Halogen Abstraction Studies. VI. Abstraction of Bromine by Phenyl Radicals from C_3–C_8 Cycloalkyl Mono- and *trans*-1,2-Dibromides[1]

Wayne C. Danen* and Kenneth A. Rose

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

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The rates of abstraction of bromine by phenyl radicals from the cyclic C_3 to C_8 monobromides and *trans*-1,2-dibromides and *meso*- and *dl*-2,3-dibromobutanes relative to the rate of chlorine abstraction from carbon tetrachloride are reported. The rates of bromine abstraction from the cycloalkyl monobromides vary with ring size in a manner similar to that observed for endothermic homolytic and carbonium ion processes which suggests that there is considerable bond breaking in the transition states leading to the cycloalkyl radical intermediates in the present study. A comparison of the monobromide:dibromide rate ratios for the different-sized rings reveals decisive variations depending upon ring size which suggests that anchimeric assistance to bromine abstraction in the dibromides is related to the ease of attainment of a trans periplanar alignment of the adjacent bromine atoms. After correcting for the slight influence of polar effects in the abstraction from 1,2-dibromoethane, it is concluded from the rate data that the 2-bromoethyl radical is stabilized by ~2 kcal/mol relative to the ethyl radical itself.

We have demonstrated in previous papers in this series that the free radical abstraction of a halogen atom is a convenient and unambiguous method of generating a specific free radical for the purpose of studying homolytic processes in organic compounds. In particular, we have elucidated a unique polar effect operative in the homolytic abstraction of a halogen atom,[2] determined the occurrence of neighboring halogen participation in such processes,[3] provided an assessment of the relative rates of formation of various bridgehead radicals,[4] investigated electronic–steric effects in ortho-substituted iodobenzenes,[5] and determined the relative ease of iodine abstraction from the isomeric iodonaphthalenes, iodopyridines, and iodothiophenes.[1a]

We presently wish to report the rates of abstraction of bromine by the phenyl radical from the cyclic C_3 to C_8 monobromides and *trans*-1,2-dibromides (with the exception of 1,2-dibromocyclobutane) relative to the rate of abstraction of chlorine from carbon tetrachloride. Ring size is known to be an important factor influencing the rate of formation of cycloalkyl cations, radicals, and anions.[6] It will be shown that the rate of homolytic bromine removal varies with ring size in a manner which parallels endothermic homolytic and carbonium ion processes. A comparison of the rate ratio for a given cycloalkyl monobromide with the corresponding cycloalkyl 1,2-dibromide reveals decisive differences with ring size which suggest that anchimeric assistance in the dibromides is related to the ease of attainment of a trans periplanar alignment of the adjacent bromine atoms. It is concluded that the 2-bromoethyl radical is stabilized by *ca.* 2 kcal/mol relative to the ethyl radical itself.

Results

The rate data reported in Table I were obtained by the competitive technique employed in our earlier studies in which phenyl radicals were allowed to react with a large excess of both alkyl bromide and carbon tetrachloride. The phenyl radicals were generated by thermal decomposition of phenylazotriphenylmethane at 60.0 ± 0.1° and the k_{Br}/k_{Cl} values were calculated from eq 3. The values for the dibromides were statistically corrected to give the relative rate per bromine atom. The combined yields of chlorobenzene and bromobenzene totaled 20–30% for the monobromides and 60–90% for the dibromides reflecting the enhanced reactivity of the latter; the remainder of the phenyl radicals presumably abstract hydrogen atoms to form benzene. The second bromine is eliminated from the β-bromoalkyl radical generated in the abstraction from the dibromides to give the corresponding olefin which was identified in most cases by glpc retention time with that of an authentic sample and by disappearance of olefin product upon addition of bromine to the reacted solution. The amounts of olefin produced were not determined. With phenylazotriphenylmethane as a precursor to the phenyl radicals the triphenylmethyl radical also produced presumably reaches a reasonably high steady state concentration and serves as a scavenger for the second bromine atom.

$$\mathrm{R{-}Br} + \mathrm{Ph}\cdot \xrightarrow{k_{Br}} \mathrm{R}\cdot + \mathrm{Ph{-}Br} \tag{1}$$

$$\mathrm{CCl_4} + \mathrm{Ph}\cdot \xrightarrow{k_{Cl}} \mathrm{CCl_3}\cdot + \mathrm{Ph{-}Cl} \tag{2}$$

$$k_{Br}/k_{Cl} = [\mathrm{PhBr}][\mathrm{CCl_4}]/[\mathrm{PhCl}][\mathrm{RBr}] \tag{3}$$

Table I
Relative Rates of Bromine Abstraction by the Phenyl Radical from Alkyl and Cycloalkyl Mono- and 1,2-Dibromides at 60°[a]

Monobromides	Registry No.	k_{Br}/k_{Cl}[b]	1,2-Dibromides	Registry No.	k_{Br}/k_{Cl}[b]	k_{di}/k_{mono}[c]
c-C_3H_5Br	4333-56-6	0.035	c-*trans*-$C_3H_4Br_2$	16837-83-5	0.31	8.9
c-C_4H_7Br	4399-47-7	0.18				
c-C_5H_9Br	137-43-9	0.26	c-*trans*-$C_5H_8Br_2$	10230-26-9	1.48	5.7
c-$C_6H_{11}Br$	108-85-0	0.16	c-*trans*-$C_6H_{10}Br_2$	7429-37-0	1.32	8.3
c-$C_7H_{13}Br$	2404-35-5	0.34	c-*trans*-$C_7H_{12}Br_2$	52021-35-9	1.52	4.5
c-$C_8H_{15}Br$	1556-09-8	0.58	c-*trans*-$C_8H_{14}Br_2$	34969-65-8	1.36	2.3
CH_3CH_2Br	74-96-4	0.076	CH_2BrCH_2Br	106-93-4	0.37	4.9
sec-C_4H_9Br	78-76-2	0.24	*meso*-$CH_3CHBrCHBrCH_3$	5780-13-2	1.49	6.2
			dl-$CH_3CHBrCHBrCH_3$	598-71-0	1.22	5.1

[a] Estimated accuracy ±5%. [b] The relative rates are corrected to a per bromine atom per molecule of CCl_4 basis. [c] Ratio of rate of bromine abstraction from dibromide relative to rate from corresponding monobromide.

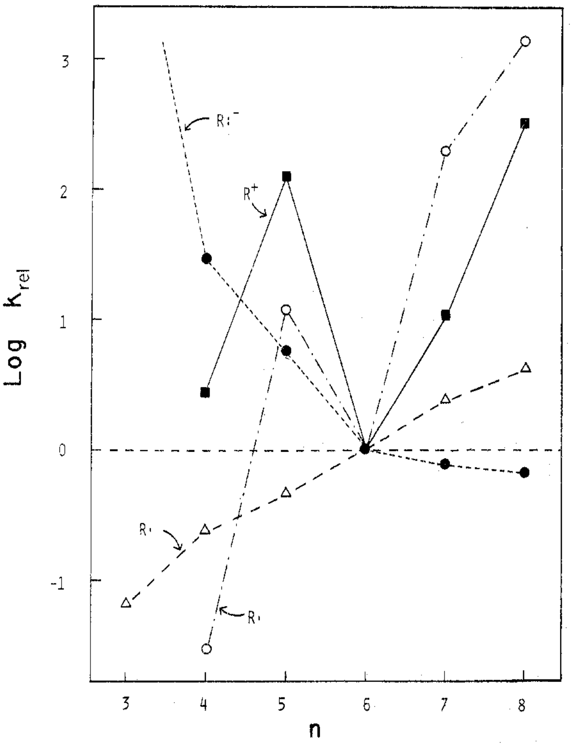


Figure 1. Dependence of ring size (n) on the rate of formation of cyclic carbonium ions, carbanions, and free radicals. (●) Rate of formation of carbanions from reaction of cycloalkanes with cesium cyclohexylamide. (■) Rate of formation of carbonium ions by solvolysis of 1-methylcyloalkyl chlorides in 80% ethanol. (△) Rate of formation of free radicals by thermal decomposition of cycloalkyl peresters. (○) Rate of formation of free radicals by thermal decomposition of cycloalkylazonitriles.

Discussion

(a) Monobromides. From the data in Table I, it is seen that the values of k_{Br}/k_{Cl} of the cycloalkyl monobromides range from 0.035 for cyclopropyl bromide to 0.58 for cyclooctyl bromide, a range of *ca.* 16-fold. However, the reactivities do not follow a regular progression depending on ring size and the rates provide an interesting correlation with data obtained from other reactions performed on the cycloalkane series. Rüchardt[6] has summarized the reaction rate data for several different types of reactions including carbonium ion, free radical, and carbanion processes. The data for the C-3 to C-8 rings are reproduced here (Figure 1).

There are at least three factors competing in the rate of reaction of cyclic compounds: hybridization differences, ring strain, and polar effects. Hybridization differences are expected to be particularly pronounced in the cyclopropyl and cyclobutyl compounds. The relatively high percentage of s character in the exocyclic bonds should facilitate carbanion and retard carbonium ion formation in these small rings. In those carbonium ion and free radical reactions in which the transition state is well along in the reaction coordinate, *i.e.*, in more endothermic reactions, the ring strain effects become more pronounced. This is because the carbon at which the reaction is taking place is going from an sp^3 to an sp^2 hybridization which relieves eclipsing effects in the cyclopentyl ring and transannular interactions in the cycloheptyl and cyclooctyl rings. In the smaller rings, especially the cyclopropyl and cyclobutyl, this rehybridization increases ring strain, thus slowing the reaction. Likewise, cyclohexyl is retarded because the almost perfectly tetrahedral arrangement is disrupted upon forming an sp^2 center. Finally, one would expect the inductive effects of added chain length in the cyclic chain to slow the rate of formation of carbanions and increase the rate of formation of carbonium ions. This effect would be the largest in going from cyclopropyl to cyclobutyl and cyclopentyl compounds and would be considerably attenuated for the larger rings. These effects are expected to be relatively small although the electronegativity differences resulting from hybridization changes can also influence polar effects.

From Figure 1 it is seen that hybridization-electronegativity effects predominate in the formation of the cyclic carbanions while ring strain effects have a pronounced effect on the formation of carbonium ions. Free radical reactions can be correlated with these effects depending upon the extent of radical character developed in the transition state. For an exothermic reaction the transition state comes early in the reaction and is structurally more similar to starting material than product according to the Hammond postulate. If polar effects are not significant an exothermic radical reaction should correlate with the carbanion reaction in Figure 1. Conversely, endothermic reactions should feel the effects of ring strain as the transition state will have considerable radical character developed and hence should correlate with the carbonium ion reactions.

In the homolytic decomposition of peresters the hybridization and polar effects appear to predominate with the rate decreasing roughly as the electronegativity of the ring carbon increases suggesting an early transition state with little radical character. However, a rigorous interpretation of these data is difficult. Two extreme mechanisms involving either one-bond or two-bond homolysis have been postulated for perester decompositions and it is possible that there is a change in the amount of radical character developed on the cycloalkyl group in the transition state depending upon ring size. The endothermic azo decomposition reaction, however, closely parallels the carbonium ion reaction, indicating a transition state late enough along the reaction coordinate to feel ring strain effects. Smith and Mead[7] have recently determined the rates of amine oxidation for a series of N-methyl nitrogen heterocycles. The results closely paralleled the decomposition of azo compounds showing the importance of ring strain effects in the transition state leading to the planar[8] aminium radical cations.

The rates of bromine abstraction from the C_3 to C_8 monobromides relative to cyclohexyl bromide are plotted in Figure 2. The values obtained are seen to correlate with the carbonium ion and azo decomposition reactions although the rate differences relative to the six-membered ring are much smaller in magnitude. According to Rüchardt's arguments, this suggests considerable bond breaking in the transition state leading to the cycloalkyl radical intermediate.

Although the abstraction of a bromine by a phenyl radical is a mildly exothermic reaction ($\Delta H = -3$ kcal/mol for abstraction from isopropyl bromide[9]) the transition state must be coming late enough along the reaction coordinate to allow ring strain effects to influence the rates of the reaction. From polar effects alone one might expect the trend to follow that of the formation of a carbanion since it has been shown that halogen abstraction reactions exhibit a positive ρ value and are accelerated by electron-withdrawing substituents.[2,3] These results also closely parallel the trend found in the abstraction of hydrogen from the cycloalkanes C_5 through C_8 by the phenyl radical reported by Bridger and Russell,[10] although the rate differences for bromine abstraction are about half again larger in magnitude relative to the six-membered ring than in the hydrogen abstraction reaction (ΔH = *ca.* -9.5 kcal/mol[9]). A re-

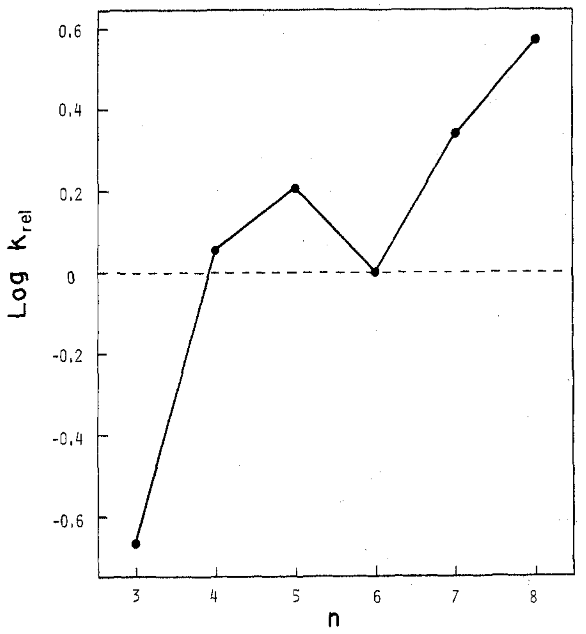


Figure 2. Dependence of ring size (n) on the rate of abstraction of bromine from cycloalkyl bromides by phenyl radicals at 60°.

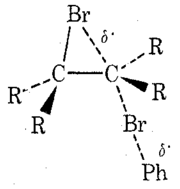
cent study by Bunce and Hadley shows similar trends.[31]

(b) 1,2-Dibromides. The rates of bromine abstraction from *trans*-1,2-dibromides reported in Table I were all considerably faster than the rates for the corresponding monobromides. We have concluded in a previous study[3] that the bromine atom in 1-iodo-2-bromoethane enhances the rate of iodine abstraction by a favorable polar effect influence as well as by anchimeric assistance. In the 1,2-dibromides of the present study the second bromine atom, like other electron-withdrawing substituents, enhances the rate of halogen abstraction because of a polar effect. From eq 4 it

$$\overset{\delta^+}{R}—\overset{\delta^-}{Br} + \cdot Ph \longrightarrow \left[\overset{\delta\delta\cdot+}{R}\text{-----}\overset{\delta^-}{Br}\text{-----}\overset{\delta\delta\cdot+}{Ph}\right]^{\dagger} \longrightarrow R\cdot + \overset{\delta^-}{Br}—\overset{\delta^+}{Ph} \quad (4)$$

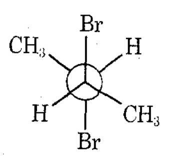
can be seen that the carbon atom to which bromine is bonded in the original alkyl bromide is somewhat electron deficient at the onset of homolytic bromine removal because of the polarized C–Br bond resulting from the inductive effect of the electronegative bromine and that this carbon atom acquires an increased amount of electron density in the transition state relative to the ground state. It has been observed in both aromatic[2] and aliphatic[3] iodides that electron-withdrawing groups enhance and electron-donating groups retard the rate of iodine abstraction by phenyl radicals and that the substituent effects can be correlated reasonably well with the Hammett and Taft relationships, respectively. For 1-iodo-2-bromoethane, however, the rate of iodine abstraction was still 90% faster than that expected based only on polar effect considerations; this enhancement was attributed to anchimeric assistance to removal of the iodine by the adjacent bromine. The present results on the *meso*- and *dl*-2,3-dibromobutanes and *trans*-1,2-dibromocycloalkanes support this conclusion and lend further insight into the stereochemical aspects of neighboring bromine participation.

It is generally accepted that anchimeric assistance by a neighboring bromine atom occurs most readily through an antiperiplanar arrangement of atoms[11] similar to the preferred orientation for an ionic E2 elimination process. It should be noted, however, that some of the data cited as evidence for homolytic anchimeric assistance has been questioned[12] and some controversy has enshrouded the topic although the most recent work of Skell and coworkers[11] and others[13] appears quite definitive and should suffice to lay this controversy to rest. In addition, there is considerable evidence from electron spin resonance studies that an adjacent chlorine,[14] bromine,[15] or iodine[15] atom (as well as sulfur, silicon, germanium, tin, phosphorus, and arsenic groups[16]) exhibits a preferred conformational orientation in which the heteroatom eclipses the p orbital of the radical center. Although the precise mode of interaction of the heteroatom with the unpaired electron is not fully understood, the results indicate that these radicals do not possess truly symmetrically bridged structures (the results for β-Br and I are not definitive in this regard) but that the interaction of orbitals is sufficient to cause hindered internal rotation about the C_α–C_β bond. This interaction must be stabilizing and the reduction in energy of the product radical should exert itself in the transition state leading to formation of the radical. It might also be pointed out that the controversy over the importance of anchimeric assistance in bromination studies stems largely from attempting to relate ratios of products possibly formed *via* several competing pathways with the rates of initial abstraction of hydrogen. Such complications are not inherent in the present study since the value of k_{Br}/k_{Cl} is a function only of the rate of abstraction of bromine from the substrate molecule.

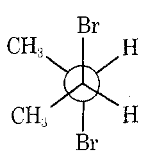


If anchimeric assistance by a β-bromine is equally effective for all the 1,2-dibromides investigated in this study, then the ratio of rates for bromine abstraction from a dibromide relative to the rate of abstraction from the corresponding monobromide, k_{di}/k_{mono}, should be reasonably constant. The last column in Table I illustrates that this ratio varies considerably from a high of 8.9 for the cyclopropyl compounds to a low of only 2.3 for the cyclooctyl bromides. We believe that the variation in this ratio reflects the relative importance of anchimeric assistance to abstraction of bromine for each dibromide since the enhancement in rate due to a polar effect should be similar for all the dibromide–monobromide pairs. It can be shown that the ratio varies qualitatively with the relative population of that conformation for each 1,2-dibromide in which the two bromine groups are antiperiplanar to each other.

Consider the *meso*- and *dl*-2,3-dibromobutanes. The lowest energy conformation of the meso isomer is that in which the bromines are trans to each other, whereas the conformation of the *dl* isomer which has the bromines trans requires the CH_3 groups to be gauche to each other, a somewhat higher energy conformation. This results in a faster rate of bromine abstraction for the meso isomer as compared to the *dl* compound since the β-bromine in the former compound is better aligned to contribute to lowering the activation energy barrier for abstraction. A similar



meso



dl

mode of reasoning can account for the relatively small difference of 4.9 in the rate of abstraction of bromine from 1,2-dibromoethane as compared to ethyl bromide. A significant proportion of molecules of 1,2-dibromoethane exists in the less reactive gauche conformation in solution since the difference in energy between the trans and the gauche isomers is only 0.7 kcal/mol.[17] On the other hand, the rigidity of the three-membered ring and the relatively wide Br–C–H angles in *trans*-1,2-dibromocyclopropane (HCH angle = 115.12° in cyclopropane[18]) place the two bromine atoms in an alignment approaching the optimal trans arrangement accounting for the enhanced dibromo:monobromo ratio of 8.9. Likewise, in *trans*-1,2-dibromocyclopentane the flexibility of the five-membered ring allows for various conformations but it has been determined that the two bromines exist >90% in the diaxial form.[19] Similarly, *trans*-1,2-dibromocyclohexane is known to exist as an equilibrium mixture of diaxial and diequatorial conformers in an essentially equimolar proportion.[20] The diaxial conformation is perfectly aligned, of course, for assistance by the adjacent bromine and an enhancement in rate of 8.3 over that observed for bromocyclohexane results. From Table I it may be noted that the dibromo:monobromo ratio drops rather significantly for the cycloheptyl and, particularly, the cyclooctyl compounds. This is in accord with conformational studies on *trans*-1,2-dibromocyclooctane in which it was concluded that there is a significant population of conformations having the bromines in a "diequatorial" arrangement.[21] An inspection of molecular models suggests that transannular interactions increase as the bromines approach an anti conformation.

Although variation in k_{di}/k_{mono} ratios for the various cycloalkyl di- and monobromides can be qualitatively rationalized as reflecting the relative populations of conformations in which the two bromines in the dibromides approach a trans alignment, this reasoning should not be overextended. In particular, free radical hydrogen bromide additions to 1-bromocycloalkenes were observed to be trans-stereospecific suggesting the intermediacy of a bromine-bridged radical but alteration of the ring size made the additions monostereospecific.[22] Stereoselectivity decreased in the order $C_6 > C_5 > C_7 > C_4$ and it has been suggested[23] that the stability of the bromine-bridged radicals (probably not symmetrically bridged) relative to the classical radicals may be altered by strain. Extension of this reasoning would suggest that the cyclopropyl system would produce the most strained intermediate which is not reflected in the high k_{di}/k_{mono} value in the present study. The addition of HBr to a 1-bromocycloalkene and the abstraction of bromine from a *trans*-1,2-dibromocycloalkane differ significantly, however, and perhaps are not comparable. The former requires a bridged-bromine radical intermediate to abstract hydrogen from HBr to produce a *cis*-1,2-dibromocycloalkane whereas the present study involves removal of a bromine atom from a *trans*-1,2-dibromocycloalkane.

An alternate explanation of our data cannot be ruled out.[32] It is observed that the k_{Br}/k_{Cl} values for the 1,2-dibromides listed in Table I are reasonably constant except for the cyclopropyl and ethyl systems. If assistance by neighboring bromine is significant, it is plausible that this factor is dominant over conformational effects for all the secondary systems except cyclopropyl and the k_{di}/k_{mono} ratios thus reflect mainly on reactivity differences among the monobromides where conformational effects appear to be more important. The cyclopropyl and ethyl systems react slower in both series presumably due to C–Br bond strength considerations.

It may be noted that a crucial feature of either of the above explanations of the k_{di}/k_{mono} data is the involvement of anchimeric assistance by the neighboring bromine for the 1,2-dibromides.

In our previous work we concluded that a concerted elimination of the β-bromine was probably not responsible for the enhanced rate of iodine abstraction from 1-bromo-2-iodoethane.[3] The present results confirm this conclusion. The k_{di}/k_{mono} value of 8.9 for the cyclopropyl pair is the largest observed in the present work yet the elimination of β-bromine from the 2-bromocyclopropyl radical should be the least favored. Heat of formation data indicate an increase of 25.4 kcal/mol in ring strain in going from cyclopropane to cyclopropene whereas there is a loss of ring strain for the cyclopentyl through cyclooctyl counterparts.[24]

(c) Estimate of Stabilizing Influence of β-Bromine Substituent. It was concluded in the above section that a β-bromine substituent can stabilize a radical center although the precise mode of this stabilization is not yielded by these studies. It would seem important to be able to obtain an estimate of this stabilizing influence. Krusic and Kochi have obtained barriers to rotation in alkyl radicals of 1.2, 1.6, and 2.0 kcal/mol for the β substituents Si, Ge, and Sn, respectively.[16a] A barrier as high as 5 kcal/mol was noted for Sn in the adduct of tributylstannyl radical to butadiene.[16c] Alternatively, the stabilization energy in the 2-bromoethyl radical due to interaction of the unpaired electron with the β-bromine substituent may be defined as $D(CH_3CH_2–H) - D(BrCH_2CH_2–H)$.[25] We have observed in previous studies that the abstraction of iodine from β-bromoethyl iodide is *ca.* 90% faster than the expected rate after correcting for inductive effects.[3] From this rate enhancement an estimate of the stabilizing influence of the β-bromine can be calculated since there is an excellent correlation between the rate of abstraction of iodine from aliphatic iodides and the respective thermodynamic C–H bond dissociation energies, providing the kinetic k_I/k_{Br} values are first corrected for the slight polar effects of the groups attached to the carbon from which the iodine is abstracted.[4] Knowing the k_I/k_{Br} abstraction rate of an alkyl iodide, it is possible to obtain its D(C–H). By calculating the D(C–H) for $BrCH_2CH_2–H$ and comparing it with the known D(C–H) for $CH_3CH_2–H$, a stabilization of 2.1 kcal/mol is obtained for the 2-bromoethyl radical relative to the ethyl radical itself.

A similar analysis utilizing k_{Br}/k_{Cl} data of the sort obtained in the present study yielded a bond dissociation energy for $BrCH_2CH_2–H$ of 96.1 kcal/mol which is lower than the D(C–H) of ethane by 1.9 kcal/mol in good agreement with the estimate from the k_I/k_{Br} data. The same treatment was applied to allyl bromide as a check on the validity of this method. From the k_{Br}/k_{Cl} value of 2.43 for allyl bromide a resonance energy of *ca.* 8 kcal/mol is estimated. This compares with a value of *ca.* 10 kcal/mol determined by other workers.[25] It appears, then, that this Polanyi type of relationship is capable of yielding at least semiquantitative estimates of stabilization energies although the true values may be underestimated somewhat possibly because of the inherent assumption of a constant ΔS^* for the reactions. In this regard, Skell, *et al.*, reported a $\Delta\Delta H^* = -3.4$ kcal/mol and a $\Delta\Delta S^* = -7.2$ eu for the β-hydrogen of 1-bromobutane relative to the α hydrogen for reaction with Br atoms and interpret the differences as resulting from bromine bridging.[11a] Thus, we conclude that a β-bromine stabilizes a radical site to the extent of *ca.* 2.0 kcal/mol although this value might underestimate the stabilization somewhat.

Experimental Section

Kinetic analysis were performed as described previously.[3]

Bromocyclopropane, bromocyclobutane, bromocyclopentane, bromocyclohexane, bromoethane, 2-bromobutane, 1,2-dibromoethane, and allyl bromide were commercially available and purified by vacuum distillation if deemed necessary by glpc analysis.

Bromocycloheptane was synthesized by adding anhydrous HBr to cycloheptene following the general procedure of Mozingo and Patterson.[26] To a solution of 0.2 mol of cycloheptene in anhydrous ether in a round-bottom flask wrapped in aluminum foil was added a slight excess of dry HBr from a gas cylinder, keeping the temperature below 5°. The reaction was allowed to stir for 20 hr. As much of the unreacted cycloheptene as possible was removed by vacuum distillation. The remaining cycloheptene was brominated by saturating with Br_2, washed with 10% $NaHSO_3$ and water, and dried, and the bromocycloheptane was obtained by distillation at 26–26.5° (0.3 mm), yielding a product >99% pure by glc and containing no detectable dibromide. This compound was very sensitive to thermal decomposition, and glpc injection port temperature and distillation pot temperatures were kept below 80°. Commercially obtained bromocycloheptane was found to contain *ca.* 10% low-boiling impurities and attempted purification by spinning band distillation at reduced pressures was unsuccessful due to thermal decomposition.

Bromocyclooctane was synthesized in a similar manner from cyclooctene. Since this compound was also quite susceptible to thermal decomposition, attempts to distill the product only yielded more impurities. The major reaction impurity was cyclooctene which was removed by washing with 85% H_2SO_4 at 5 ° following the procedure of Cope, Brown, and Woo.[27] Other low-boiling components of the mixture were removed by distillation at 50° (0.3 mm), leaving bromocyclooctane that was >99% pure by glpc.

meso- and *dl*-2,3-dibromobutane were prepared from *trans*- and *cis*-2-butene, respectively, by bubbling the butene through a 0.1 mol solution of Br_2 in CCl_4. The exothermic reaction occurred quite fast and the bromine color was discharged in 15 min. The CCl_4 was removed on a rotary evaporator and the product distilled at 29–30° (5 mm). Analysis by glpc showed each isomer >99% pure, the only detectable impurity being the other diasteriomer.

trans-1,2-Dibromocyclopropane was prepared by addition of Br_2 to cyclopropene in CH_2Cl_2. The cyclopropene was generated by the method of Closs and Krantz[28] using 22 ml (0.4 mol) of allyl bromide and 16 g (0.4 mol) of sodium amide rather than allyl chloride as reported. The higher boiling allyl bromide gave better results with less allyl compound as contaminate in the product. The cyclopropene generated escaped through the condenser as it was formed and was bubbled into 5.8 g (0.4 mol) of Br_2 in CH_2Cl_2. The CH_2Cl_2 was removed by fractional distillation and the product collected by glc and identified by nmr spectroscopy.[29]

trans-1,2-Dibromocyclopentane, -cyclohexane, -cycloheptane, and -cyclooctane were prepared by the slow addition of the respective cycloalkene to a solution of bromine (*ca.* 0.3 mol) in CCl_4 until the bromine color was just discharged. The solutions were then fractionally distilled at atmospheric pressure to remove the CCl_4 and any unreacted cycloalkene, and then were vacuum distilled utilizing either a Vigreux or spinning band distillation apparatus: *trans*-1,2-dibromocyclopentane (bp 53–56° (4.5 mm)); *trans*-1,2-dibromocyclohexane (bp 55–57° (0.4 mm)); *trans*-1,2-dibromocycloheptane (bp 42–46° (0.1 mm)); *trans*-1,2-dibromocyclooctane (bp 71–73° (0.1 mm)). All products were determined to be >99% pure by glpc although all the dibromides were found to be quite sensitive to injection port temperature.[30]

Registry No.—HBr, 10035-10-6; cycloheptene, 628-92-2; cyclooctene, 931-88-4; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; bromine, 7726-95-6; cyclopropene, 2781-85-3; cyclopentene, 142-29-0; cyclohexene, 110-83-8.

References and Notes

(1) (a) For paper V in this series, see W. C. Danen, D. G. Saunders, and K. A. Rose, *J. Amer. Chem. Soc.*, **96**, 4558 (1974). (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

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