Free-Radical Addition Reactions with Cyclic Olefins. Role of Medium Ring Size Effect

L. H. GALE

Shell Development Company, Emeryville, California 94608

Received June 14, 1968

A study of free-radical addition reactions with cyclic olefins has demonstrated a marked difference in relative reactivity depending on whether the radical addition step is reversible or nonreversible. The reactivity of cyclic olefins with nonreversible addends, acetaldehyde, and bromotrichloromethane is not very sensitive to ring size, and it decreases in the order cyclooctene > cyclopentene > cycloheptene > cyclohexene. The order of reactivity with reversible addends, hydrogen bromide, and ethanethiol is nearly the opposite—cyclohexene > cyclopentene > cycloheptene ≫ cyclooctene—and the decrease with cyclooctene is 10- to 100-fold. This inverse behavior is attributed to the role of the "medium ring size" effect (also known as I strain) in the reversible additions.

The free-radical addition reactions of thiol compounds[1] and hydrogen bromide[2] with *cis,cis*-1,5-cyclooctadiene at low temperature (ambient and −10°, respectively) give high yields of 5-substituted cyclooctenyl derivatives. These results suggest that the reactivity of the cyclooctenyl double bond is low. The reduced reactivity of the cyclooctenyl double bond was confirmed by competitive addition of hydrogen bromide to cyclic olefins.[2] The order of reactivity was cyclohexene > cyclopentene > cycloheptene ≫ *cis*-cyclooctene, and the relative rates were 1:0.93:0.48:0.06, respectively, at −17°. These results are in marked contrast to available data for the relative rate constants for addition of free radicals to various cyclic olefins. Gresser, Rajbenbach, and Szwarc[3] have reported that the rate constants for addition of methyl radical decreases in the order cyclooctene > cyclopentene > cycloheptene > cyclohexene at 65° in the gas phase. Walling and Helmreich[4] have reported that at 60° the rate constants for addition of dodecanethiyl radical to cyclopentene is 2.6 times larger than to cyclohexene. Also at ambient temperature the addition of trichloromethyl radical is 3.2 times faster to cyclopentene than cyclohexene.[5] The present paper describes a study of the relative reactivities of cyclic olefins in radical addition reactions which was initiated to determine the origin of these differences in reactivity. It was felt that reversibility of the radical addition step might play a role. Therefore addends were selected which give both reversible and nonreversible addition steps. Acetaldehyde and bromotrichloromethane form new carbon–carbon bonds in the radical addition step and the addition is not reversible. Ethanethiol and the previously studied hydrogen bromide form carbon–sulfur and carbon–bromine bonds, and the addition steps are reversible.[4,6]

Results

The several techniques for evaluating the relative reactivities of olefins using competitive addition of an addend have been discussed critically by Cadogan and Sadler.[7] In the present study the relative reactivity, $\bar{P}$, of olefins M_1 and M_2 was determined from the actual yields of 1:1 adducts measured at low conversion of olefins. Thus $\bar{P}$ was calculated from the expression

$$\bar{P} = \frac{[M_2]_{av}}{[M_1]_{av}} \frac{[AM_1B]}{[AM_2B]}$$

High addend–olefin molar ratios were used to minimize telomerization. Addends with large chain transfer constants were used, ensuring long kinetic chain lengths, and thus minimizing the effects of termination reactions. The alternative method of measuring $\bar{P}$ based on determining the relative amounts of olefins reacted is subject to considerable error because of the possibility of olefin consumption by allylic hydrogen abstraction reactions. (Allylic hydrogen abstraction is a significant reaction of trichloromethyl radicals with cyclic olefins.)[8]

Acetaldehyde.—The relative reactivities of cyclic olefins with acetaldehyde at 52° are summarized in Table I. These data demonstrate that the differences in reactivity of cyclic olefins are small and decrease in the order cyclooctene > cyclopentene > cycloheptene > cyclohexene. The relative reactivity values, $\bar{P}$, were shown to be independent of olefin ratios and dose rate (*i.e.*, rate of initiation).

TABLE I

RELATIVE REACTIVITY OF CYCLIC OLEFINS TO ADDITION OF ACETALDEHYDE AT 52 ± 3°

	Relative reactivity, $\bar{P}$				
Unsaturate	*a*	*b*	*c*	*d*	Av
Cyclopentene	2.8	2.5	2.4	2.6	2.6 ± 0.1
Cyclohexene	1.0	1.0	1.0	1.0	1.0
Cycloheptene	2.3	2.1	2.2	2.2	2.2 ± 0.1
Cyclooctene	3.2	2.9	2.7	2.9	2.9 ± 0.1

[a] R = [acetaldehyde]/[Σ(olefin)] = 11.3–12.2; [cycloolefin]/[cyclohexene] = 3.5–4.0; dose rate 0.0913 Mrad/hr. [b] R = 13.1–15.3; [cycloolefin]/[cyclohexene] = 0.93–0.97; dose rate 0.0913 Mrad/hr. [c] R = 15.2; [cyclopentene]:[cyclohexene]:[cycloheptene]:[cyclooctene] = 1.14:1.00:0.98:0.96, dose rate 0.0913 Mrad/hr. [d] Same as *c*, except dose rate is 0.016 Mrad/hr.

Bromotrichloromethane.—The relative reactivities of cyclic olefins to addition of bromotrichloromethane were determined at −20.5° in order to compare directly with the low-temperature results from addition of hydrogen bromide. The data are summarized in Table II. These data demonstrate that the relative order of reactivity is the same as found with acetaldehyde. The differences in reactivity are greater because of the lower temperature. The relative reactivities with

(1) J. M. Locke and E. W. Duck, *Chem. Commun.*, **8**, 151 (1965).
(2) L. H. Gale, *J. Org. Chem.*, **33**, 3643 (1968).
(3) J. Gresser, A. Rajbenbach, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 3005 (1961).
(4) C. Walling and W. Helmreich, *ibid.*, **81**, 1144 (1959).
(5) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 254.
(6) See ref 5, p 302.
(7) J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc., B*, 1191 (1966).
(8) E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961).

TABLE II
RELATIVE REACTIVITY OF CYCLIC OLEFINS TO ADDITION OF BROMOTRICHLOROMETHANE AT −20.5 ± 1°

Unsaturate	Relative reactivity, $\bar{P}$ a	b	c	Av
Cyclopentene	4.8	5.6	6.3	5.6 ± 0.4
Cyclohexene	1.0	1.0	1.0	1.0
Cycloheptene	3.3	4.2	4.2	3.9 ± 0.4
Cyclooctene	7.1	9.4	7.5	8.0 ± 0.9

[a] R = [$BrCCl_3$]/[Σ(olefin)] = 3.6–4.2; [cyclopentene]/[cycloolefin] = 0.54–0.78; dose rate 0.134 Mrad/hr. [b] R = 3.8–4.0; [cyclopentene]/[cycloolefin] = 0.41–0.46; dose rate 0.134 Mrad/hr. [c] R = 6.4–6.8; [cyclopentene]/[cycloolefin] = 0.71–0.85; dose rate 0.134 Mrad/hr.

bromotrichloromethane were shown to be independent of addend concentration and ratios of olefins.

Ethanethiol.—The relative reactivity of cyclohexene and cyclooctene was determined with ethanethiol. These cyclic olefins represent the extremes in reactivity toward addition of acetaldehyde, bromotrichloromethane, and hydrogen bromide. The effect of ethanethiol concentration was determined by diluting the reactants with chlorobenzene while still maintaining the ratio of [ethanethiol]/[Σ(cycloolefin)] >3 to minimize telomer formation. The results are summarized in Table III. These data demonstrate that (1) cyclohexene is

TABLE III
RELATIVE REACTIVITY OF CYCLOOCTENE AND CYCLOHEXENE WITH ETHANETHIOL[a]

Temp, °C	[Ethanethiol], mol/l.	$\bar{P}$ = −d(cyclooctene)/d(cyclohexene)
−78	8.30	0.64 ± 0.08[b]
−21 ± 2	9.08	0.17
	4.51[c]	0.10
	2.47[c]	0.067
	1.54[c]	0.051
53 ± 1	9.08	0.061
	4.51[c]	0.053
	2.42[c]	0.045
	1.58[c]	0.036

[a] R = [ethanethiol]/[Σ(cycloolefins)] = 3.21; [cyclooctene]/[cyclohexene] = 0.97. [b] Average of two experiments. [c] Chlorobenzene diluent.

more reactive than cyclooctene, in agreement with their reactivities with HBr; (2) the reactivity of cyclooctene relative to cyclohexene, $\bar{P}$, decreases with increasing temperature; and (3) $\bar{P}$ decreases with decreasing ethanethiol concentration.

Discussion

The results of the competitive addition of four addends to cyclic olefins demonstrate a difference in relative reactivity for reversible and nonreversible addends. Walling and Helmreich[4] have developed the expressions for the experimentally determined reactivity ratio, $\bar{P} = -dM_1/dM_2$, for two olefins in a competitive experiment. The reactions involved are

$$B\cdot + M_1 \underset{k_{a1}'}{\overset{k_{a1}}{\rightleftharpoons}} BM_1\cdot \xrightarrow[[AB]]{k_{d1}} BM_1A + B\cdot$$

$$B\cdot + M_2 \underset{k_{a2}'}{\overset{k_{a2}}{\rightleftharpoons}} BM_2\cdot \xrightarrow[[AB]]{k_{d2}} BM_2A + B\cdot$$

From this scheme it can be shown that

$$\bar{P} = \frac{k_{a1}k_{d1}(k_{a2}' + k_{d2}[AB])}{k_{a2}k_{d2}(k_{a1}' + k_{d1}[AB])}$$

Thus in this general case $\bar{P}$ is a function of not only the relative rate of addition of B· to M_1 and M_2, but also of the rates of elimination of B· from the adduct radicals, of the rates of abstraction of A by adduct radicals and of the concentration of AB. If M_1 and M_2 are specifically assigned to two olefins, there are eight limiting conditions which can lead to simplification of the general equation.

If radical additions to both olefins are not reversible ($k_d[AB] \gg k_a'$), then

$$\bar{P} = \frac{k_{a1}}{k_{a2}} \quad (1)$$

If radical addition to both olefins is highly reversible ($k_a' \gg k_d[AB]$), then

$$\bar{P} = \frac{k_{a1}k_{d1}k_{a2}'}{k_{a2}k_{d2}k_{a1}'} \quad (2)$$

If $k_{d1}[AB] \gg k_{a1}'$ and $k_{d2}[AB] \simeq k_{a2}'$, then

$$\bar{P} = \frac{k_{a1}k_{a2}'}{k_{a2}k_{d2}}\frac{1}{[AB]} + \frac{k_{a1}}{k_{a2}} \quad (3)$$

If $k_{a1}' \gg k_{d1}[AB]$ and $k_{d2}[AB] \simeq k_{a2}'$, then

$$\bar{P} = \frac{k_{a1}k_{d1}}{k_{a2}k_{a1}'}[AB] + \frac{k_{a1}k_{a2}'k_{d1}}{k_{a2}k_{a1}'k_{d2}} \quad (4)$$

If $k_{a1}' \simeq k_{d1}[AB]$ and $k_{d2}[AB] \gg k_{a2}'$, then

$$\frac{1}{\bar{P}} = \frac{k_{a2}k_{a1}'}{k_{a1}k_{d1}}\frac{1}{[AB]} + \frac{k_{a2}}{k_{a1}} \quad (5)$$

If $k_{a1}' \simeq k_{d1}[AB]$ and $k_{a2}' \gg k_{d2}[AB]$, then

$$\frac{1}{\bar{P}} = \frac{k_{a2}k_{d2}}{k_{a1}k_{a2}'}[AB] + \frac{k_{a2}k_{d2}k_{a1}'}{k_{a1}k_{d1}k_{a2}'} \quad (6)$$

If $k_{a1}' \gg k_{d1}[AB]$ and $k_{d2}[AB] \gg k_{a2}'$, then

$$\bar{P} = \frac{k_{a1}k_{d1}}{k_{a2}k_{a1}'}[AB] \quad (7)$$

If $k_{d1}[AB] \gg k_{a1}'$ and $k_{a2}' \gg k_{d2}[AB]$, then

$$\bar{P} = \frac{k_{a1}k_{a2}'}{k_{a2}k_{d2}}\frac{1}{[AB]} \quad (8)$$

These limiting expressions provide a basis for interpreting our results. First, considering the relative reactivities of cyclic olefins with the nonreversible addends, bromotrichloromethane and acetaldehyde, k_a' is always zero at these temperatures and eq 1 applies. Thus the experimentally determined reactivity ratio, $\bar{P}$, is a measure only of the ratio of rate constants for addition of trichloromethyl and acetyl radical to the double bonds. From Tables I and II the rate constants for addition of these radicals to the double bonds of cyclic olefins are similar, and decrease in the order cyclooctene > cyclopentene > cycloheptene > cyclohexene. This same order of reactivity has been reported for methyl radical addition.[3]

Second, in the reactions of cyclic olefins with the reversible addends, hydrogen bromide and ethanethiol, it is apparent that in these systems $\bar{P}$ must be dependent on a number of rate constants, for k_a' is not zero. The question arises as to which one of the other seven limiting conditions is applicable to the additions of these reagents to cyclic olefins. Equation 2 can be ruled out because $\bar{P}$ was found to depend on addend concentration in the addition of ethanethiol to cyclohexene and cyclooctene. The dependence of

$\bar{P}$ on ethanethiol concentration provides information on the most likely kinetic expression. $\bar{P}$ as shown in Table III was calculated on the basis that M_1 is cyclooctene and M_2 is cyclohexene. The experimentally determined values of $\bar{P}$ were found to decrease with decreasing ethanethiol concentration. This result rules out eq 3, 6, and 8. Equations 5 and 7 incorporate the assumption that the addition to cyclohexene is effectively nonreversible due either to a low rate constant for the elimination reaction, k_{a2}', or a high rate of transfer $k_{d2}[AB]$. This assumption seems unlikely based on the results of Sivertz;[9] from a kinetic study of the photolytic addition of *n*-butyl mercaptan to cyclohexene, Sivertz concluded that the elimination reaction is important. Further arguments against application of eq 5 arise from a plot of $1/\bar{P}$ *vs.* [ethanethiol]$^{-1}$. While reasonably straight lines are obtained at both -21 and 53° as predicted by eq 5, the intercepts on the y axis do not correspond to the predicted values for k_{a2}/k_{a1}.[10] It is concluded that eq 4 is the best limiting kinetic expression to describe the observed dependence of $\bar{P}$ on ethanethiol concentration. A plot of $\bar{P}$ *vs.* concentration of ethanethiol is shown in Figure 1. Reasonably straight lines are obtained, particularly at $-21°$. The effect of ethanethiol concentration on $\bar{P}$ is much smaller at 53°, suggesting that at this temperature ethylthiyl addition to both olefins is highly reversible and eq 2 is becoming applicable.

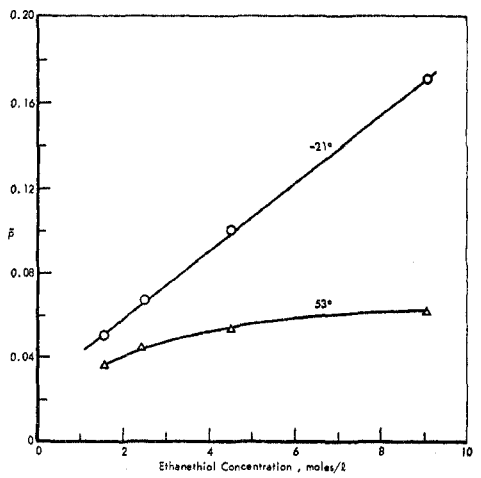
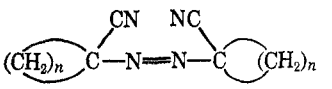


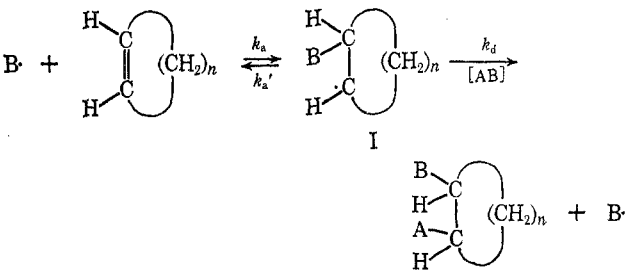
Figure 1.—Plot of $\bar{P}$ *vs.* ethanethiol concentration for addition to cyclohexene and cyclooctene.

Based on the above considerations, it is concluded that the low reactivity with reversible addends of cyclooctene relative to cyclohexene is due to an abnormally high reversibility of the addition step with cyclooctene, *i.e.*, $k_{a1}' \gg k_{d1}[AB]$. The role of reversibility in altering olefin reactivity in free radical addition reactions has been demonstrated previously in the addition of thiols to bicycloalkenes.[11] There remains the question of whether the high reversibility is due to an unusually large rate constant for the reverse reaction, k_{a1}', or to an unusually small rate constant for abstraction, k_{d1}. The high reversibility of the addition step with cyclooctene is likely a manifestation of the "medium ring size effect" (also known as I strain).[12] Consideration of the role of this effect in radical addition reactions suggests an answer to whether k_a' is enhanced or k_d reduced for cyclooctyl radical. The basis for the "medium ring size effect" is that saturated carbon rings with eight to eleven carbon atoms can exist only in conformations which contain a number of nonbonded hydrogen–hydrogen repulsive interactions. Thus medium size rings have a higher energy content than rings containing five to seven or twelve or more atoms where staggered conformations exist which reduce or eliminate these interactions. This effect is shown in the lower exothermicity for hydrogenation of cyclooctene compared to smaller ring olefins.[13] Two studies have been reported which illustrate the role of this effect in free radical reactions. Overberger and coworkers[14] reported that the rate of thermal decomposition of azobisnitriles of the type



is fastest with the cyclooctyl compound and decreases in the order cyclooctyl > cycloheptyl > cyclopentyl > cyclohexyl. Similarly, Russell[15] has reported that the rate of hydrogen abstraction from cycloalkanes by chlorine atom decreases in the order cyclooctane > cycloheptane > cyclopentane > cyclohexane. In both of these studies the rate-determining step converts an sp^3 carbon atom to sp^2 hybridization. This transformation reduces the number of hydrogen–hydrogen nonbonded interactions in cyclooctyl rings, and thus the rates of reactions with cyclooctane or its derivatives are enhanced.

In the present study the reverse reaction sequence occurs, *i.e.*, the addition of an addend to a double bond converts a cyclic olefin to a saturate. In successive steps, two sp^2 carbons are converted into sp^3 hybridization. From methyl radical addition data[8]



and our results with addition of acetaldehyde and bromotrichloromethane, it is concluded that the "medium ring size effect" does not influence the rate constant for addition of B·. Apparently when Ia is substituted cyclooctyl radical, the presence of one sp^2 carbon center imparts sufficient flexibility to minimize hydrogen–hydrogen nonbonded interactions. Thus it

(9) C. Sivertz, *J. Phys. Chem.*, **63**, 34 (1959).

(10) From eq 5 the y intercept should equal k_{a2}/k_{a1}, the relative rate of addition of a radical B· to cyclohexene and cyclooctene. The data in Tables I and II demonstrate that k_{a2}/k_{a1} for addition of acetyl radical is 0.34 at 52° and for trichloromethyl radical is 0.12 at $-21°$. Making the reasonable assumption that ethylthiyl radical should have about the same values of k_{a2}/k_{a1}, the y intercept in Figure 1 should equal *ca.* 0.34 at 53° and 0.12 at $-21°$. The actual intercepts are vastly different, 13 at 53° and 3 at $-21°$.

(11) E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, **30**, 3003 (1965).

(12) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 265.

(13) R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).

(14) C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker, and J. Herbert, *ibid.*, **75**, 2078 (1953).

(15) G. A. Russell, *ibid.*, **80**, 4997 (1958).

is also likely that the rate constant for elimination of B· from cyclooctyl radical, k_a', will not be enhanced. It is concluded that the role of the "medium ring size effect" is principally to decrease greatly the rate constant for the abstraction reaction, k_d, with cyclooctyl radical. This conclusion is consistent with the known rate enhancement for the reverse reaction, formation of cyclooctyl radical *via* hydrogen abstraction from cyclooctane or decomposition of the azobisnitrile.

Experimental Section[16]

Reagents.—The purification of the cyclic olefins was described previously.[2] Acetaldehyde (Eastman Organic Chemicals, White Label) was distilled from a mixture of calcium hydride and alumina through a 20-in. tantalum helices packed column in a nitrogen atmosphere, bp 22.0°. The purified acetaldehyde was stored at −10° until used. Bromotrichloromethane (Eastman Organic Chemicals, practical) was fractionally distilled through a 20-in. tantalum helices packed column in a nitrogen atmosphere. The distillation apparatus was protected from light. A center cut was collected with bp 104.0–104.8°. The purity based on glpc is 99.9% (0.10% CCl_4). Ethanethiol (Eastman Organic Chemicals, White Label) and chlorobenzene (Matheson Coleman and Bell) were used directly with no purification.

Irradiation Procedure.—Samples were irradiated in the 8000-Ci cobalt-60 facility. The dose rates were determined by ferrous dosimetry using identical geometry.

Competitive Addition of Acetaldehyde.—Accurately weighed mixtures of acetaldehyde and cyclic olefins (total volume of reactants *ca.* 3 ml) were placed in 13 mm o.d. × 100 mm long heavy walled Pyrex ampoules and were degassed and sealed *in vacuo*. The samples were irradiated at the desired temperature, ±3°, in the cobalt-60 facility. Irradiation times were varied to achieve *ca.* 10% conversion of unsaturates. The reactivity of each cyclic olefin was determined using cyclohexene as the reference unsaturate. Several multicompetitive experiments were carried out using all four cyclic olefins together.

The products from all competitive additions of acetaldehyde to cyclic olefins were analyzed by glpc using a Ucon 50HB2000–Chromosorb W column (6 mm o.d. × 3.0 m long) programmed from 40 to 175° at 6°/min with a helium flow rate of 85 cc/min. All glpc analyses were performed in triplicate.

In order to identify unambiguously the various cycloalkyl methyl ketones (1:1 adducts), individual mixtures of acetaldehyde and each cyclic olefin were prepared in Pyrex ampoules and handled as above. These samples were irradiated for 72 hr at 52.5° at a dose rate of 0.0913 Mrad/hr. Identification of each product was accomplished by trapping the glpc separated components and analyzing each one by mass and infrared spectrometry. The mass spectra of each cycloalkyl methyl ketone was consistent with the structural assignment. Cyclopentyl methyl ketone exhibited an infrared spectrum with $\nu_{max}^{CCl_4}$ 2900 m, 2850 sh, 1720 s, 1450 w, 1425 vw, 1360 m, 1175 w, 1160 w, and 970 cm^{-1} vw. Cyclohexyl methyl ketone exhibited an infrared spectrum with $\nu_{max}^{CCl_4}$ 2900 m, 2850 sh, 1710 s, 1450 m, 1425 vw, 1380 w, 1350 m, 1310 vw, 1290 vw, 1240 w, 1165 m, 960 vw, and 885 cm^{-1} vw. Cycloheptyl methyl ketone exhibited an infrared spectrum with $\nu_{max}^{CCl_4}$ 2900 m, 2850 sh, 1715 s, 1460 m, 1445 m, 1425 sh, 1380 sh, 1360 m, 1265 w, 1235 w, 1165 m, and 950 cm^{-1} w. Cyclooctyl methyl ketone exhibited an infrared spectrum with $\nu_{max}^{CCl_4}$ 2900 s, 2850 sh, 1710 s, 1470 m, 1440 m, 1420 sh, 1380 sh, 1350 m, 1165 m, and 970 cm^{-1} vw.

Competitive Addition of Bromotrichloromethane.—Accurately weighed mixtures of bromotrichloromethane and cyclic olefins (total volume of reactants *ca.* 3.5 ml) were placed in 13 mm o.d. × 100 mm long heavy walled Pyrex ampoules wrapped with aluminum foil to exclude light. The samples were degassed and sealed *in vacuo*. All samples were stored at −10° until irradiated and analyzed. The samples were irradiated in the cobalt-60 facility at −20.5 ± 1° using a cooling bath maintained at this temperature by circulating Dry Ice cooled isopropyl alcohol. Irradiation times were varied to achieve *ca.* 10% conversion of unsaturates. Conversions of cyclopentene in cyclopentene–cyclohexene mixtures were higher (25–29%). The reactivity of each cyclic olefin was determined using cyclopentene as the reference unsaturate rather than cyclohexene. The reaction with cyclohexene is complicated by extensive allylic hydrogen abstraction.

The products from all competitive additions of bromotrichloromethane to cyclic olefins were analyzed by glpc using a SE 30/Chromosorb W column (3 mm o.d. × 1.5 m long) programmed from 35 to 150° at 4°/min with a helium flow rate of 100 cc/min. All glpc analyses were performed in triplicate.

In order to identify the various 1-bromo-2-trichloromethylcycloalkanes (1:1 adducts) individual mixtures of bromotrichloromethane and each cyclic olefin ($[BrCCl_3]/[cycloolefin] = 4$) were prepared. About 2-ml samples were irradiated for 4.0 hr at ambient temperature at 0.0913 Mrad/hr. These reaction conditions resulted in high conversions into the 1:1 adduct with each cyclic olefin except cyclohexene. Identification of each product was accomplished by a combination of nmr, infrared, and mass spectrometry. Samples of each 1:1 adduct for infrared and mass spectral analyses were obtained by trapping glpc separated products. Samples of 1:1 adducts from cyclopentene, cycloheptene, and cyclooctene for nmr analyses were obtained by pumping off the unreacted cyclo olefin and the bulk of the bromotrichloromethane (any remaining $BrCCl_3$ would not interfere with the nmr analyses) from the above reaction products. In order to obtain a sample of 1-bromo-2-trichloromethylcyclohexane for nmr analysis a larger scale reaction was carried out. Bromotrichloromethane, 59.75 g (0.30 mol), and cyclohexene, 6.23 g (0.076 mol), were placed in a 50-ml heavy-walled Pyrex ampoule and degassed and sealed off *in vacuo*. The sample was irradiated for 15.8 hr at 0.0913 Mrad/hr at ambient temperature. The product was distilled at reduced pressure using an 8-in. vacuum-jacketed Vigreux column. The unreacted cyclohexene, chloroform, and bromotrichloromethane were removed at 15 mm. The remainder was distilled at reduced pressure yielding the following three fractions: 2.3 g of 3-bromocyclohexene (0.014 mol), bp 33–35° (1 mm); 1.9 g, bp 42–93° (1 mm); and 10.6 g of 1-bromo-2-trichloromethylcyclohexane (0.039 mol), bp 100–104° (1 mm). The reported boiling point for 1-bromo-2-trichloromethylcyclohexane is 71–73° (0.2 mm).[17] It was demonstrated as glpc that the 1:1 adduct from cyclohexene consisted of two isomers formed in nearly equal amounts.

The mass spectrum of each 1-bromo-2-trichloromethylcycloalkane was consistent with the structural assignment.

The nmr spectral data and assignments are summarized in Table IV. The nmr spectrum of 1-bromo-2-trichloromethylcyclooctane is in good agreement with previously reported spectra.[18] 1-Bromo-2-trichloromethylcyclooctane has previously[18] been shown to be an equimolar mixture of *cis–trans* isomers which are not separable by glpc. The *cis–trans* isomers are characterized by >CHBr absorptions at 4.95 and 4.65 ppm, respectively. In the present study 1-bromo-2-trichloromethylcyclohexane was separated by glpc into two isomers which also were present in equimolar amounts. The nmr spectra of the glpc trapped isomers differed in their >CHBr absorptions. One isomer gave a broad singlet at 5.0 ppm which was assigned to the equatorial hydrogen in the *cis* isomer, while the other isomer exhibited a multiplet at 4.8 ppm due to the axial hydrogen of the *trans* isomer. The relative positions and structures of these absorptions are consistent with those observed for the known equatorial and axial hydrogen absorptions in bromocyclohexane. *cis–trans* isomers have been identified previously from the addition of iodoperfluoroalkanes to cyclohexene.[19] The chemical shift due to the $HCCl_3$ proton appears to vary with ring size. In general, this absorption in all 1:1 adducts occurs further downfield than expected for this proton (expected location *ca.* 2.2 ppm). This shift is attributed to the influence of the bromine atom attached to the adjacent carbon atom. The

(16) Infrared spectra were measured using a Perkin-Elmer Model 21 double-beam recording spectrophotometer with sodium chloride optics. The control settings were resolution, 927; response, 1; gain, 6.5 speed, 5; and suppression, 2. Infrared spectra were recorded of samples as solutions in spectrograde solvents in 0.05-mm sodium chloride microcavity cells (Type D, Barnes Engineering Co.) using a 4X beam condenser. Nmr spectra were measured on a Varian A-60 spectrometer. Gas–liquid partition chromatographs were obtained with an Aerograph Model 350B dual column unit. The relative peak areas were assumed to represent relative per cent by weight. Mass spectra were obtained using a CEC 21-103 mass spectrometer.

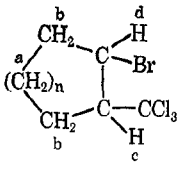
(17) E. I. Heiba and L. C. Anderson, *J. Amer. Chem. Soc.*, **79**, 4940 (1957).

(18) J. G. Traynham and T. M. Couvillon, *ibid.*, **87**, 5806 (1965); J. G. Traynham, T. M. Couvillon, and N. S. Bhacca, *J. Org. Chem.*, **32**, 529 (1967).

(19) N. O. Brace, *ibid.*, **28**, 3093 (1963).

TABLE IV

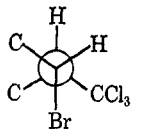
CHEMICAL SHIFT ASSIGNMENTS FOR NMR SPECTRA OF 1-BROMO-2-TRICHLOROMETHYLCYCLOALKANES[a]



	Chemical shift values[b]				
	n[c]				
H	1	2 *trans*	2 *cis*	3	4
a	1.9 } (6)	1.8 } (8)	1.8 } (8)	1.55 } (10)	1.65 (8)
b	2.15 }	2.05 }	2.05 }	1.9 }	2.1 (4)
c	3.65 (1)	3.06 (1)	2.38 (1)	2.1 }	2.8 (1)
d	4.45 (1)	4.8 (1)	5.0 (1)	3.2 (1)	4.65 } (1)
				4.8 (1)	4.95 }

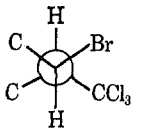
[a] The number of hydrogens is indicated in parentheses. [b] In parts per million from tetramethylsilane. [c] Registry numbers are as follows: n = 1, 17827-32-6; n = 2 (*trans*), 17831-06-0, (*cis*), 17831-07-1; n = 3, 17827-33-7; n = 4, 17827-34-8.

influence of the bromine atom will depend on the distance between the hydrogen and the bromine atom. This distance will be greatest in a conformation where the dihedral angle is 180° as in the *cis* isomer of 1-bromo-2-trichloromethylcyclohexane.



cis

In this conformation the $HCCCl_3$ shift should be nearly normal, and the signal at 2.4 ppm is consistent with this conformation. On the other hand, in the *trans* isomer of 1-bromo-2-trichloromethylcyclohexane, the bromine–hydrogen angle is much smaller and



trans

the $HCCCl_3$ signal is shifted downfield to 3.0 ppm. If one assumed predominant *trans* addition to cyclopentene, Dreiding stereomodels demonstrate that the bromine and hydrogen atoms can be nearly eclipsed, and thus the bromine–hydrogen interaction is greatest giving the largest shift downfield to 3.65 ppm. Apparently in the larger ring 1:1 adducts the greater flexibility with increasing ring size decreases the bromine–hydrogen interaction.

1-Bromo-2-trichloromethylcyclopentane exhibited an infrared spectrum with $\nu_{max}^{CCl_4,CS_2}$ 2950 s, 2875 sh, 1465 w, 1445 s, 1435 sh, 1305 m, 1290 m, 1275 m, 1260 m, 1195 s, 1130 m, 1070 m, 1053 m, 1008 m, 940 w, 900 s, 862 s, 825 w, 790 vs, 760 vs, and 720 cm^{-1} m. *trans*-1-Bromo-2-trichloromethylcyclohexane exhibited an infrared spectrum with $\nu_{max}^{CCl_4,CS_2}$ 2925 s, 2860 sh, 1455 sh, 1445 s, 1335 w, 1320 w, 1295 w, 1255 w, 1235 w, 1195 m, 1078 w, 1040 w, 1020 w, 960 s, 940 w, 906 m, 888 w, 872 w, 860 m, 818 s, 777 vs, 759 vs, and 688 cm^{-1} m. *cis*-1-Bromo-2-trichloromethylcyclohexane exhibited an infrared spectrum with $\nu_{max}^{CCl_4,CS_2}$ 2910 s, 2850 sh, 1460 sh, 1445 s, 1300 w, 1265 w, 1240 m, 1190 s, 1076 m, 1051 m, 952 s, 920 m, 905 m, 856 s, 840 s, 810 w, 775 vs, and 755 cm^{-1} vs. 1-Bromo-2-trichloromethylcycloheptane exhibited an infrared spectrum with $\nu_{max}^{CCl_4,CS_2}$ 2900 s, 2850 sh, 1455 m, 1445 sh, 1430 sh, 1315 w, 1275 m, 1265 m, 1185 s, 1128 w, 1078 w, 1028 m, 1003 m, 968 m, 955 m, 875 w, 858 m, 786 vs, 765 vs, and 728 cm^{-1} m. 1-Bromo-2-trichloromethylcyclooctane exhibited an infrared spectrum $\nu_{max}^{CCl_4,CS_2}$ 2900 s, 2850 sh, 1465 m, 1445 m, 1282 w, 1230 w, 1215 w, 1172 w, 1152 w, 1085 w, 1045 w, 1010 w, 976 w, 961 sh, 915 sh, 903 w, 890 w, 862 w, 840 sh, 832 m, 818 w, 765 vs, and 720 cm^{-1} m.

Competitive Addition of Ethanethiol.—Accurately weighed mixtures of ethanethiol, cyclohexene, cyclooctene, and in some cases chlorobenzene (total volume of reactants *ca.* 3–4 ml) were placed in 13 mm o.d. × 100 mm long heavy-walled Pyrex ampoules wrapped with aluminum foil to exclude light. The samples were degassed carefully and sealed *in vacuo*. All samples were stored at −78° until irradiated and analyzed. It was demonstrated that with these precautions no reaction (thermal or light initiated) occurred in the absence of radiation. Samples were irradiated in the cobalt-60 facility at −78, −21 ± 2, and 53 ± 1°. The reaction proved to be very sensitive to trace amounts of oxygen, and even with careful degassing the level of conversion varied greatly and was difficult to reproduce.

The products from all competitive additions were analyzed by glpc using a SE-30 firebrick column (6 mm o.d. × 1.5 m long) programmed from 40 to 220° at 10°/min with a helium flow rate of 100 cc/min. All glpc analyses were performed in duplicate.

Samples of ethyl cyclohexyl sulfide and ethyl cyclooctyl sulfide for analytical purposes were obtained by irradiating individual mixtures of ethanethiol and each cyclic olefin. A sample of ethanethiol and cyclohexene (R = [ethanethiol]/[cyclohexene] = 4.0) was irradiated for 3 hr at 0.0913 Mrad/hr at 30°. A sample of ethanethiol and cyclooctene (R = 4.5) was irradiated for 20.9 hr at 0.0913 Mrad/hr at 30°. Identification of each 1:1 adduct was accomplished by trapping the glpc separated components and analyzing each one by nmr, mass, and infrared spectrometry. The mass spectra of each ethyl cycloalkyl sulfide was consistent with the structural assignment. The nmr spectrum of ethyl cyclohexyl sulfide was characterized by the following chemical shifts (parts per million from tetramethylsilane): 1.20 (triplet, CH_3–), 1.78 (broad singlet, $-CH_2-$), 2.5 (quartet, $-CH_2S-$), and 2.65 ppm (broad multiplet, –SCH<). The nmr spectrum of ethyl cyclooctyl sulfide was characterized by the following chemical shifts parts per (million from tetramethylsilane): 1.20 (triplet, CH_3–), 1.58 (singlet, $-CH_2-$), 2.48 (quartet, $-CH_2S-$), and 2.75 ppm (broad multiplet, –SCH<). The relative intensities of peaks were consistent with the proposed structures. Ethyl cyclohexyl sulfide exhibited an infrared spectrum with $\nu_{max}^{CCl_4,CS_2}$ 2925 s, 2850 sh, 2650 vw, 1455 s, 1375 w, 1340 w, 1260 s, 1200 m, 1180 w, 1120 w, 997 m, 885 m, 855 w, 820 m, 780 w, 763 w, 745 sh, and 734 cm^{-1} m. Ethyl cyclooctyl sulfide exhibited an infrared spectrum with $\nu_{max}^{CCl_4,CS_2}$ 2925 s, 2850 sh, 2675 vw, 1470 m, 1445 s, 1375 w, 1260 m, 1240 w, 1045 w, 1015 vw, 972 w, 916 vw, 855 vw, 830 vw, 810 vw, 785 vw, 755 w, and 730 cm^{-1} vw.

Registry No.—Cyclopentyl methyl ketone, 6004-60-0; cyclohexyl methyl ketone, 823-76-7; cycloheptyl methyl ketone, 6713-48-0; cyclooctyl methyl ketone, 6713-50-4; ethyl cyclohexyl sulfide, 7133-25-7; ethyl cyclooctyl sulfide, 17827-73-5.

Acknowledgments.—The author wishes to thank Mr. R. E. Thorpe for obtaining and interpreting the mass spectra, and Mr. J. L. Jungnickel for aid in interpreting nmr spectra. The author also acknowledges Dr. C. D. Wagner for helpful discussions which aided in interpreting the kinetic expressions. The capable assistance of Messrs. M. O. Babcock and E. J. Wong is gratefully acknowledged.