Hz splitting) at 6.12 ppm.

The spectrum of the cis 3,5 isomer (**3**) consists of four types of protons in the ratio of 1:1:2:2 and should be of the AA′BB′CD symmetry type.[13] Indeed, two types of methylene protons are evident at 2.62 and 3.09 ppm. A geminal coupling of −17.4 Hz is evident for $J_{44'}$.[15] Proton H_4' is identified from the observed splitting patterns as having a chemical shift of 2.62 ppm. This proton's signals exhibit a resolvable 2.2-Hz triplet splitting, which should be an accurate measure of $J_{34'}$, in the A_2BC system of protons 3,5,4,4′.[14a] Thus, $J_{34'}$ is rather larger than expected for a trans J_{HCCH} coupling in a cyclopentene ring.[14b,16] Perhaps the bromine atoms perturb the $H_{4'}$ proton so that the angle between the C–C–H_3 and C–C–H_4 planes is reduced away from 90°, where the vicinal coupling would be zero.[18] The assignment of proton H_4 to the signals centered at 3.09 ppm follows from its geminal coupling with the H_4' proton and its 6.6-Hz triplet splitting, which is a good measure of J_{34} in the A_2BC spin system of the 3,5,4,4′ protons. The assignment of the H_3 and H_5 protons to the doublet (6.6-Hz splitting) of doublets (2.2-Hz splitting) of doublets (1.5-Hz splittings) at 5.01 ppm then follows. The first two splittings arise as discussed above and the last one arises from couplings with the vinyl protons. Finally, the vinyl protons are assigned to the deceptively simple doublet at 6.12 ppm.

In summary, the nmr spectral symmetries, integrated intensities, chemical shifts, and observed splitting patterns for the isomers **1**, **2**, and **3** allow unequivocal assignment of their structure. It should be pointed out that a complete analysis of their nmr spectra to obtain exact proton–proton coupling constants would require a great amount of effort, as their nmr spectra are really quite complex. What we have done here is to skim off and use available splitting and chemical-shift information from the observed spectra. As discussed above, the observed splittings are expected to be reasonable approximations to the coupling we have identified. Thus, the nmr results discussed here are in complete agreement with the earlier assignments based on dipole moments and chemistry[10a,11] and other nmr results in related systems.[14,16]

Three dibromide isomers from the bromination of 1,3-cyclohexadiene were isolated many years ago by Farmer and Scott.[10b] The straightforward manner by which the isomeric five-membered ring dibromides were assigned, as described above, gave us hope that with these data as examples the assignments in the six-membered series could be accomplished. In our work in the later series, as before,[10b] two solid isomers, mp 108 and 68°, were isolated along with a very labile liquid dibromide which rearranges to mixtures of the two solid isomers. As described below, the three dibromides had different infrared spectra such that it was possible to devise a quantitative ir analysis procedure to measure the ratio of **4** to **6** and **5** to **6** from the brominations. However, the infrared spectra were not much help in establishment of the structures of the three dibromides.

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[15] The sign of this geminal coupling is based on analogy to other systems; see, for example, ref 14b and 14c.

[16] See A. K. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965).

[17] For discussion of the spectra of AA′BB′ spin system see (a) D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963); (b) B. Dischler and G. Englert, *Z. Naturforsch. A*, **16**, 1180 (1961); (c) R. C. Hirst and D. M. Grant, *J. Chem. Phys.*, **40**, 1909 (1964).

[18] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

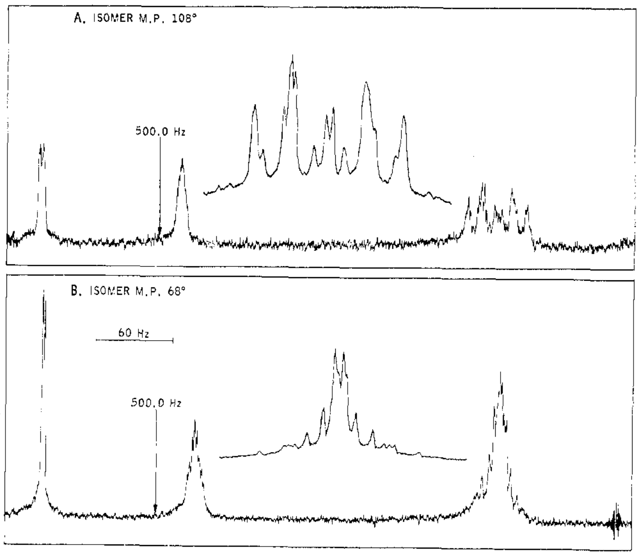

Figure 1.—Proton 100-MHz spectra of 3,6-dibromocyclohexene isomers in CCl_4. Point in spectra 500.0 Hz downfield from tetramethylsilane indicated. Inserts show methylene protons regions when methine protons irradiated.

In the case of a trans 3,4 isomer (**4**) we expected to observe a proton nmr spectrum somewhat analogous to that of **1** in the five-membered series and exhibiting two types of vinyl protons, two types of methine protons, and possibly four types of methylene protons or at least a complex methylene region. For the trans 3,6 and cis 3,6 isomers we expected to observe one type of vinyl proton, one type of methine proton, and two types of methylene protons. The symmetry of these proton nmr spectra were expected to be characteristic of very complex AA'BB'CC'DD' systems. If these spectra could be completely analyzed to provide vicinal proton–proton coupling constant data, then it would be possible to assign the cis and trans structures. The information which would be pivotal in deciding the issue would be the coupling parameters between the sets of chemical shift equivalent, magnetically nonequivalent methylene protons on the 4 and 5 carbon atoms. These protons form, within the eight-spin systems, two distinct types of AA'BB' spin systems. For the trans 3,6 isomer we would expect to extract a set of vicinal coupling parameters between the methylene protons which exhibit one vicinal coupling of a magnitude about 12–13 Hz which is characteristic of two C–C–H planes with a dihedral angle close to 180°. The two other vicinal couplings should be characteristic of dihedral angles close to 60°, which would give rise to vicinal coupling in the range of 3–5 Hz.[14c,18] Molecular models of a trans 3,6 isomer strongly suggest that a reasonably rigid conformation is favored. For the cis 3,6 isomer, models suggest the possibility of a rapid interconversion between two conformations having one bromine nearly axial and one equatorial or possibly a semirigid conformation with both bromines nearly equatorial. In either case, on an nmr time scale, one would expect to find a set of vicinal coupling constants, none of which are characteristic of a dihedral angle close to 180°. Instead, vicinal couplings for the methylene protons characteristic of the averages for two conformations like that in **6** [*i.e.*, $J^{\text{obsd}} = {}^1/_2 \cdot (J^{\text{trans}}_{4'5'} + J^{\text{gauche}}_{45})$, $J^{\text{obsd}}_{45'} = J^{\text{gauche}}_{4'5'}$, and $J^{\text{obsd}}_{4'5} = J^{\text{gauche}}_{4'5}$][19] or of one rigid one similar to **6'** would be expected. A confirmation like **6'** would possess two vicinal couplings characteristic of a 0° dihedral angle and one characteristic for 60°.[20] Thus, extraction of the vicinal coupling information and subsequent assignment would seem to depend on the iterative analyses of two complex eight-spin systems. Analyses of such eight-spin systems are very formidable tasks and very costly in computer time. It seemed to us that it might be possible to greatly simplify the problem for the two 3,6 isomers if the methine protons could be decoupled in double-resonance experiments from the methylene protons. This would reduce the problem to analyses of two AA'BB' systems, which are much more tractable. It was expected that the vinyl protons would have only very small long-range couplings to the methylene protons. In addition, the nature of these two AA'BB' spin systems could be expected to be significantly different not only from the standpoint of the coupling parameters which would be obtained but from another more subtle standpoint. Thus, the trans 3,6 isomer would give rise to an AA'BB' system characteristic of a reasonably large *M* value, whereas we would expect the cis 3,6 isomer to possess a spectrum characteristic of small (about 1–2 Hz) or zero *M*.[21]

The labile liquid dibromide was never obtained in a reaonably pure state at a time convenient to record its nmr spectrum. Spectra were taken of mixtures of the three bromides and numerous extra signals not assignable to the two solid dibromides were evident. Unfortunately, it turned out that the signals from the various protons of the liquid isomer were masked by those of the other two isomers, even at 220 MHz. However, we felt that, if the configuration of the two solid dibromides turned out to be assignable to the trans 3,6 and cis 3,6 isomers, and from the fact that the liquid dibromide isomerized to the other two isomers, it would be quite reasonable to assign the liquid isomer the trans 3,4 structure. In addition, its boiling point was essentially identical with that of the 1,4 isomer, its melting point is much lower than those of either of the other isomers, thus suggesting a lower molecular symmetry, and the infrared spectrum is consistent and similar to those of the other isomers. The firm assignment of the structures of the two solid isomers then becomes crucial.

The 100-MHz nmr spectra of the two crystalline dibromides are shown in Figure 1. Indeed, both exhibit one type of vinyl proton, one type of methine proton, and a complex methylene region in the intensity ratio of 1:1:2. Both the vinyl and methine signal are characteristic of deceptively simple spectra which could be part of AA'BB'CC'DD' spin systems. To carry out fully the analyses of the spectra as they stand would be tedious and time-consuming tasks. We proceeded to carry out double-resonance experiments on each molecule where the methine protons were irradiated with a large modulation (about 40 Hz). The inserts in Figure 1 show that indeed the methylene proton regions in both cases were reduced to sym-

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(19) See, for example, R. J. Abraham and G. Gatti, *J. Chem. Soc. B*, 961 (1969).

(20) The spectrum and vicinal coupling parameters for 1,2-dihydronaphthalene appear to be close to this situation; see ref 14c.

(21) $M = J_{AA'} - J_{BB'}$; see ref 17.

metrical patterns characteristic of AA'BB' spin systems. These two experiments then establish unequivocally that we are dealing with molecules with a symmetry correct for the 3,6-dibromocyclohexene isomers. Iterative analyses on the AA'BB' spectrum with the largest chemical shift and dibromide, mp 108°, with the computer program NMRENIT[22] yielded vicinal coupling constants of 12.79, 2.64, and 4.27 Hz.[23] The large vicinal coupling is characteristic of a trans vicinal coupling and the two small ones of vicinal gauche ones.[16,18,19] Thus, based on these parameters, we assign the trans structure to the isomer with mp 108°. The iterative analysis of the AA'BB' spectrum for the isomer with mp 68° is still in progress.[23] This particular spectrum has proved difficult to assign in detail because of its small chemical shift between the protons (see Figure 1) and the fact that its parameter *M* is apparently zero. Thus far, two assignments have been found which correspond closely to the experimental spectrum. The two assignments yield vicinal couplings of 10.2 ± 0.5 and 2.2 ± 0.5 and 7.5 ± 0.5 and 3.2 ± 0.5 Hz, respectively.[23] The first pair would fit conformation **6'** and the second pair a fast interconversion of two conformations such as **6**. Significantly, in both of these assignments *M* is zero and no vicinal couplings as large as that observed in the case of the isomer with mp 108°, and consistent with vicinal $J_{180°}$,[19] are found. Thus, we assign the cis 3,6 configuration to the isomer with mp 68°.

The assignments and chemical shifts for five of the cylic dibromide isomers discussed above are summarized in Table IV.

TABLE IV

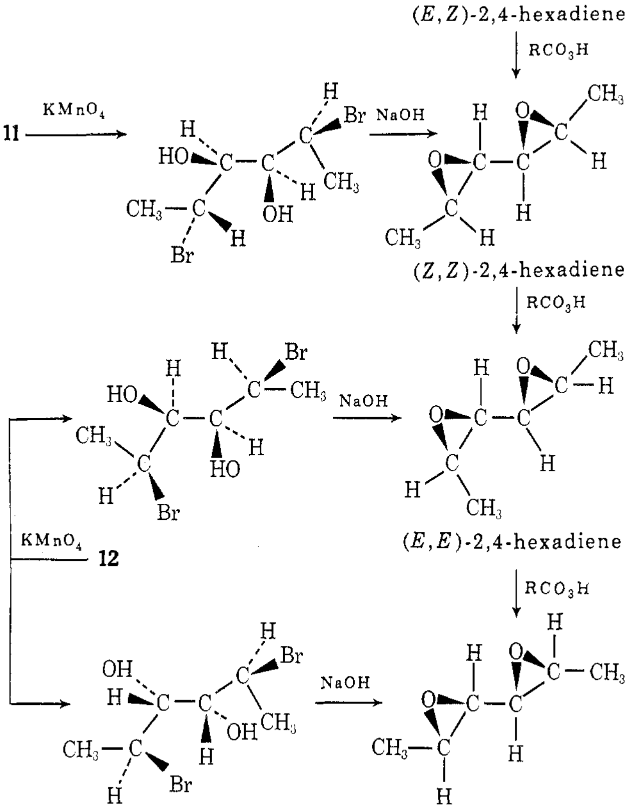
SUMMARY OF CHEMICAL SHIFT ASSIGNMENTS FOR DIBROMIDES IN CCl_4[a]

Compd	Methylene	Methine	Vinyl
trans-3,4-Dibromocyclopentene (**1**)	2.72, 3.31	4.72, 5.22	6.05
trans-3,5-Dibromocyclopentene (**2**)	2.96	5.12	6.12
cis-3,5-Dibromocyclopentene (**3**)	2.62, 3.09	5.01	6.12
trans-3,6-Dibromocyclohexene (**5**)	2.154, 2.454	4.826	5.942
cis-3,6-Dibromocyclohexene (**6**)	2.144, 2.304	4.700	5.906

[a] In parts per million downfield from tetramethylsilane.

Establishment of the Structures of Acyclic Dibromides 11 and 12.—Dibromides **11** and **12** were separated from each other and the 1,2-dibromides by fractional recrystallization. The proton nmr spectra of **11** and **12** were consistent with their expected compliment of protons. However, to obtain any configurational information from these spectra would have required fitting two complex ten-spin systems, which would be a formidable task, and detailed nmr studies of some model compounds. Thus, a chemical approach to assignment of their structures was sought. A feasible approach to this goal seemed to be through conversion to the diepoxides as indicated in Scheme I. The diepoxides which were obtained from the dibromides were identified by comparison with the diepoxides produced by direct treatment of the 2,4-hexadienes with peroxy acids. The meso dibromide (**11**) yielded a single cis,trans diepoxide which was identical with one[24] of the diepoxides obtained by treatment of (*E*,*Z*)-2,4-hexadiene with peroxy acid. The racemic dibromide **12** formed two diepoxides. One of these diepoxides was identical with one of the diepoxides from peroxy acid reaction with (*Z*,*Z*)-2,4-hexadiene, and the other was identical with one of the diepoxides resulting from peroxy acid reaction with (*E*,*E*)-2,4-hexadiene. Using these procedures we were able to establish the structures of diastereomers **11** and **12**. The assumptions that we made in pursuing this line of structure proof are that (1) glycol formation with permanganate is a cis addition;[25] (2) formation of an epoxide from a bromohydrin occurs with inversion of configuration;[26] and (3) epoxidation of the diene is a stereospecific cis addition.[27]

SCHEME I



Methods for Analysis of the 4,5-Dibromo-2-hexenes.—The amounts of 4,5-dibromo-2-hexenes (1,2-dibromides) which were formed in the brominations of the 2,4-hexadienes were obtained by direct vpc analysis of the bromination products, and by analysis of the

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[22] M. T. Bowers, T. I. Chapman, and S. L. Manatt, *J. Chem. Phys.*, **50**, 5412 (1969); this program was adapted for use on a Hewlett-Packard 2116B with 16k of memory, 7900A Disc Drive, and 7970B Digital Tape Unit.

[23] S. L. Manatt, S. P. Sander, P. A. Kroon and V. Heasley, details to be published subsequently; for the mp 108° isomer the average observed minus calculated line position for 24 lines was 0.03 Hz.

[24] When the 2,4-hexadienes react with peroxy acid, two diastereomeric diepoxides are expected from each diene, assuming cis addition to each double bond. See ref 27.

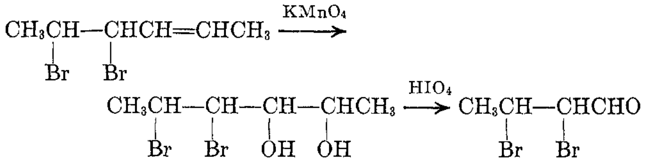
[25] K. Wiberg and K. Saegebarth, *J. Amer. Chem. Soc.*, **79**, 2822 (1957).

[26] S. Winstein and H. Lucas, *J. Amer. Chem. Soc.*, **61**, 1576 (1939).

[27] For example, see J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, p 619.

crotonaldehyde dibromides which were formed from the 1,2-dibromides as indicated in Scheme II.

SCHEME II

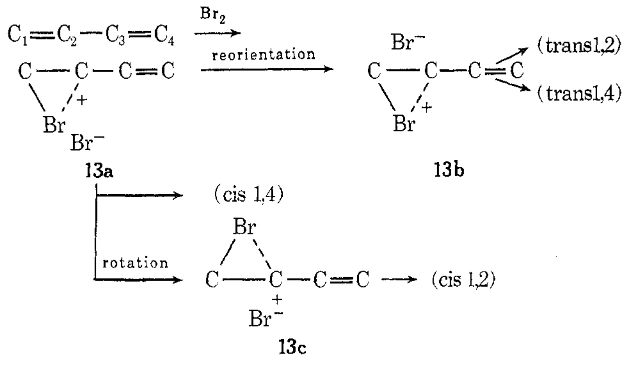

$CH_3CHBr-CHBrCH=CHCH_3 \xrightarrow{KMnO_4} CH_3CHBr-CHBr-CH(OH)-CH(OH)CH_3 \xrightarrow{HIO_4} CH_3CHBr-CHBrCHO$

Crude 2,4-hexadiene bromination mixtures were converted to glycol mixtures, which were subjected to reaction with periodic acid. The crotonaldehyde dibromides (diastereomers) were analyzed by vpc. Authentic crotonaldehyde dibromides were obtained by brominating commercial crotonaldehyde (mainly *E*). The principle diastereomer from the bromination of crotonaldehyde was assumed to be the erythro dibromide on the basis that trans addition would predominate. The crotonaldehyde dibromides formed from the 1,2-dibromides (*via* Scheme II) were shown to be identical with the authentic crotonaldehyde dibromides by vpc and ir. Good agreement was observed between analyses obtained *via* crotonaldehyde dibromides and direct vpc analyses of 2,4-hexadiene bromination mixtures. A check on this method of analysis was made by subjecting a (*Z*)-1,3-pentadiene bromination product to the reactions of Scheme II. Only a single crotonaldehyde dibromide isomer (threo) was obtained, which is in accord with our previous finding that bromine addition to the 3,4 bond in the 1,3-pentadienes is stereospecific.[3]

Discussion

The mechanism which we are suggesting to account for the different dibromide products in the polar bromination of conjugated dienes is shown in Scheme III. In this mechanism a bromine molecule attacks a particular double bond of the diene, yielding a bromonium ion–bromide ion[28] pair, **13a**. Both the 1,2 adduct and the 1,4 adduct then arise from the same intermediate. Cis 1,4 addition results when the anion of this pair effects essentially an SN2′ attack on carbon atom 4. It is possible that some reorientation of the ion pair (perhaps solvent separation) would be necessary before this attack could occur. Trans 1,4 addition could result if a *reorientation* of the initial ion pair occurred to give **13b**. This same reorientation of the ion pair would normally be required for 1,2 addition, unless bridging in the brominium ion were so weak that the rate of *rotation* about the C_1–C_2 bond competed with the rate of reorientation, and 1,2 addition occurred *via* **13c** (possible with acyclic dienes only). However, SN2′ attack (1,4 addition) by anion in **13c** would still result in cis 1,4 product.

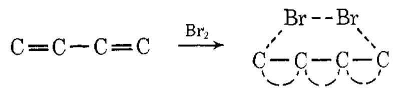
SCHEME III



The fact that 1,4 addition is predominantly a cis addition for all of the cases in Tables I and II would seem to be due to the fact that collapse of ion pair **13a** is apparently a facile process, which may result from the fact that the anion in **13a** is generated in close proximity to carbon atom 4. We observe that where the ratio of 1,4 to 1,2 addition is particularly large [cyclohexadiene and (*Z,Z*)-2,4-hexadiene in CCl_4 and CH_2Cl_2; all dienes in CH_2Cl_2] the stereospecificity of 1,4 addition is also high. On the other hand, where 1,4 addition occurs to a lesser extent (that is, 1,2 addition is relatively more rapid) then the amount of 1,4 addition which is trans increases. This is reasonable if we assumed that trans 1,4 addition is occurring *via* the same intermediate as trans 1,2 addition, namely **13b**.

The substantially lesser amount of cis 1,4 addition with cyclopentadiene can also be explained by this mechanism. Studies with models indicate that considerable steric interaction would be expected when ion pair **13a** from cyclopentadiene collapses to cis 1,4 product, particularly if the anion should be the tribromide ion. This steric interaction would be substantially less with the other dienes. The unusually high percentage of cis 1,4 addition observed with cyclohexadiene (96 and 98% in CCl_4 and CH_2Cl_2, respectively) may be due to the fact that the geometry is most favorable in this case, so that collapse of ion pair **13a** *via* cis SN2′ attack by anion can occur with a minimum of steric interaction between bromines and with a minimum of reorientation within the ion pair.

Other mechanisms for 1,4 addition could be considered. A "Diels–Alder"-type addition to the cisoid form of the diene was formerly proposed, but the possibility of this mechanism has been eliminated for acyclic dienes by the finding that the remaining double bond in the 1,4 adduct is always trans.[2–5] A concerted Diels–Alder-type mechanism, where fission of the Br–Br bond is synchronous with formation of bonds to the 1,4 carbon atoms, is still a possibility for cyclic dienes and could also occur with acyclic dienes provided that addition occurred to the transoid form of the diene. Such a mechanism is indicated as follows.



The data in Tables I and II provide evidence against such a concerted 1,4 addition mechanism or at least against the consideration of this as being the sole mechanism responsible for 1,4 addition. The most obvious fact revealed by our data is that the 1,4 addition is in all cases predominantly a cis

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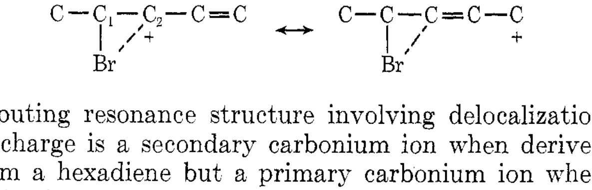
[28] We show the anion to be the bromide ion; however, from various kinetic studies,[29] it seems likely that our reaction conditions (addition of neat bromine) would lead to a mechanism in which more than one bromine molecule would be involved in the rate-determining step. Therefore, it is possible that the tribromide ion is the chief anionic species.

[29] For example, see J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1483 (1969).

process—*i.e.*, both bromine atoms are added to the same side of the molecule—but the degree of stereospecificity varies widely, meaning that either two mechanisms of 1,4 addition compete or the single mechanism which is occurring allows for both cis and trans 1,4 addition. If we look at the effect of structure of the diene, it is seen that 1,4 addition is most stereospecific (in the cis sense) with cyclohexadiene and least with cyclopentadiene. Examination of molecular models indicates that alignment of a bromine molecule for a concerted Diels–Alder-type addition should be nearly perfect for cyclopentadiene but that the alignment would not be as good for cyclohexadiene and would be still poorer for the 2,4-hexadienes. Since in comparable solvents, cyclopentadiene gives the lowest amount of cis 1,4 addition of any of the dienes, we feel that it is unlikely that a concerted mechanism contributes significantly. Further evidence against the concerted mechanism is that the amount of cis 1,4 addition (compared to trans 1,4 addition) tends for each diene to be low in the most nonpolar solvent, pentane. A concerted mechanism with little development of charged species ought to be favored (over competing ionic processes) in a nonpolar solvent.

An observation of considerable interest in this study has to do with the stereospecificity of 1,2 addition to the 2,4-hexadienes. Table II shows that the percentage of trans 1,2 addition varies between 91 and 69% depending upon diene and solvent. This result came as a considerable surprise, since in our studies on the 1,3-pentadienes[3] we found that addition to the 3,4 bond was stereospecific and we concluded on this basis that the intermediate in diene bromination (**13a**) should be viewed as a tightly bridged bromonium ion with little delocalization of charge into the vinyl group. The percentage of trans 1,2 addition which we observe here with the 2,4-hexadienes is very comparable to that observed by others[30] for the bromination of the 1-phenylpropenes in several solvents. The above workers did not observe significant difference in the degree of stereospecificity between the cis and trans olefin, an observation with which we concur in the present study (Table II).

The fact that 1,2 addition to the 2,4-hexadienes is not stereospecific is probably related to the slightly greater stabilization of intermediate **13a** in the hexadiene system over the same intermediate in the pentadiene system. As shown in the structures below, the contributing resonance structure involving delocalization of charge is a secondary carbonium ion when derived from a hexadiene but a primary carbonium ion when derived from a pentadiene. Our interpretation is that delocalization of charge away from carbon 2 (in the accompanying structures) weakens interaction between bromine and carbon 2 so that the rate of rotation about the 1,2 bond (**13a** → **13c**) becomes competitive with the rate of reorientation of the ion pair (**13a** → **13b**). We assume, as have previous workers,[30] that direct collapse of the initially formed ion pair, **13a**, to the cis 1,2 adduct does not occur because excessive steric interaction between the attached bromine and the bromide ion would occur.



A further interesting comparison can be made between the stereospecificity of 1,4 addition and that of 1,2 addition. With two exceptions—(*Z,Z*)-2,4-hexadiene in CH_2Cl_2 and CCl_4—the data in Table II show that the stereospecificity for trans 1,2 addition is higher than that for cis 1,4 addition. This observation is consistent with the mechanism proposed in Scheme III, and suggests that intermediate **13b** plays an important role in the reaction (along with **13a**) since involvement of **13b** would lead to a stereospecific 1,2 addition but would diminish the ratio of cis to trans 1,4 addition. On the other hand, intermediate **13c** does not seem to play a significant role, since the stereospecificity of 1,2 addition is higher than that of 1,4 addition; the opposite observation would be expected if the contribution of **13c** were substantial.

Conclusion

This paper provides conclusive data on the structures of products obtained from several important conjugated diene systems, thus opening the way for a variety of bromination studies. The 2,4-hexadienes have been identified as a system having particular appeal for studying the factors effecting 1,2 and 1,4 addition, since each of these processes may be evaluated simultaneously *via* stereochemical results. The fact that 1,4 addition to a variety of dienes was found to be nonstereospecific but largely cis points to the lack of intrinsic stereochemical control in the SN2′ displacement process, which we assume is operative here, and at the same time provides insight into the specific nature of the ion pair intermediates involved in these additions.

Experimental Section

General.—Melting points are uncorrected. Nuclear magnetic resonance spectra were obtained with Varian A-56/60, A-60, and HA-100 instruments. The 100-MHz spectrometer was based on three Hewlett-Packard 5100 Frequency Synthesizers. The frequency sweep was generated by a Barry Research LSC-7A Digital Programmer which drove one of the synthesizers. The decoupling modulation was supplied by a Hewlett-Packard 200 AB Oscillator. An Allison Labs Bond Rejection Filter Model 210R set at the decoupling audio modulation was inserted between the V-4311 unit and the V-4354 unit. In the decoupling experiments 4–16 spectra were accumulated in a Hewlett-Packard 5480 Averager which was triggered by the LSC-7A Digital Programmer. Unless otherwise stated, infrared spectra were obtained on a Beckman IR-10 spectrophotometer. Cyclohexadiene, (*E,Z*)-2,4-hexadiene (99%), and (*E,E*)-2,4-hexadiene (99%) were obtained from Aldrich Chemical Co. (*Z,Z*)-2,4-hexadiene (98%) was from Chemical Samples Co. Purities were confirmed by vpc. Cyclopentadiene was prepared from its dimer just prior to use.

Bromination Procedure.—Reactions were done in the dark at −15°. The diene concentrations were 0.02 mol fraction with respect to solvent.[31]

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(30) J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469 (1969); R. C. Fahey and H. J. Schneider, *ibid.*, **90**, 4429 (1968).

(31) In our previous studies on butadiene,[3] isoprene,[3] and the piperylenes,[3] we concluded that only a polar bromination mechanism occurred under these conditions. The known radical inhibitors, oxygen (all three dienes) and 2,6-di-*tert*-butyl-4-methylphenol (2,4-hexadiene and cyclopentadiene), were found to have no effect on product compositions in the present study.

Bromine was added neat from a small capillary dropper to well-stirred solutions. Reactions were carried to 20–25% of completion. Yields of dibromide products were found to be between 90 and 100% based on direct isolation of products (cyclohexadiene, 2,4-hexadienes) or use of vpc internal standards (cyclopentadiene).

Analysis of Cyclopentadiene and Hexadiene Dibromides.—Vpc analyses of the dibromides from cyclopentadiene and the 2,4-hexadienes were done on a Hewlett-Packard 7620A hydrogen flame chromatograph. Analysis conditions are (2,4-hexadiene dibromides): 6 ft × 0.25 in. SS, 2.5% SE-30 on 60–80 mesh Chromosorb W (AW-DMCS), 40°, 125 ml/min (N_2). Retention times under these conditions for **7**, **8**, **9**, **10**, **11**, and **12** are 17.0, 19.6, 17.8, 19.7, 23.2, and 25.8 min, respectively. Analysis conditions for the cyclopentadiene dibromides follow: 6 ft × 0.125 in. SS, 2.5% SE-30 on 80–100 mesh Chromosorb W (AW-DMCS), 55°, 55 ml/min (N_2). Retention times under these conditions for **1**, **2**, and **3** are 4.4, 5.4, and 8.0 min, respectively.

Reaction mixtures were analyzed directly without work-up.[32] Direct on-column injection of samples was generally employed. In the case of the cyclopentadiene dibromides the area/weight ratios for each dibromide were found to be identical. Because of their very similar structures, **11** and **12** would be expected to have similar area/weight ratios. Owing to the limited amounts of the 1,2-dibromides (also they were contaminated with some **11** and **12**) the area/weight ratios of the 1,2-dibromides with respect to **11** and **12** were not determined.

The cyclopentadiene dibromide mixtures were also analyzed by nmr and found to give results consistent with those obtained by vpc.

Analyses of the Cyclohexadiene Dibromides.—Attempts to analyze **4**, **5**, and **6** by vpc were unsuccessful since extensive rearrangement of the isomers occurred under all conditions. [Numerous liquid phases, column lengths (copper and steel) and temperatures were examined.]

The dibromide mixtures were analyzed by quantitative ir analysis using the following noninterfering absorption bands: **4** (590 cm^{-1}), **5** (1080 cm^{-1}), and **6** (980 cm^{-1}). Standard curves were prepared by plotting the ratio of **4**:**6** (and **5**:**6**) against a ratio of their respective absorbancies (at the wavenumbers mentioned above). **5** and **6** were obtained without traces of the other isomers. **4** contained traces of **5** and **6**. Solvent was removed from the bromination mixtures *in vacuo* without heat. It was established that no rearrangement occurred or dibromides were lost during this operation. The analyses were carried out using a Perkin-Elmer 337 grating spectrophotometer, KBr cells (0.05 mm), and CCl_4 as the solvent. At least two brominations were run for each set of reaction conditions. Most of the duplicate runs gave results which were within 1–2% of each other; none showed more than 4% difference.

meso- **and** *dl-***2,5-Dibromo-(*E*)-3-hexene (11 and 12).**—**11** was prepared in the following manner. The solvent was removed *in vacuo* from the product of bromination of (*E*,*Z*)-2,4-hexadiene. The residue was dissolved in pentane and fractionally recrystallized twice at Dry Ice temperatures to give **11** (98% pure by vpc): mp 35–37°; ir (CCl_4) trans CH=CH, 960 cm^{-1}; nmr (CCl_4) δ 1.84 (d, 6, CH_3), 4.68 (m, 2, CHBr), 6.03 (d d, 2, CH=CH). A similar recrystallization of the bromination product from the *E*,*E* isomer gave **12** (98% pure by vpc): a liquid; ir (CCl_4) trans CH=CH, 960 cm^{-1}; nmr (CCl_4) δ 1.84 (d, 6, CH_3), 4.68 (m, 2, CHBr), 6.06 (d d, 2, CH=CH). Both **11** and **12** rearranged when heated in sealed tubes for several days at 80° to identical mixtures of dibromides.

Assignments of stereochemical structures to **11** and **12** were based on the reactions described in Scheme I above. Dibromides **11** and **12** were converted to glycols by reaction with permanganate in aqueous ethanol at −30° according to the procedure of Winstein.[10a] For example, 2 g of **11** yielded 2 g of crude product which melted at 103.5–105° after washing with pentane. The product from **12** melted at 90–92° after similar treatment. Both products showed strong ir absorption at 3400 cm^{-1} (KBr disk).

Conversion of the glycols from **11** and **12** to diepoxides was accomplished as follows. For example, 1.0 g of the glycol from **11** was stirred with 9.3 ml of 0.77 *M* NaOH for a few minutes at 0°. Titration of an aliquot showed that 2 equiv of base was consumed. The diepoxide was isolated by repeated ether extraction. After distillation of ether, the residue was distilled, yielding 0.3 ml, bp 80–82° (30 mm) [reported for a mixture of hexadiene diepoxides,[33] 175–177° (760 mm)]. The diepoxide from **12** was obtained in similar quantity with similar boiling point.

Vpc analysis (DEGS, 8 ft × 0.25 in., 60°) of the diepoxide from **11** showed a single peak (retention time 11.5 min) identical in ir spectrum and retention time with the minor diepoxide obtained by reaction of (*E*,*Z*)-2,4-hexadiene with peroxy acid.[34] The diepoxide from **12** showed two peaks, A and B, in its vpc in a ratio (A:B) of 0.13, retention times 9.7 and 12.1 min, respectively. Diepoxides A and B were isolated and found to be identical (retention times and ir) with the minor diepoxides obtained from (*E*,*E*)- and (*Z*,*Z*)-2,4-hexadiene (and peroxy acid), respectively.

4,5-Dibromo-2-hexenes (7, 8, 9, and 10).—The 1,2-dibromides were isolated by preparative vpc. The compounds collected from a (*Z*,*Z*)-2,4-hexadiene bromination product were identified as a mixture of **7** and **8** by the ir spectra: cis CH=CH (CS_2), 740 cm^{-1} (strong). Similarly, the collected compounds from the (*E*,*E*)-2,4-hexadiene bromination product were identified as **9** and **10** by the ir spectra: trans CH=CH (CS_2), 960 cm^{-1} (strong). Also, each of the collected 1,2-dibromides rearranged upon heating in CCl_4 at 80° to give the identical equilibrium mixtures of **7**, **8**, **9**, **10**, **11**, and **12** as were formed on equilibration of **11** and **12** under identical conditions.

Further proof for the structures of the 1,2-dibromides was obtained by converting them to known crotonaldehyde dibromides as outlined in Scheme II above. For example, 3.20 g of the crude dibromide mixture [from bromination of (*Z*,*Z*)-2,4 hexadiene] was oxidized to a glycol mixture as described for **11** and **12** above. The glycol was isolated, it was dissolved in 25 ml of water and 15 ml of alcohol, a solution of 3.5 g of periodic acid in 10 ml of water was added, and the mixture was stirred at 25° for 30 min. The crotonaldehyde dibromides were extracted from the reaction mixture with ether and isolated by preparative vpc [6 ft × 0.25 in., 2.5% SE-30 on 60/80 mesh Chromosorb W (AW-DMCS), 42°, 125 ml/min (N_2)]. The crotonaldehydes obtained from dibromide mixtures and authentic crotonaldehyde dibromides were found to have identical retention times (erythro, 12.6 and threo, 14.0 min) and ir spectra: (CCl_4) HC=O, 2820 and 2720 cm^{-1}, and C=O, 1740 cm^{-1}. The authentic crotonaldehyde dibromides were prepared by bromination of commercial crotonaldehyde and were obtained, bp 95–97° (30 mm) [lit.[35] by 75–82° (14 mm)], in a ratio of 6:1 (erythro:threo).

Cyclopentadiene Dibromides (1, 2, and 3).—Winstein, *et al.*,[10a] have previously identified **1**, **2**, and **3** as products in the bromination of cyclopentadiene. Samples of **1** (5% **2**) and **3** (99%) were obtained using essentially the procedure of Winstein, *et al.* A mixture of **1** and **2** containing 70% **2** was obtained. Nmr measurements at 60 MHz in CCl_4 gave the following: **1**, 2.72 [dd, 1, cis CBrC(**H**)H, J = 20.3 Hz, other fine coupling], 3.31 [dd, 1, trans CBrC(**H**)H, J = 20.3, J' = 5.4 Hz, other fine coupling], 4.72 (d, 1, CH_2C**H**Br, J = 5.4 Hz, other fine coupling), 5.22 (s, 1, CH=CHC**H**Br, fine coupling), 6.05 (s, 2, C**H**=C**H**, fine coupling); **2**, 2.96 (t, 2, CH_2, J = 5 5 Hz), 5.12 [d t, 1, CBr(H), J = 5.5, J' = 1.1 Hz], 6.12 (d, 2, C**H**=C**H**, J = 1.1 Hz); **3**, 2.62 [d t, 1, cis CBrC(**H**)H, J = 17.4, J' = 2.2 Hz], 3.09 [d t, 1, trans CBrC(**H**)H, J = 17.4, J' = 6.6 Hz], 5.01 [d of dd, C(H)-Br, 2, J = 6.6, J' = 2.2, J'' = 1.5 Hz], 6.06 (d, 2, C**H**=C**H**, J = 1.5 Hz).

Cyclohexadiene Dibromides (4, 5, and 6).—These dibromides were prepared essentially as described previously.[10b] The liquid

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[32] Control experiments were performed to show that rearrangement of isomers did not occur under conditions of bromination. Cyclopentadiene was brominated in the presence of pure **11** and also in the presence of a hexadiene dibromide mixture; (*E*,*Z*)-2,4-hexadiene was brominated with pure **3** added. No rearrangement of the above added dibromides was detected in these experiments. The absence of rearrangement during vpc analyses is established as follows. (a) Single vpc peaks were obtained from purified isomers, showing no injection port rearrangement. (b) Samples collected from the vpc showed the same composition after reinjection, demonstrating absence of injection-port and column rearrangement. The routine observation of a sharply returning base line between well-separated peaks of isomers also rules out on-column rearrangement.

[33] J. L. Everett and G. A. R. Kon, *J. Chem. Soc.*, 3131 (1950).

[34] The 2,4-hexadienes were converted to diepoxides by reaction for 3 days at 0° with excess *m*-chloroperoxybenzoic acid in chloroform. Each diene yielded two diepoxides in about 2:1 ratio. Each of the six diastereoisomeric diepoxides was isolated in pure form and an ir and nmr spectrum was obtained for each compound. The isomers are readily distinguished by their spectra. A paper is in preparation which will report the details *of this study.*

[35] P. L. Viguir, *C. R. Acad. Sci.*, **150**, 1431 (1910).

dibromide was isolated by removing through fractional recrystallization (of a bromination product) at Dry Ice temperature (*n*-pentane) as much of the solid 3,6 isomers as possible and then flash distilling [bp 40° (0.07 mm)] a small amount of the liquid. Only a very small amount of the pure isomer (nearly free of the 3,6 isomers) could be isolated with each distillation. The liquid (pure) was found to be extremely labile and rearranged to the 3,6 isomers.

The liquid dibromide was assigned the trans 3,4 structure (**4**) on the following basis: its boiling point was essentially identical with those of the 3,6 isomers; its melting point was much lower than those of the 3,6 isomers, which suggests lower molecular symmetry; the C–H absorption bands in the ir spectrum were very similar to those of the 3,6 isomers; and it (**4**) rearranged on standing in CCl_4 to give **5** and **6**. [The liquid isomer (**4**), **5**, and **6** all rearranged to identical equilibrium mixtures.] Also, nmr spectra of mixtures containing **4** did not show any signals inconsistent with its structure. Unfortunately, signals attributable to it were masked by the overlapping signals from the other two isomers, even at 220 MHz. Nmr spectra of both pure solid dibromides were recorded in CCl_4 at 60, 100 (see Figure 1), and 220 MHz: **5**, 4.304 (complex multiplet, 2, $-CH_2CH_2-$protons), 4.8268 (complex multiplet, 1, $-CHBr-$), 5.942 (broad d, $J = 3$ Hz, 1, $-CH{=}CH-$); **6**, 2.224 (complex multiplet, 1, $-CH_2CH_2-$protons), 4.700 (complex multiplet, 1, $-CHBr-$), 5.906 (sharp d, $J = 1.7$ Hz, 1, $-CH{=}CH-$). The infrared spectra (CCl_4) of **4**, **5**, and **6** all showed a fairly similar C–H stretching region (3150–2850 cm^{-1}) and additional strong–medium absorptions as follows: **4**, 1435, 1440, 1280, 1210, 1222, 1145, 1018, 922, 730, 655, 590, 545 cm^{-1}; **5**, 1440, 1400, 1201, 1080, 995, 565 cm^{-1}; **6**, 1450, 1440, 1350, 1301, 1214, 1165, 1175, 1130, 1068, 980, 887, 730, 668 cm^{-1}.

Equilibration Studies.—The equilibrium mixtures shown in Table III were obtained in every case by approaching the equilibrium position from more than one direction; *e.g.*, pure samples of two of the three cyclohexadiene dibromides (**5** and **6**) and nearly pure samples of **4** in carbon tetrachloride were allowed to stand at room temperature until each showed the same composition of dibromides (about 3 months). Equilibration times at room temperature for the other dibromides follow: cyclopentadiene dibromides, 1–2 months; 2,4-hexadiene dibromides, 75% complete in 3 months (CCl_4); bromination mixtures (in CH_3NO_2) from (*E*,*Z*)- and (*E*,*E*)-2,4-hexadiene, 1.5 months. Heating at 78–80° caused equilibration of all of the dibromides within 1–2 weeks.

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Registry No.—**1**, 42086-50-0; **2**, 42086-51-1; **3**, 17040-70-9; **4**, 42086-52-2; **5**, 42086-53-3; **6**, 42086-54-4; **7**, 42086-55-5; **8**, 42086-56-6; **9**, 42086-57-7; **10**, 42086-58-8; **11**, 42086-59-9; **12**, 42086-60-2; 1,3-cyclohexadiene, 592-57-4; cyclopentadiene, 542-92-7; (*Z*,*Z*)-2,4-hexadiene, 6108-61-8; (*E*,*Z*)-2,4-hexadiene, 5194-50-3; (*E*,*E*)-2,4-hexadiene, 5194-51-4.

Study of a Cope-Related System. *trans,trans*-1,5-Cyclodecadiene and *trans*-1,2-Divinylcyclohexane[1,2]

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Rate constants were determined for the forward and reverse rearrangements of the Cope-related pair, *trans*,-*trans*-1,5-cyclodecadiene (**3**) and *trans*-1,2-divinylcyclohexane (**4**). The rate of **4** → **3** was determined from the rate of racemization of (+)-**4** (the two rate constants are identical), an indirect approach necessitated by the large equilibrium constant favoring **4**; the ratio of forward and reverse rate constants yielded $K_{200°} = 2 \times 10^4$ with $\Delta G_{200°} = 9.4$ kcal mol^{-1}. The individual rate constants yielded $E_a = 25.0$ and 31.6 kcal mol^{-1} for **3** → **4** and **4** → **3**, respectively. The ring strain of **3** is estimated to be 12 kcal mol^{-1} relative to **4**.

trans,trans-1,5-Cyclodecadienes and *trans*-1,2-divinylcyclohexanes are formally interconvertible *via* the Cope rearrangement, and several such related pairs are now known as a result of the isolation of many sesquiterpene cyclodecadienes. In some instances there is an observable equilibrium, *e.g.*, **1**–**2**, as a result of differential effects of methyl substitution of the double bonds and the presence of a trans-fused lactone[3] which offset the strain of the cyclodecadiene. For the unsubstituted pair **3**–**4** there is insufficient counterbalancing of the high energy of the medium ring and the conversion to **4** is virtually complete. It is nevertheless still possible to explore the relationship from both sides. The rate constant k_1 for the forward Cope rearrangement can be measured directly; and the rate constant k_{-1} for the reverse Cope rearrangement can be obtained from the rate of racemization of optically active **4**, which involves Cope rearrangement to an optically active conformation of **3**, racemization of the cyclodecadiene (a relatively rapid process[4]), and reversion of the Cope rearrangement.[5] For this relationship $k_{obsd} = k_{rac} = k_{-1}$. The present paper reports on the determination of these rate constants and related thermodynamic parameters.

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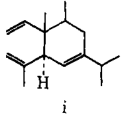
(1) The investigation was supported by Public Health Service Research Grants GM 14133 and 16338 from the Division of General Medical Sciences, U. S. Public Health Service.

(2) The article is abstracted from the Ph.D. Thesis of D. W. J., University of Wisconsin, 1970. The last year of research was carried out at Wesleyan University.

(3) T. C. Jain, C. M. Banks, and J. E. McCloskey, *Tetrahedron Lett.*, 841 (1970).

(4) For 1,5-dimethyl-*trans,trans*-1,5-cyclodecadiene, interconversion of enantiomeric conformations has been shown to be fast on the nmr time scale between temperatures of 40 and 90°. It is therefore not possible for the energy of activation for interconversion of enantiomeric conformations of **3** to be rate determining. See ref 6.

(5) This sequence corresponds to the interconversion at 200° of δ- and epi-δ-elemenol (i and ii) reported by K. Morikawa and Y. Hirose, *Tetrahedron Lett.*, 869 (1969).



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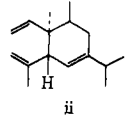

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