4.2–4.9 (0.8 H), a multiplet at 5.3–5.5 (1 H), and a multiplet at 5.7–6.0 ppm (1.2 H). This material was reinjected under conditions identical with those above and collected. The nmr of the collected material, which glpc[7] showed to consist of *ca.* 80 and 20% A and B, respectively,[16] was identical and superimposable with the one described above.

Irradiation of 2-Methylene-3,7,7-trimethyl-3,5-cycloheptadiene (8) and (8-d_2).—A solution of 200 mg of **8** in 3 ml of benzene was irradiated in a Pyrex tube for 9 hr. Gas chromatography[5] showed 95% **15** and 5% **8** as determined from relative peak areas. The new product was collected. The nmr spectrum of **15** showed two singlets at 0.58 and 0.74 (6 H, *gem*-dimethyl), a singlet at 1.08 (3 H, bridgehead CH_3), two one-hydrogen doublets at 1.64 and 2.44 (J = 15 Hz, $=CH_2$), a singlet at 2.18 (1 H, bridgehead H), a two-hydrogen absorption at 4.50–4.60 consisting of two peaks, and a two-hydrogen doublet of doublets at 5.72 and 5.84 ppm (J = 2.5 Hz, cyclobutenyl hydrogens). The uv spectrum of **15** showed only end absorption [210 mμ (ϵ 2476)]. The ir spectrum[18] of **15** showed a weak band at 1645 and a strong band at 885 cm^{-1} ($=CH_2$). *Anal.* Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.28; H, 10.82.

A solution of 350 mg of **8**-d_1 in 5 ml of benzene was irradiated for 14 hr. Analysis[5] showed 55% **15**-d_1 and 45% **8**-d_1. The mixture was concentrated and a sample of **15**-d_1 was collected. The nmr spectrum of **15**-d_1 showed loss of the doublets at 1.64 and 2.44 ppm. The absorption at 4.50–4.60 ppm had collapsed to a singlet. The remainder of the spectrum is unchanged.

Reduction of 9.—A solution of 172 mg (1.165 mmol) of **9** in 5 ml of carbon tetrachloride containing the catalyst from 40 mg of platinum oxide was permitted to absorb 0.9 equiv of hydrogen. The reaction mixture was filtered and concentrated. Gas chromatography[15] showed one major component (*ca.* 95%) which was collected. The 100-Mc nmr spectrum of this material showed singlets at 0.58 and 0.82 (*gem*-dimethyl), absorption at 1.0–1.5, and singlets at 2.65 and 3.10 ppm (bridgehead hydrogens). The cyclopentenyl absorption at 5.0–5.4 ppm had disappeared. Mass spectrum (80 eV) showed m/e (rel intensity) 150 (15), 135 (80), 122 (38), 107 (100), etc.

Reduction of 10.—A solution of 38 mg (0.27 mmol) of **10** in 1 ml of carbon tetrachloride containing the catalyst from 10 mg of platinum oxide was permitted to absorb 1.1 equiv of hydrogen. The reaction mixture was filtered and concentrated. Gas chromatography[15] showed one major component (*ca.* 85%) which was collected. The nmr spectrum of this material showed loss of the cyclobutenyl hydrogen absorption. The allylic hydrogen could not be distinguished. Mass spectrum (80 eV) showed m/e (rel intensity) 150 (11), 135 (24), 122 (100), 107 (78), etc.

Reduction of 11.—A solution of 65 mg (0.44 mmol) of **11** in 1 ml of carbon tetrachloride containing the catalyst from 30 mg of platinum oxide was permitted to absorb 0.9 equiv of hydrogen. The mixture was filtered and concentrated. Gas chromatography[15] showed one major compound (*ca.* 95%) which was collected. The nmr spectrum of this material showed loss of the cyclobutenyl hydrogen absorption. The allylic hydrogen could not be distinguished, and the spectrum was very similar to that of reduced **10**. Mass spectrum (80 eV) showed m/e (rel intensity) 150 (13), 135 (25), 122 (100), 107 (77), etc.

Registry No.—**7**, 19566-41-7; **8**, 19566-42-8; **9**, 19566-43-9; **10**, 19566-44-0; **11**, 19566-45-1; **13**, 19566-47-3; **15**, 19566-48-4.

Acknowledgment.—The authors are grateful to the National Aeronautics and Space Administration for an institutional grant which was used in part to support this work.

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[18] Determined as a solution in carbon tetrachloride.

Stereochemistry of Radical Additions of Bromotrichloromethane to Some Cyclic Olefins[1]

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In order to assess the importance of some factors which may influence the stereochemistry of additions of reagents which are sources of carbon radicals to alkenes, we have investigated the photoinitiated additions of bromotrichloromethane to several cycloalkenes. Nmr data have been used to assign stereochemistry to the 1-bromo-2-trichloromethylcycloalkane adducts. Like cyclooctene,[2] cyclohexene affords a mixture of *cis* and *trans* adducts. *trans*-1,4,5,6,7,8,9,10-Octahydronaphthalene, cyclopentene, indene, and norbornene yield only *trans* adducts, and cycloheptene only the *cis* adduct. The over-all stereochemical results are most readily rationalized in terms of addition of both portions of the addend (in separate steps) from an axial-like direction. Abstraction of Br from $BrCCl_3$ by the intermediate 2-trichloromethylcycloalkyl radical may occur before or after ring flipping in flexible systems, but it does not occur to form product with eclipsed Br and CCl_3 substituents.

Recent investigation of the photoinitiated addition of bromotrichloromethane to *cis*-cyclooctene demonstrated that the 1,2-addition product consists of a 1:1 mixture of *cis*- and *trans*-1-bromo-2-trichloromethylcyclooctane.[2,3] While a mixture of geometrical isomers was expected for this radical addition reaction, the 1:1 proportion obtained was surprising. Both highly stereoselective and nonselective radical additions of hydrogen bromide, halogens, thiols, and hydrogen sulfide have been reported.[4] Reaction conditions, identity of substituents on the alkene linkage, and steric factors have been found to affect significantly the stereoselectivity of these additions.[4] Few data are available however, on the stereochemistry of additions of carbon tetrahalide (or of other reagents which are sources of carbon radicals) to alkenes.[5] Therefore, in order to assess the importance of some factors which may influence the stereochemistry of such additions, we have

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[1] (a) We gratefully acknowledge partial support of this research by a grant from the National Science Foundation (Grant No. GP 5749). (b) Presented in part at the Southwest Regional Meeting of the American Chemical Society, Little Rock, Ark., Dec 1967, paper 170.

[2] J. G. Traynham, T. M. Couvillon, and N. S. Bhacca, *J. Org. Chem.*, **32**, 529 (1967). Although the addition product appeared to be a single component by gas chromatographic (gc) analysis, nuclear magnetic resonance (nmr) data clearly established it to be a mixture.

[3] The 1,2-addition product formed in minor amounts (3%) from addition of carbon tetrachloride to *cis*-cyclooctene was likewise shown to be a 1:1 mixture of *cis* and *trans* isomers: J. G. Traynham and T. M. Couvillon, *J. Amer. Chem. Soc.*, **89**, 3205 (1967).

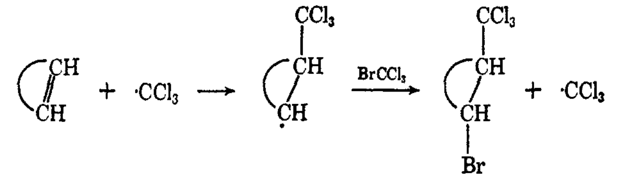
[4] For brief reviews, with references, see (a) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 206–218; (b) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962).

[5] (a) E. S. Fawcett, *ibid.*, **47**, 219 (1950). (b) E. Tobler and D. J. Foster, *J. Org. Chem.*, **29**, 2839 (1964). (c) J. Weinstock (Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept 1955, p 19-20) reported that radical addition of $BrCH_2COOEt$ to norbornene appeared to give the *exo-cis* product. (d) NOTE ADDED IN PROOF.—L. H. Gale [*J. Org. Chem.*, **34**, 81 (1969)] has reported radical additions of $BrCCl_3$ to cycloalkenes (ring sizes 5–8, γ radiation). He reports single adducts with cyclopentene and cycloheptene but does not identify them as *cis* or *trans* isomers. He does report *cis* and *trans* adducts with cyclohexene.

cis-1-Bromo-2-trichloromethylcyclohexane	$J_{xa} + J_{xb} = 7.8$; $J_{mx} = 2.2$; $J_{mc} = 3.3$; $J_{md} = 10.5$
trans-1-Bromo-2-trichloromethylcyclohexane	$J_{xa} = 5.5$; $J_{xb} = 3.5$; $J_{mx} = 4.0$; $J_{mc} = 6.0$; $J_{md} = 6.0$
trans 2	$J_{xa} + J_{xb} + J_{mx} \simeq 10$; $J_{md} = 6.0$; $J_{mx} + J_{mc} \simeq 5$
cis-1-Bromo-2-trichloromethylcycloheptane	$J_{mx} = 3.0$; $J_{ma} = 11.0$; $J_{mb} = 3.0$
trans-1-Bromo-2-trichloromethylcyclopentane	$J_{xa} = 3.0$; $J_{xb} = 6.0$; $J_{mx} = 3.0$; $J_{mc} = 8.0$; $J_{md} = 8.0$
trans-1-Bromo-2-trichloromethylindane	$J_{mx} = 3.2$; $J_{mc} = 8.8$; $J_{md} = 5.0$; $J_{cd} \simeq 18$
trans-2-*endo*-Bromo-3-trichloromethylnorbornane	$J_{2ex,3en} = 6.0$; $J_{2,ex1} = 4.0$; $J_{2ex,6ex} = 1.5$; $J_{3en,4} = 0.0$; $J_{3en,7a} = 1.7$; $J_{7a,1} = 1.3$; $J_{7a,4} = 1.3$; $J_{7a,7s} = 11.0$

Figure 1.—Summary of vicinal coupling constants (in hertz). The subscripts designate hydrogens according to the following key: H_x is HCBr, H_m is $HCCCl_3$, H_a and H_b are geminal hydrogens vicinal to CCl_3; H_c and H_d are geminal hydrogens vicinal to Br; *ex*, *en*, *s*, and *a* refer to *exo*, *endo*, *syn*, and *anti* hydrogens, respectively.

extended this study to include other cycloalkenes and bicycloalkenes, chosen to reveal the influence of steric effects and relative ease of ring flipping in different ring systems. The over-all stereochemical results are most readily rationalized in terms of addition of both portions of the addend (in separate steps) from an axial-like direction. After initial addition of $\cdot CCl_3$ to the cycloalkene, the second step (abstraction of Br from $BrCCl_3$ by the substituted cycloalkyl radical) may occur before or after ring flipping in flexible systems, but it does not occur to form product with eclipsed Br and CCl_3 substituents.

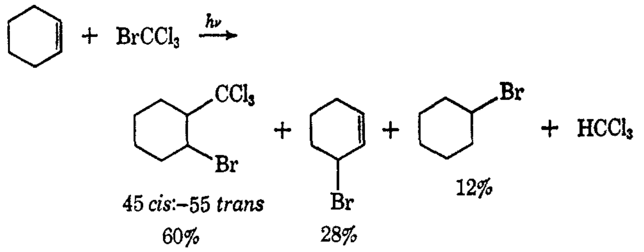


Each addition was carried out under an atmosphere of nitrogen by irradiating a deoxygenated mixture of cycloalkene and $BrCCl_3$ (1:2 or 1:4 molar ratio) with 3500-Å light for a few hours.[2] Nmr spectra periodically obtained on small samples of the mixture were used to estimate the progress of the reaction. After irradiation, excess $BrCCl_3$ was removed, and nmr spectra (60, 100, and 220 MHz) of the 1,2-addition product(s) were recorded. These spectra clearly revealed whether the 1,2-addition product consisted of a single compound or was a mixture of geometrical isomers.[2] The stereochemistry of individual 1,2-addition products was assigned by comparing the relative magnitude of the experimental coupling constants with that expected from application of the Karplus relation[6] to molecular models of the isomeric products.

Results

Cyclohexene.—Additions of $BrCCl_3$ to cyclohexene have been described previously.[5d,7] Although monosubstituted cyclohexane derivatives were reported to be among the products, no hint is given in these papers[7] that the 1,2 adduct was regarded as anything other than a single isomer. Dehydrohalogenation rate data[7a,b] and acid hydrolysis[7c] were used to identify the adduct as the *trans* isomer.

Our addition product from photoinitiated addition of $BrCCl_3$ to cyclohexene possessed the same physical properties as those previously reported for 1-bromo-2-trichloromethylcyclohexane.[7] Its nmr spectrum, however, is quite similar to that of the 1,2-adduct mixture obtained from cyclooctene.[2] Decoupling and selective dehydrohalogenation[2] experiments were used to establish that this product is also a mixture and consists of *cis*- and *trans*-1-bromo-2-trichloromethylcyclohexane (45:55).[8] The nmr spectrum includes four multiplet signals downfield from −2.55 ppm, each of which has an area equivalent to approximately $^1/_{20}$ of the total area of the spectrum. (The adduct has ten protons per molecule.) In accord with our study of cyclooctene adducts,[2] we assign the more upfield pair of these signals (M) to $HCCCl_3$ and the more downfield pair (X) to HCBr. The decoupled spectra not only revealed that the outer pair of these four signals (X_c and M_c) are coupled, as are the inner pair (X_t and M_t), but also afforded the coupling constants which we used to assign *cis* and *trans* labels to the isomeric components of the mixture. The single large J_{vic} (J_{md} = 10.5 Hz) for one isomer, and the lack of a $J_{vic} > 6$ Hz for the other isomer, together with the relative magnitude of the other coupling constants (Figure 1), permit us to assign the signals X_c and M_c to the *cis* isomer and the signals X_t and M_t to the *trans* isomer. While the coupling constants are consistent with a chair conformation for the *cis* isomer (with the bulky CCl_3 substituent equatorial), they are not consistent with a chair conformation with both substituents equatorial for the *trans* isomer (J_{ax}, J_{md}, each expected to be *ca.* 10–11 Hz). These coupling constants require that the *trans* isomer exist either in the sterically unfavorable chair conformation with both substituents axial or in a twist (flexible) form.[9]



Electrical repulsions between the *trans* (diequatorial) Br and CCl_3 substituents, and unfavorable axial substituent–axial H interactions, are relieved by the change

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(6) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963). Most of our applications were qualitative rather than quantitative; that is, we examined models to see if the probable dihedral angle led one to expect a "large" or a "small" vicinal coupling constant.

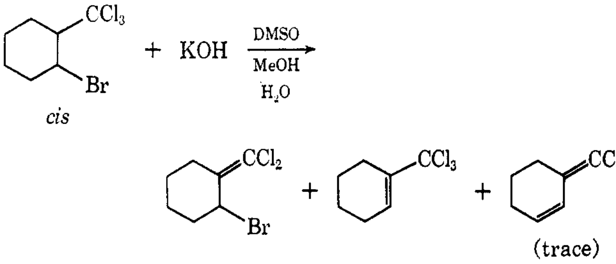
(7) (a) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949). (b) M. S. Kharasch and M. Sage, *ibid.*, **14**, 537 (1949) (these authors used ultraviolet irradiation). (c) E. I. Heiba and L. C. Anderson, *J. Amer. Chem. Soc.*, **79**, 4940 (1957) (these authors used γ radiation). While this reference reports the hydrolysis of the addition product to the previously known *trans*-2-bromocyclohexanecarboxylic acid, the authors do not ever label the addition product *trans*, and they mildly disfavor the *trans* label earlier in the paper.

(8) This mixture is apparently that formed by kinetic control, for, in a separate experiment (by Dr. F. Schweinsberg), a sample of *cis*- and *trans*-1-bromo-2-trichloromethylcyclohexane (approximately 28:72) in $BrCCl_3$ did not change composition when irradiated under the addition reaction conditions for 22 hr.

(9) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, pp 36–42.

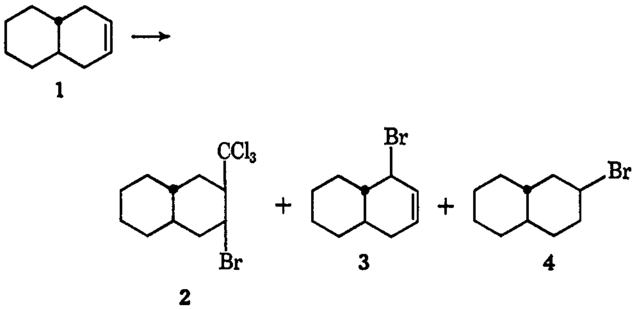
from chair to twist conformation, but the repulsions are probably increased by the similar change for the *cis* isomer. The only monocyclic cyclohexanes known to exist largely in the flexible form have a *t*-butyl substituent which would have to be axial if the chair form were used.[9] Although the conformation energy of the trichloromethyl substituent apparently has not been estimated,[10a] it is probably at least as large as that of *t*-butyl.[10b] We favor the twist (flexible) conformation, rather than the diaxial chair, for *trans*-1-bromo-2-trichloromethylcyclohexane.[10c]

In experiments paralleling those with the mixed 1,2 adducts obtained from cyclooctene,[2] treatment of the mixture of *cis*- and *trans*-1-bromo-2-trichloromethylcyclohexane with 0.5 molar equiv of base under essentially E2 conditions led to the selective dehydrohalogenation of the *cis* isomer and the subsequent isolation of pure *trans* isomer.[11,12] The dehydrohalogenation products were analyzed and characterized by use of gc, infrared (ir), and nmr data. The *cis* isomer was partially separated from the *trans* isomer by repeated fractional distillation at reduced pressure.



In addition to the mixture of *cis* and *trans* addition products, reaction of $BrCCl_3$ with cyclohexene produced substantial amounts of products arising from hydrogen abstraction processes,[7c] namely, 3-bromo-1-cyclohexene (28%) and chloroform in approximately equimolar amounts during the progress of the reaction. The product mixture also contained another product, tentatively identified by nmr data as bromocyclohexane (12%), and whose origin is, at best, speculative.[13]

trans-1,4,5,6,7,8,9,10,-Octahydronaphthalene (1).[14]—When a mixture of bromotrichloromethane and 1 was irradiated with 3500-Å light for 4 hr, 84% of the olefin was converted into a product mixture which consisted of $BrCCl_3$ addition product (2, 50%), allylic bromide (3, 20%), and HBr addition product (4, 30%).[13] Products 3 and 4 depend upon allylic hydrogen abstraction from 1; their formation is competitive with but otherwise not related to the addition of $BrCCl_3$ to 1.



The 60-, 100-, and 220-MHz nmr spectra of 2, which included a single, narrow multiplet for HCBr (H_x) and a broad doublet for $HCCCl_3$ (H_m), revealed that this $BrCCl_3$ addition product was a single isomer. There are four possible geometrical isomers for this 2,3-disubstituted *trans*-decalin: two *trans* (both substituents axial or both equatorial) and two *cis* (one substituent axial, one equatorial). Figure 1 summarizes the coupling constants from the nmr spectrum of 2. The magnitudes of these coupling constants are correct for the *trans*, diaxial isomer, but they are too small for any of the other possible isomers. If either or both of the substituents were equatorial, at least one coupling constant would be expected to be about 10 Hz.[15] (See earlier discussion about cyclohexene adduct.)

Cycloheptene.—Irradiation of a mixture of cycloheptene and $BrCCl_3$ for 16 hr led to an 81% yield of products consisting of the adduct, 1-bromo-2-trichloromethylcycloheptane (32%), and hydrogen-abstraction products (3-bromo-1-cycloheptene, 40%, and trichloromethylcycloheptane, 28%).[16] The nmr spectra of the adduct demonstrated that it was a single isomer; in contrast to the spectra for the cyclooctene and cyclohexene adducts, only single multiplet absorptions were recorded for HCBr (H_x) and $HCCCl_3$ (H_m). The coupling constants obtained by decoupling experiments are summarized in Figure 1. On the basis of molecular models and the probable conformation of a vicinally substituted

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(10) (a) J. A. Hirsch in "Tropics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967, pp 199–222. (b) E_s values: *t*-Bu, −1.54, and CCl_3, −2.06 (R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 598). (c) Professor M. Hanack, University of Tübingen, has informed us, by private communication, that *trans*-1,2-di-*t*-butylcyclohexane exists in the diequatorial conformation. The twist conformation for *trans*-1-bromo-2-trichloromethylcyclohexane must be favored by electrical repulsions in the diequatorial conformer rather than by steric repulsions.

(11) The nmr spectrum of the recovered 1-bromo-2-trichloromethylcyclohexane included absorptions X_t and M_t of the original spectrum but not X_c and M_c. Treatment of this isomer with more base, under the same mild conditions which led to dehydrohalogenation of the other isomer, failed to bring about any dehydrohalogenation.

(12) Dehydrohalogenations of 1-bromo-2-trichloromethylcyclohexane (from cyclohexene + $BrCCl_3$) to 3-dichloromethylene-1-cyclohexene have been effected with 2 molar equiv of sodium ethoxide in ethanol.[7a,c] In one study, a 39% yield of diene was obtained, and 13% of starting material (which we presume to have been the less reactive *trans* isomer) was recovered.[7c]

(13) No proposal that has occurred to us for the formation of bromocycloalkane is uniquely or completely satisfying.

The reaction mixtures did contain an acidic gas, presumed to be HBr. Hydrogen abstraction by Br· (generated by dissociation of $BrCCl_3$) would lead to HBr and allylic radical, which could subsequently react with cyclohexene and with $BrCCl_3$, respectively, to give the observed bromides. Alternatively, Br· could add to cyclohexene to give an intermediate radical which abstracts hydrogen from cyclohexene (or chloroform) to form bromocyclohexane. The large amounts of bromocycloalkane formed in the several reactions observed here seem incompatible with the requirement that all Br· (and HBr) arise from dissociation of $BrCCl_3$, and substantial amounts of 1,2-dibromide would be expected if 2-bromocycloalkyl radical figured importantly in the over-all reaction.

(14) Prepared from benzoquinone–butadiene adduct by the procedure of W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. D. Dreger, and W. M. Hubbard, *J. Amer. Chem. Soc.*, **83**, 606 (1961). The mixture of *cis*- and *trans*-octahydronaphthalene obtained in this procedure is conveniently separated by fractional distillation through an annular Teflon spinning-band column.

(15) A referee suggested that the twist form for the substituted ring in **2** should be considered. While Dreiding models indicate that one ring of a *trans*-decalin can be twist rather than chair, the twist form is not so flexible as it is for cyclohexane. The models indicate that, in the twist form for **2**, the Br and CCl_3 substituents are about as close together as in a diequatorial conformation and at least one large (∼10 Hz) coupling constant would be expected.

(16) The relative amounts of addition and hydrogen abstraction reactions vary greatly with ring size and probably depend in part on the relative stabilities of the different allylic radicals.[8] Trichloromethylcycloheptane may arise from hydrogen abstraction from cycloheptene by 2-trichloromethylcycloheptyl radical or by the radical addition of $HCCl_3$, itself formed by hydrogen abstraction by ·CCl_3.

cycloheptane (chair or twist-chair),[17] we were led to expect H_m in *cis*-1-bromo-2-trichloromethylcycloheptane to exhibit two small (J_{mx} and J_{mb}) and one large (J_{ma}) vicinal coupling constants, and H_m in the *trans* isomer to exhibit one small (J_{mb}) and two large (J_{mx} and J_{ma}) ones. The experimental J values are consistent with those expected for the *cis* isomer but not the *trans*.

Cyclopentene and Indene.—Radical additions of $BrCCl_3$ to cyclopentene and to indene have been reported to give single vicinal addition products,[7a,c] but the stereochemistry of the products received no comment or was only tentatively assigned. We have repeated these photoinitiated additions and obtained nmr data which confirm that each of these olefins yields a single adduct and establish that *trans* addition of $BrCCl_3$ does occur.[5a]

For both the 1-bromo-2-trichloromethylcyclopentane and 1-bromo-2-trichloromethylindan[7c] products (isolated in 84 and 72% yields, respectively), each nmr spectrum includes only single absorptions for HCBr (H_x) and $HCCCl_3$ (H_m), with $J_{mx} \simeq 3$ Hz. This small vicinal coupling constant is that expected for the *trans* isomer (vicinal torsion angle approximately 120°) but not for the *cis* isomer (vicinal hydrogens substantially eclipsed). The nmr spectrum of the indene adduct easily confirms its identity as *trans*-1-bromo-2-trichloromethylindan; the signal for H_x is a sharp doublet while that for H_m is a complex multiplet.

Norbornene.—Radical additions of $BrCCl_3$ to norbornene have been reported by several investigators, but the stereochemistry of the adduct has not been firmly established.[18] The photoinitiated addition is much more rapid than the previous reports led us to expect; after 15 min, addition was essentially complete, and the mixture had become quite warm. The product, 2-bromo-3-trichloromethylnorbornane,[5b] was obtained in 95% yield and was shown by 60- and 100-MHz nmr spectra to be a single adduct. The coupling constants, which are summarized in Figure 1 and which are comparable to those reported for the CCl_4 addition product,[5b,18c] establish the complete identity as *trans*-2-*endo*-bromo-3-trichloromethylnorbornane. The greater multiplicity in the signal for H-2, compared to that for H-3, as well as the relative magnitudes of the coupling constants, clearly requires the *exo*-H-2,*endo*-H-3 configuration. That is, $BrCCl_3$ addition, like CCl_4[5b,18c] but unlike HBr[19a] additions, is *trans*, with the initial attack by $\cdot CCl_3$ from the *exo* direction.

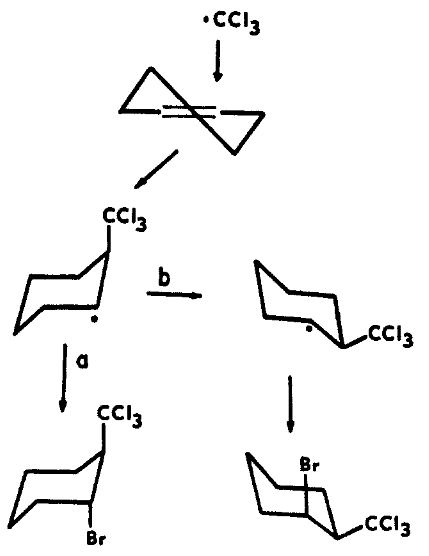

Figure 2.—Alternate pathways for the addition of $BrCCl_3$ to cyclohexene.

The dipole moment of the norbornene–$BrCCl_3$ adduct has previously been taken to indicate *cis* rather than *trans* addition.[19b] By using appropriate bond moments for C–Br (1.7 D) and C–CCl_3 (1.6 D),[19c] and the unit vectors proposed by Wilcox for calculating dipole moments of norbornane derivatives,[19d] one calculates that the dipole moment of the *cis* (*exo*) adduct will be near 3.1 D and that of the *trans* isomer near 1.5 D. The experimental dipole moment for the adduct is 2.6 D[20] and does indeed favor the *cis* isomer. We believe, however, that the nmr data are a more reliable revelation of stereochemistry in the rigid norbornane derivative than a comparison of calculated and experimental dipole moments. The applicability of the Wilcox parameters for dipole moment calculations is apparently more limited than initially proposed.[19d]

Discussion

Formation of *cis* and *trans* isomers by addition of bromotrichloromethane to cyclohexene could arise from either ring flipping or inversion of the radical center without ring flipping (or both) in the initially formed 2-trichloromethylcyclohexyl radical. Addition to a locked cyclohexene was investigated to distinguish between these possible paths. The rigid framework in *trans*-1,4,5,6,7,8,9,10-octahydronaphthalene (**1**) precludes ring flipping, but the remoteness of the saturated ring from the olefin site should minimize any other alterations in the radical addition reaction.

The flexible (monocyclic) cyclohexene adds $BrCCl_3$ to give geometrical isomers, but the rigid one (**1**) gives a single adduct, which is *trans* diaxial. These results seem to require that both portions of the addend ($BrCCl_3$) add from an axial direction. The 2-*axial*-trichloromethylcyclohexyl radical initially formed from cyclohexene may abstract Br from $BrCCl_3$ directly (Figure 2, path a) to form the *trans* product, or it may do so after ring flipping, which puts the bulky CCl_3 substituent in the more favorable equatorial conformation

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[17] J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7043 (1967), and previous papers cited there.

[18] (a) See ref 5b for the brief summary of previous reports and references. Tobler and Foster[5b] report the use of nmr data to identify the norbornene–CCl_4 adduct as *trans*-2-*endo*-chloro-3-trichloromethylnorbornane and state that "a similar stereochemistry may be inferred for the addition of bromotrichloromethane to norbornene." The nmr spectrum of 2-bromo-3-trichloromethylnorbornane was not described. These additions were effected by refluxing mixtures of norbornene, carbon tetrahalide, and benzoyl peroxide for several hours. (b) L. E. Barstow and G. A. Wiley [*Tetrahedron Lett.*, 865 (1968)] report, without any details about identification, that $BrCl_3$ adds to benzonorbornadiene to form the *trans*-2-*endo*-bromo-3-trichloromethyl product in 95% yield. (c) After this paper had been submitted for publication, the stereochemistry of the norbornene–CCl_4 adduct was discussed in some detail by C. L. Osborn, T. V. Van Auken, and D. J. Trecker, *J. Amer. Chem. Soc.*, **90**, 5806 (1968); the magnitudes of $J_{2ex,1}$ and $J_{2ex,3}$ are reversed in that paper and in the present one.

[19] (a) N. A. LeBel, *J. Amer. Chem. Soc.*, **82**, 623 (1960); (b) V. A. Rolleri, *Dissertation Abstr.*, **19**, 960 (1958); (c) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman Co., San Francisco, Calif., 1963, pp 42, 56; (d) C. F. Wilcox, *J. Amer. Chem. Soc.*, **82**, 414 (1960).

[20] The experimental dipole moment was measured as a part of a class assignment by students in the physical chemistry laboratory at Louisiana State University, under the supervision of Professor J. H. Wharton, during the fall semester, 1967.

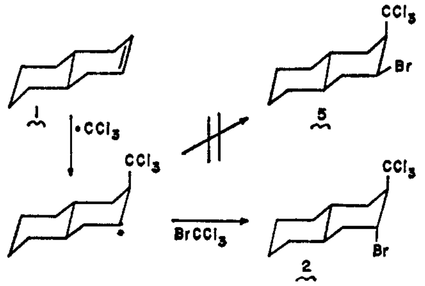

Figure 3.—Stereochemistry of the addition of $BrCCl_3$ to *trans*-1,4,5,6,7,8,9,10-octahydronaphthalene (1).

(Figure 2, path b), to form the *cis* product. By either path, the added substituents approach the ring from axial orientations.[21] The radical initially formed by axial approach of $\cdot CCl_3$ to **1**, however, cannot undergo ring flipping, and the single adduct is the *trans*-diaxial one (**2**). Were the geometric isomers formed from cyclohexene due to inversion at the radical center, rather than to ring flipping, one would expect that, with **1** as reactant, some *cis* isomer **5** would be formed along with (or instead of) the sterically unfavored *trans*-diaxial one actually obtained (see Figure 3).

Addition of $BrCCl_3$ to the nonflexible ring systems (cyclopentene, indene, and norbornene) is *trans*, probably because eclipsing approach of $BrCCl_3$ to the CCl_3 substituent in the product-forming step of the chain process is highly unfavored.[5a,b,18c] Two features of the cycloheptene addition require comment. Unlike the other flexible cycloalkenes (cyclooctene and cyclohexene), cycloheptene gives a single adduct, and unlike the other olefins for which a single adduct was obtained, cycloheptene gives the *cis* isomer, not the *trans* one. We believe that both of these features are directly associated with the very low energy barrier to conformation change (ring flipping) in cycloheptane compared to that in cyclooctane and cyclohexane.[22] We presume that every initially formed 2-trichloromethylcycloheptyl radical, with an axial-like substituent, undergoes conformational change to make the substituent equatorial-like before the product-forming step. Axial bonding to bromine (from $BrCCl_3$) by the new radical would produce *cis*-1-bromo-2-trichloromethylcycloheptane. While this picture accounts in a reasonable and qualitative way for the formation of only *cis* adduct from cycloheptene, the formation of *nearly equal* proportions of *cis* and *trans* isomers from cyclohexene and cyclooctene remains inexplicable. The slight preference for *trans* adduct (initially diaxial) from cyclohexene over cyclooctene is in accord with the higher energy barrier to conformation change with cyclohexene, but the actual outcome is undoubtedly dependent on several interrelated energy factors.

Experimental Section

Gc data were obtained with a Beckman Model GC5 instrument equipped with hydrogen flame and thermal conductivity detectors and with $^1/_8$-in. packed columns (either 6-ft SE-30 silicone or 10-ft Carbowax 20M). Ir spectra were obtained with Beckman IR-5 and IR-7 and Perkin-Elmer Model 137 instruments. Nmr spectra were obtained with Varian Associates A-60A, HA-100, and HR-220 spectrometers;[23] all chemical shifts are relative to internal tetramethylsilane reference (minus sign indicates downfield).

Addition of $BrCCl_3$ to Cyclohexene.—The general procedure used with each olefin is described only for cyclohexene. A solution of cyclohexene (1 mol) in bromotrichloromethane (2 mol) contained in a Pyrex tube was deoxygenated by a stream of nitrogen and then irradiated for 4 hr in a Rayonet photochemical reactor equipped with 3500-Å lamps. The composition of the mixture was determined periodically by gc, ir, and nmr methods. At the end of the irradiation, the conversion of cyclohexene into products was 86%, and the yield of 1-bromo-2-trichloromethylcyclohexane[7] was about 60%. The reaction mixture could be resolved by fractional distillation at reduced pressure. Gc and nmr data for the 1,2-addition product indicated that it was a mixture (45:55) of geometrical isomers: bp 73–84° (0.15 mm); $n^{20}D$ 1.5478; ir 12.8–13.5 μ (intense, CCl_3); nmr (CD_3COCD_3) −2.71 ($HCCCl_3$, *cis* isomer), −3.13 ($HCCCl_3$, *trans* isomer), −4.79 (HCBr, *trans* isomer), and −5.06 ppm (HCBr, *cis* isomer). *Anal.* Calcd for $C_7H_{10}BrCl_3$: C, 29.84; H, 3.58. Found: C, 30.3; H, 3.7.

Besides the addition product, the mixture was found to contain 3-bromocyclohexene[24,25] (28%), chloroform, and another product tentatively identified as bromocyclohexane (12%) [nmr −4.48 ppm (bm, 1 H, HCBr)]. During the course of the reaction, the molar amounts of chloroform and 3-bromo-1-cyclohexene were approximately equal.

Selective Dehydrohalogenation of 1-Bromo-2-trichloromethylcyclohexane.—During 1.5 hr, a solution of potassium hydroxide (0.02 mol) in a mixed solvent [20 ml of dimethyl sulfoxide (DMSO), 5 ml of methanol, and 5 ml of water] was added to a solution of 1-bromo-2-trichloromethylcyclohexane (0.04 mol, 45% *cis*, 55% *trans*) in a mixture of DMSO (40 ml) and methanol (10 ml).[2] The mixture was stirred at room temperature for 18 hr longer, diluted with water, and extracted three times with petroleum ether (bp 60–70°). Subsequent reduced pressure distillation of the organic material gave a mixture of dehydrohalogenation products and pure *trans*-1-bromo-2-trichloromethylcyclohexane [45% of original mixture; bp 92–99° (1.3 mm); nmr −3.05 (m, 1 H, $HCCCl_3$) and −4.80 ppm (m, 1 H, HCBr)].

The dehydrohalogenation products were shown by nmr, ir, and gc data to consist of mainly 1-bromo-2-dichloromethylenecyclohexane [ir, intense absorption at 6.23 and 11.2 μ ($C{=}CCl_2$); nmr −5.31 ppm (m, $HCBrC{=}CCl_2$)], 1-trichloromethyl-1-cyclohexene [ir, weak absorption at 6.23 (C=C) and 13.0 μ (CCl_3); nmr −5.47 ppm (m, $HC{=}CCCl_3$)], and a very small amount of 3-dichloromethylene-1-cyclohexane [nmr −6.43 (dt, J_{12} = 10 Hz, J_{26} = 1.5 Hz, $CH_2CH{=}CHC{=}CCl_2$) and −5.97 ppm (dt, J_{12} = 10 Hz, J_{16} = 4.0 Hz, $CH_2CH{=}CHC{=}CCl_2$)].

When a sample of the recovered *trans*-1-bromo-2-trichloromethylcyclohexane was treated with an equal molar amount of potassium hydroxide in the same mixed solvent used with the *cis–trans* mixture, the nmr spectrum of the organic material extracted from the diluted solution was almost totally devoid of absorptions for CH=C, but the absorptions characteristic of the *trans*-1-bromo-2-trichloromethylcyclohexane persisted.

A sample of mixed *cis*- and *trans*-1-bromo-2-trichloromethylcyclohexane spontaneously lost some hydrogen halide during storage for several weeks. Gc analysis of the sample indicated that the addition product had become contaminated with the same dehydrohalogenation product generated by potassium hydroxide treatment.

Addition to *trans*-1,4,5,6,7,8,9,10-Octahydronaphthalene (1).—Irradiation of a mixture of **1** (0.04 mol) and $BrCCl_3$ (0.16 mol) for 4 hr led to the consumption of 84% of the olefin and the formation of a product mixture consisting of *trans*-2-*axial*-bromo-3-trichloromethyl-*trans*-decahydronaphthalene (**2**, 42% yield), **3** (17%), and **4** (25%). The nmr spectrum of the mixture revealed

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[21] (a) Radical additions of HBr to cyclohexenes for which stereochemistry can be discerned are also *trans*-diaxial additions; see ref 4. (b) This suggestion does not exclude the possibility of rapid inversion at the radical center nor even of a planar radical center, but only effective approach of $BrCCl_3$ to the radical from an equatorial orientation.

[22] Reference 9, pp 41, 209, 211, records the free energy barrier to conformation interconversion in cyclohexane as 10.1 kcal/mol, that in cyclooctane as 7.7 kcal/mol, and that in cycloheptane as 2.16 kcal/mol.

[23] The 60- and 100-MHz instruments are at Louisiana State University and were purchased with the aid of equipment grants from the National Science Foundation. The 220-MHz instrument is at Varian Associates, Palo Alto, Calif., and was generously made available to N. S. B. for this study.

[24] An authentic sample of 3-bromo-1-cyclohexene for identification use was prepared from cyclohexene and N-bromosuccinimide in refluxing CCl_4 solution,[25] nmr −5.83 ppm (m, 2 H, C=CH).

[25] C. Djerassi, *Chem. Rev.*, **43**, 271 (1948).

that it also contained some chloroform, and an acidic gas (presumably HBr) was detected when the reaction flask was opened.

Adduct **2** distilled at 111-112° (0.08 mm). Its 60-MHz nmr spectrum included narrow multiplets at −5.19 (m, 1 H, HCBr) and −3.16 ppm (m, 1 H, $HCCCl_3$) which were not resolved at 100 and 220 MHz. Decoupling experiments led to the assignment of coupling constants summarized in Figure 1. *Anal.* Calcd for $C_{11}H_{16}BrCl_3$: C, 39.50; H, 4.82. Found: C, 39.75; H, 4.98.

The lower boiling components of the product mixture were not cleanly resolved by distillation, but the nearly pure distillate fractions were identified by nmr spectra. Compound **3** was the principal component in the fraction distilling at 56–60° (0.08 mm): nmr −5.72 (bm, 2 H, C=CH) and −4.52 ppm (bm, 1 H, HCBr). Compound **4** was obtained mixed with **2** and was identified by its nmr absorption at −4.67 ppm (m, HCBr); a small authentic sample for comparison was prepared in solution by the addition of hydrogen bromide to **1**.

Addition to Cycloheptene.—Irradiation of a mixture of cycloheptene (1.0 mol) and $BrCCl_3$ (4.0 mol) for 16 hr led to the formation of three products. In addition to lower boiling products tentatively identified as 3-bromo-1-cycloheptene [20% yield; decolorized Br_2 in CCl_4; ir 3.31 and 6.06 μ (olefin); nmr −5.83 (bm, 2 H, C=CH) and −4.90 ppm (m, 1 H, HCBr)] and trichloromethylcycloheptane [23% yield; did not decolorize Br_2 in CCl_4; ir 12.9-13.0 μ (intense, CCl_3)], the adduct, *cis*-1-bromo-2-trichloromethylcycloheptane, was obtained (26% yield) at 89-103° (0.1 mm). It was characterized by its ir (12.95 μ, intense, CCl_3) and nmr [C_6D_6, −4.78 (m, 1 H, HCBr) and −3.27 ppm (bm, 1 H, $HCCCl_3$)] spectra. The narrow multiplet absorption for HCBr was not resolved at 220 MHz.

Anal. Calcd for $C_8H_{12}BrCl_3$: C, 32.54; H, 4.37. Found: C, 32.89; H, 4.21.

Treatment of a sample of this adduct with a deficiency of potassium hydroxide in mixed solvent as described for the cyclohexene adduct led to a single dehydrohalogenation product, 1-bromo-2-dichloromethylenecycloheptane [ir 6.2 and 10.85 μ ($C{=}CCl_2$); nmr −5.15 ppm (m, HCBr), no absorption for C=CH], which was not separated from unconsumed adduct.

Addition to Cyclopentene.—A mixture of cyclopentene (0.18 mol) and $BrCCl_3$ (0.71 mol) afforded an 84% yield of *trans*-1-bromo-2-trichloromethylcyclopentane: bp 60° (0.05 mm); nmr −4.46 (m, 1 H, HCBr), −3.69 (m, 1 H, $HCCCl_3$), and −2.96 ppm (bm, 6 H, CH_2). Gc analysis of the product mixture revealed the presence of three minor products of significantly shorter retention time than the adduct; these products were not further characterized but are presumably hydrogen-abstraction products corresponding to those obtained from cyclohexene. When a portion of the adduct was treated with a deficiency of potassium hydroxide in mixed solvent as described for the cyclohexene adduct, it was partially dehydrochlorinated to 1-bromo-2-dichloromethylenecyclopentane: ir 6.23 and 11.1 μ ($C{=}Cl_2$); nmr −4.9 ppm (nm, HCBr). Gc analysis indicated that a single dehydrohalogenation product had been formed.

Addition to Indene.—When a mixture of indene (0.215 mol) and $BrCCl_3$ (0.86 mol) was irradiated for 6 hr, the nmr spectrum of the mixture revealed only a single component containing hydrogen, *trans*-1-bromo-2-trichloromethylindane: bp 125–129° (0.1 mm); nmr −5.72 (d, J = 3.2 Hz, 1 H, HCBr) and −4.02 ppm (m, 1 H, $HCCCl_3$).

Addition to Norbornene.—Periodic nmr spectra revealed that the addition of $BrCCl_3$ (0.64 mol) to norbornene (0.16 mol) was essentially complete after 15 min. Distillation of the mixture afforded a 95% yield of the adduct, *trans*-2-*endo*-bromo-3-trichloromethylnorbornane: bp 90–95° (0.4 mm); n^{25}D 1.5516; nmr (C_6D_6) −4.06 (m, 1 H, HCBr), −2.63 (q, 1 H, $HCCCl_3$), −2.33 (m, 1 H, H-4), −2.19 (m, 1 H, H-1), −2.1 to −1.68 (bm, 2 H, H-5 *endo* + H-6 *endo*), −1.5 to −1.0 (bm, 3 H, H-5 *exo* + H-6 *endo* + H-7 *syn*), and −0.92 ppm (dq, 1 H, H-7 anti).

Anal. Calcd for $C_8H_{10}Cl_3Br$: C, 32.85; H, 3.45. Found: C, 33.01; 3.64.

Registry No.—Bromotrichloromethane, 75-62-7; *cis*-1-bromo-2-trichloromethylcyclohexane 17831-07-1; *trans*-1-bromo-2-trichloromethylcyclohexane, 17831-06-0; **2**, 19640-04-1; *cis*-1-bromo-2-trichloromethylcycloheptane, 19640-05-2; *trans*-1-bromo-2-trichloromethylcyclopentane, 19640-06-3; *trans*-1-bromo-2-trichloromethylindan, 19640-07-4; *trans*-2-*endo*-bromo-3-trichloromethylnorbornane, 19640-08-5.

Laser Photolysis of 2-Chloro-2-nitrosobutane. Kinetics and Mechanism

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The kinetics and mechanism of the photolysis of 2-chloro-2-nitrosobutane have been investigated using the 6328-Å emission from helium–neon lasers. Concentration, oxygen, and solvent have been found to affect the mechanism and kinetics of the photodecomposition. The use of a laser as light source simplified experimental problems and reduced total irradiation time so that complications from slow dark reactions were reduced. Selective production of 2-chloro-2-nitrobutane occurred on photolysis in the presence of oxygen.

The photochemistry of 2-chloro-2-nitrosobutane and similar compounds has been previously investigated[2,3] and reviewed.[4–6] Products of the photolysis in methanol of *gem*-chloronitrosoalkanes have been reported to be 2-butanone oxime, 2,3-butanedione monoxime, and a compound with $C_8H_{16}O_3N_2\cdot HCl$ as the molecular formula,[2b] but Baldwin and Rogers[3] isolated a compound ($C_8H_{16}O_2N_2HCl$) which was shown to have a dinitrone structure. For 4-chloro-4-nitrosovaleric acid and 2-chloro-2-nitroso-1,4-diphenylbutane, Mitchell and coworkers[2a] found the primary products of the photolysis in methanol to be the respective oxime hydrochlorides. Kosinski[5] contended since experiments were carried out using light absorbed by the nitroso chromophore that the initial step of the photolysis must be the activation of the nitroso group and then its splitting off. A major role for the solvent was postulated. Artemiev[7] considered the initial step to be the formation of chlorine and nitrosoalkyl radicals. These radicals then participated in further reactions.

The photolysis of 2-chloro-2-nitrosobutane was reexamined to clarify the mechanism of the photodecom-

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