

RELATIVE RATES OF ABSTRACTION OF HALOGEN BY PHENYL RADICALS FROM
CYCLOALKYL BROMIDES, CYCLOALKYL TRANS-1,2-DIBROMIDES,
AND SELECTED AROMATIC IODIDES

by

KENNETH ALLEN ROSE

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Approved by:

Wayne C. Allen
Major Professor

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TABLE OF CONTENTS

	page
LIST OF TABLES	iv
LIST OF FIGURES.	v
PART I: RATE ACCELERATION DUE TO β -BROMINE IN HALOGEN ABSTRACTION REACTIONS OF ALKYL DIBROMIDES	1
INTRODUCTION.	1
BACKGROUND.	2
Hydrogen Abstraction Reactions	2
Halogen Abstraction Reactions.	6
Spectroscopic Studies Pertaining to β -Bromoalkyl Radicals. . .	9
OBJECTIVES.	13
RESULTS	13
DISCUSSION.	16
Abstraction of Bromine from Cyclic Mono- and 1,2-Dibromides. .	16
Stability of the β -Bromoethyl Radical.	27
CONCLUSIONS	34
EXPERIMENTAL.	36
General.	36
Syntheses.	36
Kinetic Analyses	42
PART II: LACK OF IODINE AND SULFUR ANCHIMERIC ASSISTANCE IN THE FORMA- TION OF SELECTED ARYL RADICALS	45
INTRODUCTION.	45
Section A: Lack of Iodine Migration in Thermal Decomposition of 2-Iodo-4-methylphenylazotriphenylmethane.	45
BACKGROUND	45

	page
RESULTS.	49
DISCUSSION	53
CONCLUSIONS.	55
EXPERIMENTAL	56
Section B: Lack of Anchimeric Assistance by a Neighboring Sulfide in Iodine Abstraction from 2-Iodo-2'-methylthiobiphenyl	57
RESULTS.	58
DISCUSSION	58
EXPERIMENTAL	60
BIBLIOGRAPHY	62
ACKNOWLEDGEMENTS	66
VITA	67

LIST OF TABLES

	page
TABLE I Relative Rate of Bromine Abstraction by the Phenyl Radical from Alkyl Mono- and Dibromides	15
TABLE II Relative Rate of Amine Oxidation in Nitrogen Heterocycles (N-Methylpiperidine = 1.0)	24
TABLE III Relative Rate of Bromine Abstraction by Phenyl Radical from Cycloalkyl Bromides (Cyclohexyl Bromide = 1.00)	25
TABLE IV Polar Substituent Constants and the Relative Rates of Abstraction of Bromine from Substituted Alkyl Bromides	30
TABLE V Relative Rates of Bromine Abstraction Corrected for Inductive Effects and the Respective C-H Bond Dissociation Energies for Some Alkyl Bromides	32
TABLE VI Composition and Absorbance of Standard Solutions for Infrared Calibrations	52
TABLE VII Products of IMPAT Decomposition in CCl_4	54
TABLE VIII The Rates of Abstraction of Iodine from 2-Iodo- and 2-Iodo-2'-methylthiobiphenyl by the Phenyl Radical	59

LIST OF FIGURES

	page
Figure 1. Dependence of the rate of formation of cycloalkyl carbonium ions, carbanions, and radicals on the ring size.	21
Figure 2. Dependence of the rate of abstraction of bromine from cycloalkyl bromides and <u>trans</u> -1,2-dibromides on the size of the ring.	26
Figure 3. Plot of $\log k_{\text{Br}}/k_{\text{CCl}_4}$ for the primary iodides RCH_2Br versus the Taft polar substituent constant σ^* .	31
Figure 4. Plot of log of relative rate corrected for inductive effects for R-Br vs. the respective C-H bond dissociation energies.	33
Figure 5a. IR spectra of m- & p-iodotoluene.	51
Figure 5b. IR spectrum of iodotoluene product from decomposition of IMPAT.	51

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Part I: Rate Acceleration Due to β -Bromine in Halogen Abstraction
Reactions of Alkyl Dibromides

INTRODUCTION

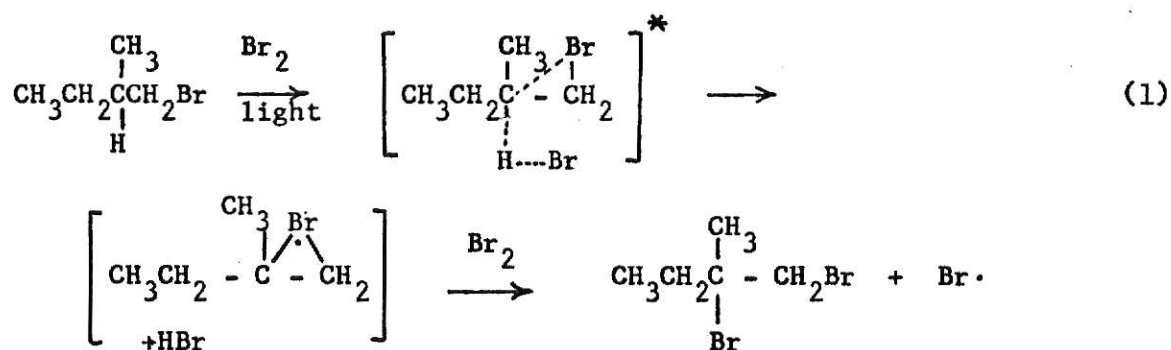
The free radical addition of HBr to an olefin is a stereoselective trans addition process. The first authors to ascribe this stereochemical control to a bridged bromine radical intermediate were Goering and co-workers.¹ The addition of HBr to 1-bromocyclohexene and 1-methylcyclohexene catalyzed by benzoyl peroxide or ultraviolet light gave cis-1,2-dibromocyclohexane and cis-1-methyl-2-bromocyclohexane, respectively. This work has led to an abundance of literature dealing with certain effects of polar substituents β to a radical site; namely the anchimeric assistance effect in abstraction reactions, the directing effects in addition reactions, and more recently analysis of the configuration of these intermediates by spectroscopic techniques. It is the anchimeric assistance effects of bromine that we are most concerned with here, although other effects will be discussed where appropriate.

In homolytic reactions anchimeric assistance is the homoconjugative donation of vacant p or low-lying d orbitals from an atom beta to a radical center, thus delocalizing the unpaired electron. This stabilizes the transition state leading to the radical intermediate and increases the rate of reaction. In abstraction reactions significant rate differences are observed when atoms such as bromine, iodine, or sulfur are substituted on the carbon adjacent to the incipient radical.

BACKGROUND

Hydrogen Abstraction Reactions

In 1963 Thaler² found that the photobromination of alkylbromides occurs preferentially at the vicinal positions. For example photobromination of cyclohexyl bromide gave trans-1,2-dibromocyclohexane in 94% yield. Independent studies by Skell and co-workers³ in 1963 demonstrated that not only is the vicinal hydrogen preferentially abstracted, but that the stereochemical integrity of the vicinal position is maintained. The liquid phase photobromination of (+)-1-bromo-2-methylbutane ($\alpha_{\text{obs}}^{27} = +4.89^\circ$) at 0° yielded (-)-1,2-dibromo-2-methylbutane ($\alpha_{\text{obs}}^{27} = -2.86^\circ$) as shown in equation 1.

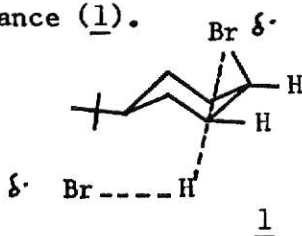


These results indicated that not only can bromine assist in the abstraction process but can also maintain the stereochemical configuration at the asymmetric center until reaction occurs with molecular bromine. The authors explained these results in terms of a bridged bromine radical as shown above. In a competitive photobromination study of cis- and trans-4-bromo-t-butylcyclohexane Skell and Readio⁴ found no detectable loss of the trans-bromide, whereas 79% of the cis-bromide had reacted to give trans-3-cis-4-dibromo-t-

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butylcyclohexane as the major product. The bulky t-butyl group can reside only in an equatorial conformation of the cyclohexane ring which locks the bromine in an axial position in the cis-bromide and in the equatorial position in the trans-bromide. It is only when in the axial position that the bromine is available for back-side anchimeric assistance in the transition state. Since the cis-bromide reacted much faster than the trans-bromide, a trans co-planar arrangement of atoms was thought to be necessary for optimum anchimeric assistance (1).

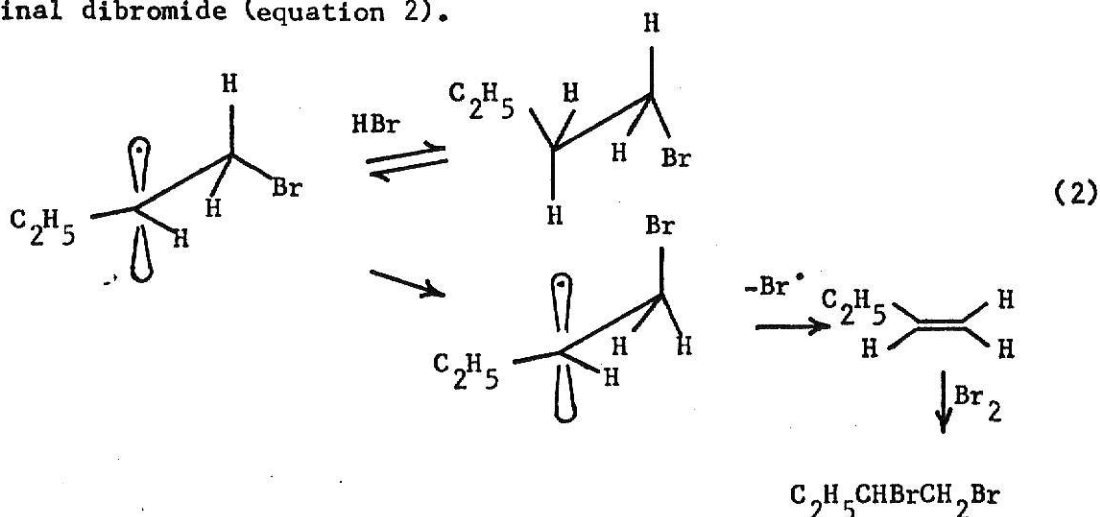


Other workers demonstrated that 1-bromobutane^{2,5} and trans-1-(bromo-methyl)-4-methylcyclohexane⁶ also gave remarkably high yields of the corresponding vicinal dibromides in photobromination reactions.

For a hydrogen atom β to an electronegative element such as bromine to be the most easily abstracted hydrogen is contrary to the theory that electronegative attacking radicals prefer positions of high electron density and preferentially abstract hydrogens from carbon atoms which are the furthest from the electron withdrawing substituents.^{5,7-9} For example, a hydrogen at the 3-position of 1-bromobutane is 0.37 times as reactive to photobromination as that of a secondary hydrogen of propane. One would predict that the reactivity at the 2-position of 1-bromobutane should be further reduced by a factor of at least 0.37.¹⁰ Thus the 2-position should be $0.37 \times 0.37 = 0.14$ times as reactive as propane. The observed relative rate of bromination at the 2-position of 1-bromobutane in the bromination of propane at 30° is 2.5, which becomes 18 when corrected for inductive effects.¹¹

How then does one explain the high reactivity of the β position?

This reactivity has traditionally been ascribed to a lowering of the transition state energy of the incipient radical by a homoconjugative donation of bromine d orbitals to the radical center, i.e., formation of a bridged bromine intermediate.^{12,7} This explanation, however, has been attacked by Tanner¹³⁻¹⁵ and questioned by Walton.¹⁶ Tanner^{13a} observed that when 1-bromobutane was brominated with molecular bromine or with N-bromosuccinimide and the reaction stopped at various stages prior to completion, different isomer distributions were obtained. Early in the reaction process the 1,3-dibromobutane was formed preferentially and it wasn't until the reaction was ca. 25% complete that the 1,2-dibromide exceeded the 1,3-dibromide. At the completion of the reaction the isomer distribution agreed with that obtained by Thaler,² Skell,⁴ and Traynham.⁶ Addition of HBr to the molecular bromine reaction gave predominantly the 1,2-dibromide even early in the reaction. Thus Tanner suggested that as the reaction progressed, the buildup of HBr affected the reaction by a reversible reaction with the β -bromo radical, as shown below. When the bromine was in the proper orientation with the radical p orbital, β -scission occurred producing an olefin which reacted rapidly with molecular bromine to produce the vicinal dibromide (equation 2).



Tanner claimed this mechanism accounted for the high proportion of the 1,2-dibromide at the completion of the reaction. Ashton, et al.,¹⁴ produced similar results for the bromination of 1-bromobutane and bromocyclohexane, and also produced evidence for 1-butene and cyclohexene in the reaction mixtures.

Attempts to verify the results of Tanner and Ashton, however, have thus far been unsuccessful. Skell and Shea¹¹ demonstrated that the ratio of 1,3/1,2 dibromides ranged from 0.15 to 0.29 at 60°C for a wide variety of reaction conditions in the photobromination of 1-bromobutane. The final HBr concentration ranged from 0 to 1.5 M for these reactions. Not once did the 1,3-dibromide exceed the 1,2-dibromide.

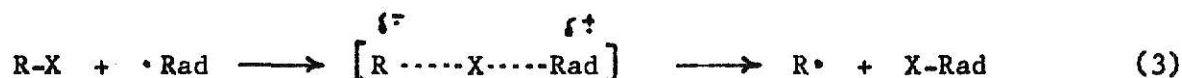
Traynham, et al.,¹⁵ obtained results for photobromination of 1-bromobutane which gave ratios of products virtually identical to Skell's. He found no substantial variation in isomer ratio from 1.7% conversion to 99.8% at 60°C, a result that is in direct conflict to Tanner's results. However, when reaction was attempted using photoiniated N-bromosuccinimide bromination of 1-bromobutane, a change in isomer distribution with time was observed, and the reaction proceeded more slowly. The isomer distribution obtained agreed qualitatively with Tanner's bromination with N-bromosuccinimide. Thus there seems to be a variance in the relative reactivities of N-bromosuccinimide, HBr, and molecular bromine in such bromination reactions. Skell recently obtained a rough estimate of the relative reactivities of molecular bromine and DBr ($k_{Br_2}/k_{DBr} = \text{ca. } 9-14$).¹⁶ He also observed that k_{HBr} is approximately 50% greater than k_{DBr} . Thus it appears that the β -bromoalkyl radical reacts with molecular bromine faster than it can abstract hydrogen from HBr.

The photobromination of 1-bromobutane in carbon tetrachloride was performed by Ronneau, et al.,¹⁷ using essentially the same reaction conditions as Tanner^{13(a)} but using 1-bromobutane that was radioactively labeled with Br⁸² as starting material. The inorganic products (HBr and Br₂) were isolated from the reaction mixture and trapped by potassium hexacyanoferrate(II) and analyzed, revealing only 3% of total activity. This low yield of activity in the inorganic products was maintained even when the reaction was allowed to proceed to large extents. This result clearly does not substantiate the mechanism proposed by Tanner in which the β -bromoalkyl radical decomposed to free olefin and a bromine atom, although this result could be reconciled to a later modified mechanism^{13(b,c)} in which Tanner suggested a cage elimination-readdition process. Ronneau also reported the ratio of dibromides 1,2/1,3 as being 5.0 and in the 1,2-dibromide the Br⁸² activity was distributed with only 10% at the 2-position but 90% at the 1-position. The cage elimination-readdition process would have to be a very tight cage process to accommodate this activity distribution.

Halogen Abstraction Reactions

Although much work has been published concerning homolytic hydrogen abstraction reactions, there is a paucity of information concerning the nature of halogen abstraction processes. Many hydrogen abstraction reactions by various free radicals have been successfully correlated with σ or σ^+ , and all such reactions occur more readily if electron-donating substituents are present, thus exhibiting a negative ρ value.¹⁸ However, Danen and co-workers in their studies of iodine abstraction reactions with

the phenyl radical successfully correlated a series of aryl iodides with the Hammett σ constants¹⁸ and a series of alkyl iodides with the Taft polar substituent constant σ^* .¹⁹ Both correlations gave a positive ρ value. Kuivila²⁰ also reported a positive ρ value in his abstraction of chlorine from aromatic acid chlorides and unsaturated bromides by the tri-*n*-butyltin radical. These results indicated that the charge distribution in the transition state of halogen abstraction reactions must involve anionic character on the carbon from which the halogen is being removed (equation 3). It should be emphasized,



however, that such a transition state description does not necessarily imply buildup of excess electron density on the carbon in the transition state but only that this atom acquires an increased amount of electron density relative to the ground state. It is possible that electron donating substituents stabilize the ground state and electron withdrawing groups destabilize the ground state while neither type strongly perturbs the transition state. The charge distribution is reversed in hydrogen abstraction reactions. Electron withdrawing substituents stabilize this anionic character in the transition state, thus enhancing the rate of halogen abstraction. Thus the rate of abstraction of bromine from vicinal alkyl dibromides should be faster than from unsubstituted alkyl bromides from polar considerations alone, neglecting any anchimeric assistance effects. Indeed the rate of abstraction of iodine by the phenyl radical from 2-bromo-1-iodoethane was expected to be ca. 60% faster²¹ than the abstraction of iodine from iodoethane due to the polar effect of the neighboring bromine. However, the actual rate turned out to

be ca. 150% faster than iodoethane, of which 90% was attributed to anchimeric assistance by the β bromine in the transition state.

Not only is anchimeric assistance by a β bromine observed in halogen abstraction reactions, but there is also a stereochemical effect exhibited in the dehalogenation of vicinal dibromides.

The first authors to propose a bridged bromine radical in dehalogenation reactions were Kray and Castro.²² The dehalogenation of vicinal dibromides by chromous sulfate in aqueous dimethylformamide at room temperature gave olefins with a quite high degree of stereochemical control. The rate of abstraction of bromine from vicinal dibromides was substantially faster than the abstraction from monobromides.

Kochi and Singleton substantiated these results²³ and showed that the reductive dehalogenation process with chromous sulfate is a two-step process, and that a β bromine greatly enhanced the rate of reaction. For example in 85% dimethylformamide containing 5% H_2O and 10% ethanol and 0.9 M perchloric acid at 0° the rate of bromine abstraction from meso-2,3-dibromobutane was 1.1×10^4 faster than abstraction from 2-bromobutane. Both the anchimeric assistance and the stereoselectivity of these reductive elimination reactions were thought to be due to a bridged bromine radical intermediate.

Using the tri-n-butyltin radical to abstract bromine from vicinal dibromides Kuivila and co-workers showed that the olefins which are produced are the result of an anti elimination.²⁴ For example debromination of meso-2,3-dibromobutane at 25° resulted in 90% trans-2-butene and 10% cis-2-butene, and debromination of dl-2,3-dibromobutane gave 34% trans-2-butene and 66% cis-2-butene. The stereoselectivity of the reaction increased as the

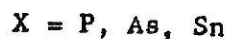
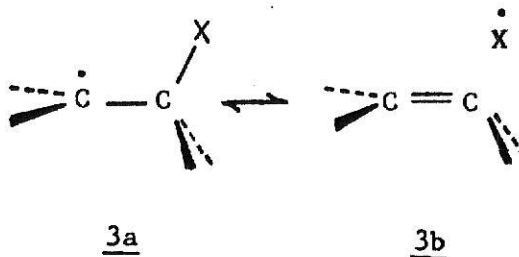
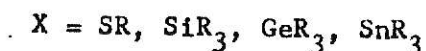
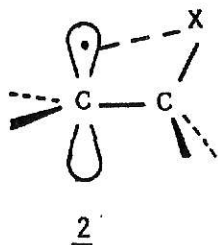
temperature was lowered or the ratio of $n\text{-Bu}_3\text{SnH}$ to alkyl dibromide was increased. With more of the tri- n -butyltin hydride present the bridged bromine intermediate is captured more rapidly thus retaining the stereochemical integrity. Kuivila calculated the percent anti elimination for the 2,3-dibromobutanes to be >90 for the meso isomer and >66 for the dl isomer.

Spectroscopic Studies Pertaining to β -Bromoalkyl Radicals

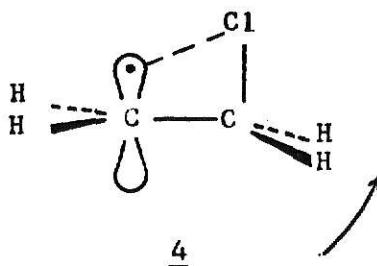
Although reaction rate data and the high degree of stereochemical control are highly indicative of a bridged bromine radical intermediate, the exact nature of the intermediate cannot be ascertained from reaction data. However, from electron spin resonance (esr) studies one should be able to obtain a much more detailed picture of the geometry of the intermediate.

Recent esr studies have suggested that the stability of the intermediate radical is due to delocalization of the unpaired electron by hyperconjugation and homoconjugation mechanisms. When alkyl radicals are substituted in the β -position with various heavier atoms of Group IV, V, and VI elements, there is a preferred conformation in which the heteroatom-carbon bond eclipses the p orbital of the radical center. Krusic and Kochi²⁵ have demonstrated this for β -sulfur, -silicon, -germanium, and -tin groups and have invoked an incipient 1,3-bonding between the unfilled 3d orbitals of the heteroatom and the p orbital of the carbon radical center (2). Although these results did not indicate a symmetrically bridged intermediate, the interaction of orbitals was sufficient to cause hindered internal rotation about the $C_\alpha\text{-}C_\beta$ bond which the authors suggested may be

sufficient to control stereochemistry. A strong hyperfine interaction between phosphorus, arsenic, and tin atoms and the radical center has been observed by Lyons and Symons,²⁶ who also demonstrated an alignment of the $C_\alpha-X$ bond with the p orbital of the radical center. These authors interpreted the interaction as being a hyperconjugation effect rather than an involvement of outer d orbitals (3). Kawamura and Kochi²⁷ have presented arguments showing both hyperconjugation and homoconjugation mechanisms to be operating, but to different extents depending on the nature of X.



Similar results have been obtained for the elusive β -haloalkyl radicals which are of prime interest to the present discussion. The well-resolved esr spectrum of the β -chloroethyl radical was reported by Kawamura, Edge, and Kochi²⁸ and interpreted to indicate that the β chlorine atom is inclined from its normal position toward the p orbital of the radical center, with the two equivalent protons displaced toward the nodal plane (4). This



asymmetric bridging interaction was believed to be due mainly to a p-p homoconjugation mechanism from arguments based on g values. Similar data has been reported by Lyons and Symons²⁹ for esr studies of β -Cl, -Br, and -I-substituted tert-butyl radicals. Again a preferred conformation alignment is observed, and the hyperfine interaction with the halogen nucleus increases steadily from Cl to I. These authors likewise ascribe this interaction to an enhanced hyperconjugation effect, although they do admit that the spectrum assigned to $(\text{CH}_3)_2\text{CCH}_2\text{-Br}$ (which showed eight almost equivalent protons) could be taken as evidence for a more symmetrically bridged structure.

Evidence that the β -bromoethyl radical is not a symmetrically bridged intermediate was obtained by Hargis and Shevlin.³⁰ The chemically induced dynamic nuclear polarization (CIDNP) during thermolysis of benzoyl β -bromopropionyl peroxide gave non-equivalent methylene protons in the resulting β -bromoethyl radical. Therefore interconversion of the methylene groups via bromine migration cannot occur at a rate greater than the rate of diffusion from cage. This result does not rule out a bridged radical in the transition state, however.

The case for radical intermediates being stabilized appreciably by β substituents which can interact with a radical site either by hyperconjugation or by homoconjugation is a very strong one indeed. If the energy of the intermediate is lowered, the transition state leading to radical intermediate is also lowered facilitating the abstraction of an atom from the carbon adjacent to the substituent. The configurational identity of the radical site can also be maintained under conditions which prevent the breaking of the 1,3-interaction, such as low temperature or rapid reaction

of the radical intermediate.

This section is not intended to be an exhaustive survey of the literature on halogen-bridged radicals. For an extensive review of literature on this topic see Bridged Free Radicals by L. Kaplan.³¹

At the beginning of this work Tanner's arguments against bridged bromine radicals had not been refuted. Since his results were determined by product yields, we thought the halogen abstraction system would be a much better test of anchimeric assistance by a neighboring bromine.

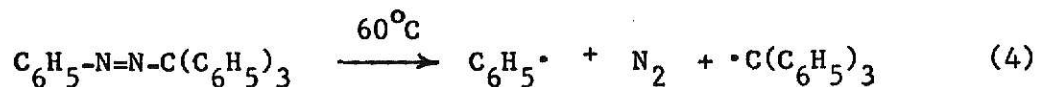
Although of little synthetic value, halogen abstraction reactions far surpass hydrogen abstractions in many aspects as a means of generating free radicals for the study of homolytic processes in organic compounds. The major advantage is that the abstraction of a halogen atom produces a free radical at a specific site within a molecule. The site may be specified exactly by the choice of appropriate organic halide substrate which can normally be synthesized without difficulty. There is usually a multitude of different types of C-H bonds within even a relatively simple organic molecule and many competitive hydrogen abstractions result. The relative abstraction rates, when corrected for inductive effects, are a measurement of the strength of a bond, and correlate quite well with the respective C-H bond dissociation energies. Thus, the relative stability of the free radical is reflected directly in the rate obtained in the competitive abstraction technique employed here, and one does not have to rely on product yields as a measure of stability of the radical intermediate.

OBJECTIVES

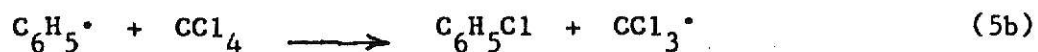
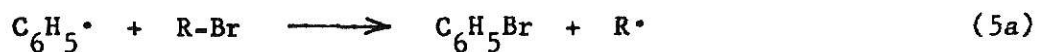
1. To determine the rates of bromine abstraction from meso- and dl-2,3-dibromobutane.
2. To compare the rates of bromine abstraction from the cycloalkyl bromides (C-3 through C-8) with the corresponding trans-1,2-dibromides and related reactions.
3. To substantiate the validity of calculations determining the stabilizing influence of a β bromine atom in the 2-bromoethyl radical.

RESULTS

The abstraction of bromine from a number of alkyl monobromides and dibromides vs. the abstraction of chlorine from carbon tetrachloride by the phenyl radical are reported here. The thermal decomposition of PAT (phenylazotriphenylmethane) at 60°C generates phenyl radicals in situ (equation 4). The phenyl radicals then react with the alkyl bromide and



CCl_4 , producing bromobenzene and chlorobenzene, respectively (equation 5).



The rates of bromine abstraction relative to carbon tetrachloride (CCl_4) were calculated from equation 6. The mmoles of R-Br and CCl_4 were obtained

$$\frac{k_{\text{Br}}}{k_{\text{CCl}_4}} = \frac{(\text{C}_6\text{H}_5\text{Br})(\text{CCl}_4)}{(\text{C}_6\text{H}_5\text{Cl})(\text{RBr})} \quad (6)$$

gravimetrically by weighing into an ampoule, and the mmoles of bromobenzene and chlorobenzene were obtained by glc analysis utilizing an internal standard. The values for the dibromides were statistically corrected to give the relative rate per bromine atom. The second bromine is eliminated from the β -bromoalkyl radical generated in the abstraction from the dibromides to give the corresponding olefins which were identified in most cases by comparison of retention times with those of authentic samples and by the disappearance of olefin product upon addition of bromine. The amounts of olefins produced were not determined. The triphenylmethyl radical reaches a reasonably high steady-state concentration and serves as a scavenger for the second bromine atom. It has been shown in hydrogen abstraction reactions that the resulting triphenylmethane does not affect the $k_{\text{H}}/k_{\text{Cl}}$ ratio due to its very small concentration.³² The presence of the triphenylmethyl radical also efficiently traps $\text{R}\cdot$ and $\text{CCl}_3\cdot$ and prevents the polymerization of olefins.

The $k_{\text{Br}}/k_{\text{CCl}_4}$ values obtained by the abstraction of bromine from aliphatic mono- and dibromides are reported in Table I, along with the percent yield of chlorobenzene and bromobenzene based on PAT. The percent yield could not be determined in cases where the substrate or other products interfered in the glc analysis.

TABLE I

RELATIVE RATE OF BROMINE ABSTRACTION BY THE PHENYL
RADICAL FROM ALKYL MONO- AND DIBROMIDES AT 60°C

Monobromides	$k_{\text{Br}}/k_{\text{CCl}_4}^a$	Yield % ^b	1,2-Dibromides	$k_{\text{Br}}/k_{\text{CCl}_4}^a$	Yield %
c-C ₃ H ₅ Br	0.035 \pm 0.002	----	c- <u>trans</u> -C ₃ H ₄ Br ₂	0.314 \pm 0.015	----
c-C ₄ H ₇ Br	0.179 \pm 0.010	23.3	c- <u>trans</u> -C ₄ H ₆ Br ₂	----	----
c-C ₅ H ₉ Br	0.255 \pm 0.010	23.3	c- <u>trans</u> -C ₅ H ₈ Br ₂	1.48 \pm 0.02	72.0
c-C ₆ H ₁₁ Br	0.160 \pm 0.007	26.2	c- <u>trans</u> -C ₆ H ₁₀ Br ₂	1.32 \pm 0.06	70.5
c-C ₇ H ₁₃ Br	0.342 \pm 0.028	----	c- <u>trans</u> -C ₇ H ₁₂ Br ₂	1.52 \pm 0.04	57.2
c-C ₈ H ₁₅ Br	0.584 \pm 0.016	----	c- <u>trans</u> -C ₈ H ₁₄ Br ₂	1.36 \pm 0.04	87.6
CH ₃ Br	0.021 \pm 0.001	72.0	CH ₂ BrCH ₂ Br ^c	0.37	----
CH ₃ CH ₂ Br ^c	0.076	----	<u>meso</u> -CH ₃ CHBrCHBrCH ₃	1.49 \pm 0.05	69.5
<u>i</u> -C ₃ H ₇ Br ^c	0.256	----	<u>dl</u> -CH ₃ CHBrCHBrCH ₃	1.22 \pm 0.04	66.5
<u>n</u> -C ₄ H ₉ Br	0.083 \pm 0.002	----			
<u>sec</u> -C ₄ H ₉ Br	0.238 \pm 0.006	----			
<u>t</u> -C ₄ H ₉ Br ^c	0.692	----			
CF ₃ CH ₂ Br	0.200 \pm 0.002	----			
N \equiv CCH ₂ CH ₂ Br	0.144 \pm 0.021	----			
CH ₂ =CHCH ₂ Br	2.43 \pm 0.02	29.1			

^a The relative rates are corrected to a per bromine atom per molecule of CCl₄ basis.

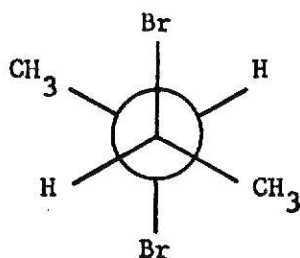
^b Yields of chlorobenzene and bromobenzene relative to PAT.

^c Rates determined by D. G. Saunders of this lab.

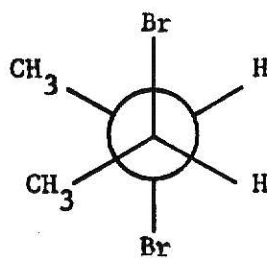
DISCUSSION

Abstraction of Bromine from Cyclic Mono- and 1,2-Dibromides

In general the rates of bromine abstraction from the dibromides were 5 to 7 times faster than the rates of abstraction from the corresponding monobromides. The difference between the rates of meso- and dl-2,3-dibromobutane were much smaller than expected (meso isomer is only 22% faster). The lowest energy conformation of the meso isomer is that in which the bromines are trans to each other (5), whereas the conformation of the dl isomer which has the bromines trans puts the CH₃ groups gauche to each other, and one would expect this to be a higher-energy conformation (6). Studies have shown that anchimeric assistance occurs most



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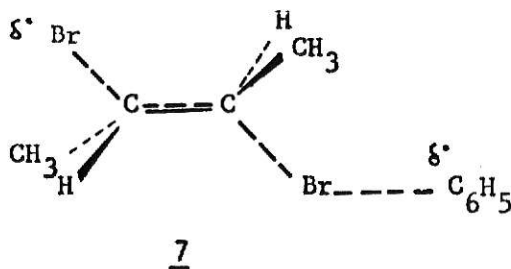


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readily through an anti-periplanar arrangement of atoms.^{4,11} Thus, it seemed at first that anchimeric assistance was not playing a part in these abstractions. However, Kuivila and co-workers observed that the products from dehalogenation of dl-2,3-dibromobutane by the tri-n-butyltin radical require an anti elimination mode,²⁴ suggesting that nonbonded interactions between the two methyl groups which are becoming eclipsed in the transition state are not significant in determining the stereochemistry of elimination.

Space-filling molecular models also indicate that the interaction between the methyl groups is small, and indeed it has been found that the gauche conformation of butane is only 0.9 kcal/mole less stable than the anti conformation.³³ Dipole-dipole interactions and van der Waals repulsion forces between the two bromines help hold the bromines anti to each other. It will be shown later that a β bromine lowers the energy of the intermediate radical by ca. 2 kcal/mole, which overcomes the 0.9 kcal/mole interactions of the methyl groups. These factors tend to increase the population of the conformation having the bromines anti in the dl isomer. From these considerations it would seem that barriers to rotation have little influence on the rates of abstraction of bromine from meso- and dl-2,3-dibromobutane.

At this point, however, it was difficult to tell whether the 6.2 fold rate enhancement of meso-2,3-dibromobutane over the rate of 2-bromobutane was due to anchimeric assistance by the adjacent bromine or if the enhancement was due to a concerted E_H2 elimination of the two bromines (7).



In order to distinguish between these two mechanisms, both of which require an anti arrangement of atoms in the transition state, the rates of bromine abstraction for the cycloalkyl dibromides from C-3 through C-8 were determined and compared to the monobromide rates. If the E_H2 mechanism is operative there should be substantial double bond character in the transition state.

As the ring size decreases to the four- and three-membered rings the ring strain increases dramatically in going from the saturated to the unsaturated ring. For example, the increase in ring strain on going from cyclopropane to cyclopropene is 25.4 kcal/mole, whereas there is a loss of ring strain for the cyclopentyl through the cyclooctyl counterparts, as calculated from heat of formation data.³⁴ The change in ring strain for the trans-1,2-dibromocycloalkanes should follow the same trend although they may be different in magnitude. This ring strain should make itself felt in the transition state, thus greatly decreasing the relative rate of bromine abstraction for the cyclopropyl and cyclobutyl systems. However the $k_{\text{Br}}/k_{\text{CCl}_4}$ results for the cyclic dibromides were quite similar for the C-5 through C-8 rings and decreased by only a factor of ca. five for the trans-1,2-dibromocyclopropane. The value for the trans-1,2-dibromocyclobutane was in question due to an interfering impurity in the starting dibromide and was not included in Table I.

This decrease of a factor of five from trans-1,2-dibromocyclopentane to trans-1,2-dibromocyclopropane was not considered significant enough to lend credence to the $E_{\text{H}}2$ mechanism but rather was attributed to the high percentage of s character in cyclopropyl exocyclic bonds which strengthens these bonds. This decrease in rate was also reflected in the abstraction from bromocyclopropane as compared to bromocyclopentane where the decrease was roughly proportional to the decrease in the dibromide series. We therefore concluded that the reaction is a two-step process involving a radical intermediate.

The abstraction of bromine from the cycloalkyl monobromides provided an interesting correlation with data obtained from other reactions performed

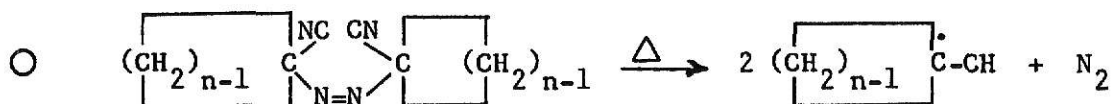
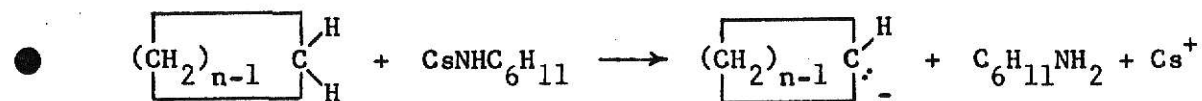
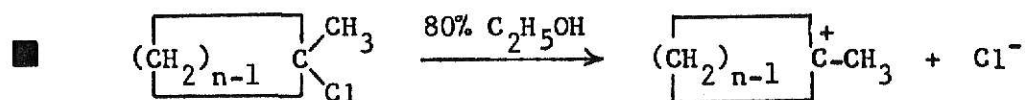
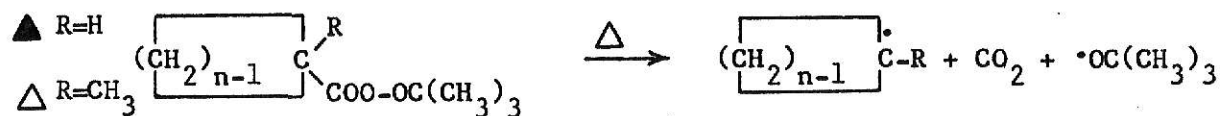
on the cycloalkane series. Ruchardt³⁵ summarized the reaction rate data from four reactions and compared the data with ring size. The data for the C-3 to C-8 rings are reproduced here (Fig. 1).

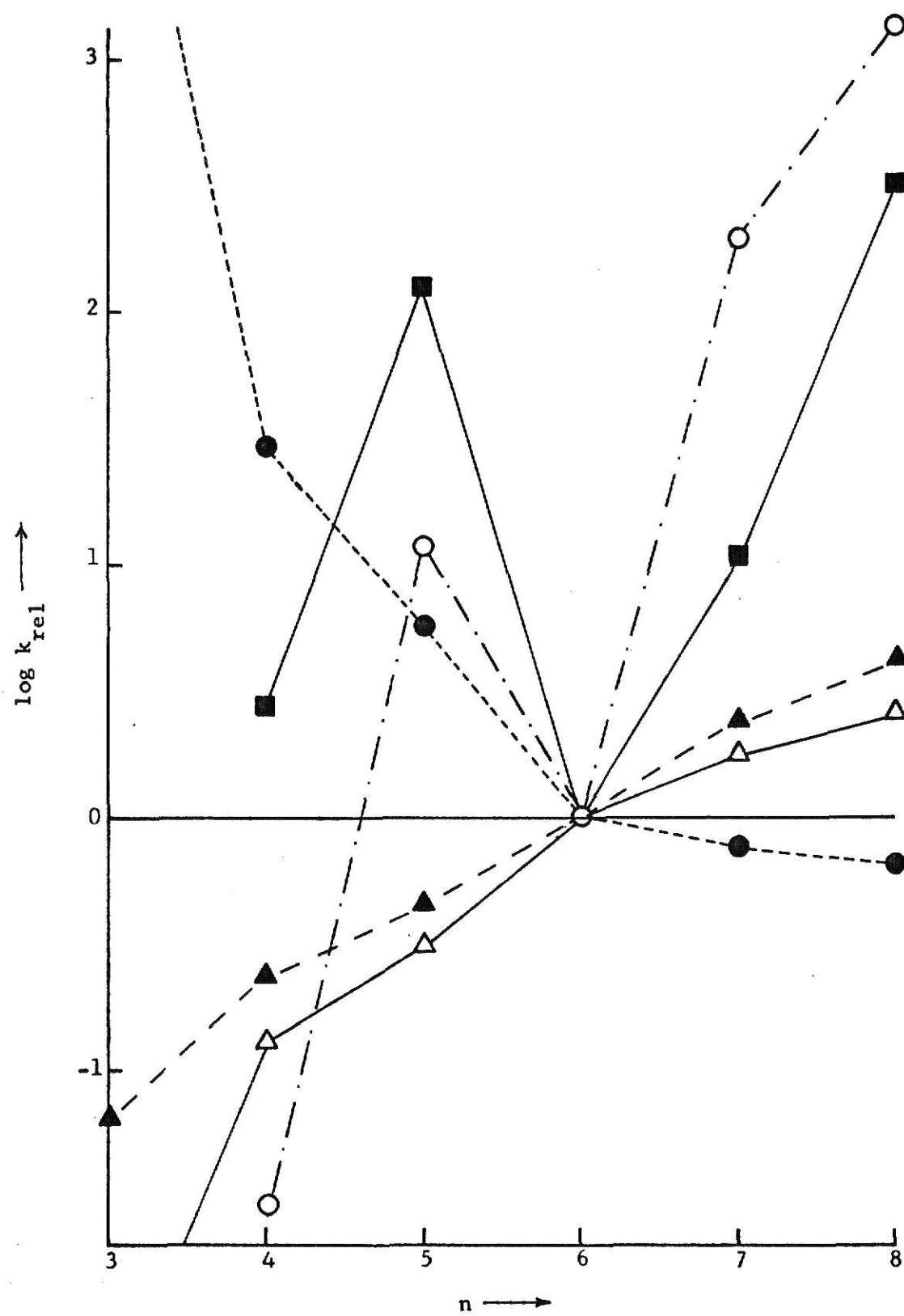
There are three factors competing in the rate of reaction of cyclic compounds; polar effects, hybridization differences, and ring strain. One would expect the inductive effects of added chain length in the cyclic chain to slow the rate of formation of carbanions and increase the rate of formation of 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. However, these effects are small. A more important effect is the hybridization differences which 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 transannular interactions in the larger rings. In the smaller rings, especially the cyclopropyl and cyclobutyl, this rehybridization increases ring strain, thus slowing the reaction.

From Fig. 1 one can see 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

Figure 1. Dependence of the rate of formation of cyclic carbonium ions, carbanions, and radicals on the ring size.

\underline{n} = number of ring members.

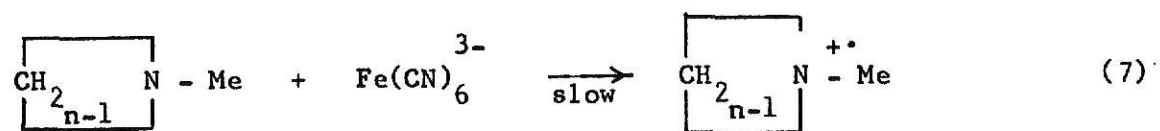




exothermic reactions the transition state comes early in the reaction and is structurally more similar to starting material than product according to the Hammond postulate. If polar effects are not significant an exothermic radical reaction should correlate with the carbanion reaction in Fig. 1. Conversely, 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 reaction.

In the decomposition of peresters the hybridization and polar effects appear to predominate, suggesting an early transition state with little radical character. 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 Mead³⁶ have recently determined the rates of amine oxidation for a series of N-methyl nitrogen heterocycles. Oxidation of the tertiary amines with alkaline potassium hexacyanoferrate(III) results in a nitrogen radical cation (equation 7). The rates obtained relative to N-methyl-



piperidine are given in Table II. These results very closely parallel the decomposition of the azo compounds, showing the importance of ring strain effects in the transition state.

Thus Ruchardt suggests that in the perester decompositions the transition state leading to the radical occurs early in the reaction coordinate while the α -C is still substantially pyramidal and little free radical character has developed. For the azo decomposition reactions and the

amine oxidation reactions the transition state occurs late in the reaction coordinate after much bond breaking has occurred. The α -atom has substantial sp^2 hybridization character and the change in ring strain in going from a tetrahedral carbon to a trigonal carbon is the significant influence.

The rates of bromine abstraction relative to cyclohexyl bromide are presented in Table III and plotted in Figure 2. The values obtained are seen to correlate with the carbonium ion reaction and azo decomposition reaction, although the rate differences relative to the six-membered ring are much smaller in magnitude. This might indicate considerable bond breaking in the transition state leading to the cycloalkyl radical intermediate, according to Ruchardt's argument.

Although the abstraction of a bromine by a phenyl radical is a mildly exothermic reaction ($\Delta H = -3$ kcal/mole for abstraction from isopropyl bromide³⁷), 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.^{18,19} 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,³² 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 ($\Delta H = \text{ca. } -9.5$ kcal/mole).³⁷

The variation in rate with ring size for the cycloalkyl trans-1,2-dibromides is plotted along with the rates for the cycloalkyl bromides in

TABLE II

RELATIVE RATE OF AMINE OXIDATION IN NITROGEN
HETEROCYCLES (N-METHYLPYPERIDINE = 1.0)³⁶

Amine	Relative Rate
N-n-butylaziridine	5.75×10^{-2}
N-Methylpyrrolidine	53.2
N-Methylpiperidine	1.0
N-Methylhexamethyleneimine	420
N-Methylheptamethyleneimine	1070

TABLE III

RELATIVE RATE OF BROMINE ABSTRACTION BY PHENYL RADICAL
FROM CYCLOALKYL BROMIDES (CYCLOHEXYL BROMIDE = 1.00)

<u>Cycloalkyl Bromide</u>	<u>Relative Rate</u>
Cyclopropyl Bromide	0.216
Cyclobutyl Bromide	1.12
Cyclopentyl Bromide	1.59
Cyclohexyl Bromide	1.00
Cycloheptyl Bromide	2.14
Cyclooctyl Bromide	3.67

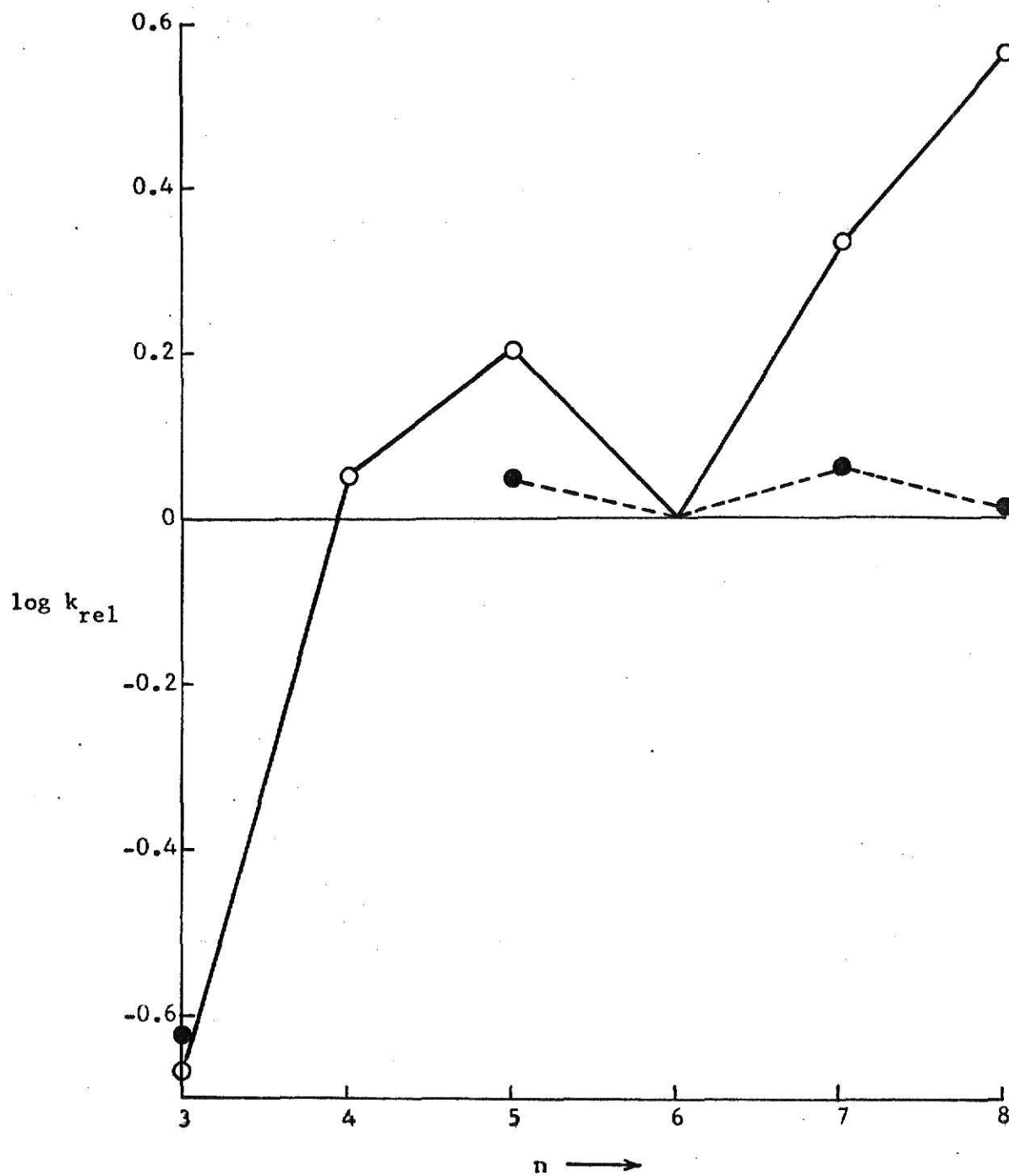


Figure 2. Dependence of the rate of abstraction of bromine from cyclic monobromides and dibromides on the size of the ring. n = number of ring members.

- Abstraction of bromine from cyclic monobromides
- Abstraction of bromine from cyclic 1,2-dibromides

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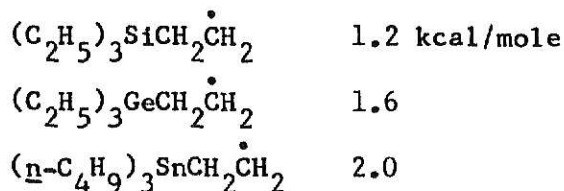
Fig. 2. The rates for the dibromides followed the same trend as the rates of the corresponding monobromides, showing the predominance of ring strain effects on the rates, although the effects were attenuated somewhat, presumably due to assistance by the adjacent bromine. Compared to the monobromides the seven and eight membered dibromide rings were considerably slower, although still slightly faster than trans-1,2-dibromocyclohexane. The transannular nonbonded interactions between the hydrogens and the bromines were considered the significant factor in slowing these dibromides. From an inspection of models of these compounds it was seen that the transannular interactions increase greatly as the bromines approach an anti conformation, making it more difficult for backside assistance in the transition state. Thus the decrease in ring strain for the C-7 and C-8 cyclic dibromides as an sp^2 carbon is generated is thought to be offset by a decrease in anchimeric assistance due to transannular interactions.

The difference between the rates for cyclopropyl bromide and cyclopropyl trans-1,2-dibromide was about the same as the differences in rates for the other rings. This was somewhat surprising in view of the fact that the anti alignment of the bromines is not possible in cyclopropyl dibromide and assistance would not be expected. Thus this rate was a little faster than anticipated.

Stability of the β -Bromoethyl Radical

In the background section the influences of a β substituent were discussed which can stabilize a radical center by delocalization of the unpaired electron by bridging, homoconjugation, and/or hyperconjugation mechanisms. It would seem very important to be able to obtain an estimate of this stabilizing influence. Krusic and Kochi²⁵ have obtained barriers

to rotation for β substituted ethyl radicals for the substituents Si, Ge, and Sn. These barriers to internal rotation were calculated from the β coupling constant that would be observed for the two equivalent β hydrogens in a "frozen" anisotropic ethyl radical assuming the $C_{\alpha}-X$ bond to be eclipsing the radical p orbital. The resulting barriers to rotation are as follows:



Danen and Winter¹⁹ have observed that the abstraction of iodine from β -bromoethyliodide is ca. 90% faster than the expected rate after correcting for inductive effects. This rate enhancement is ascribed to stabilization of the radical intermediate by the β bromine. This enhancement, although small, is substantial in view of the fact that the phenyl radical is a very reactive radical and not very selective.

From this rate enhancement an estimate of the stabilizing influence of the β bromine can be calculated. Danen, Tipton, and Saunders³⁸ reported that 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. Thus the plot of $\log (k_I/k_{Br})_{corr}$ versus $D(C-H)$ gave a line fit by the following equation (equation 8) with

$$D(R-H) = -12.083 \log (k_I/k_{Br})_{corr} + 90.70 \quad (8)$$

a correlation coefficient of 0.991. 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/mole is obtained for the 2-bromoethyl radical relative to the ethyl radical itself.³⁹

The stabilizing influence of a β bromine can also be calculated from bromine abstraction data. The rates of abstraction of bromine from a series of primary bromides with significantly different polar substituents was obtained (Table IV) and the logs of these rates were plotted versus Taft's polar substituent constants⁴⁰ (Fig. 3). This gave a $\rho = +0.158$ with a correlation coefficient $r = 0.968$. From this ρ value the rates of a series of alkyl bromides were corrected for the polar effect of the groups attached to the carbon from which the bromine was abstracted by using the Hammett relationship shown in equation 9 where $k_o = (k_{Br}/k_{CCl_4})_{corr}$ and $\Sigma\sigma^*$ is the summation of polar effects of all atoms attached including hydrogen. The

$$\log (k_x/k_o) = (+0.158) (\Sigma\sigma^*) \quad (9)$$

experimental rates, the $\Sigma\sigma^*$, the corrected rates, and the corresponding C-H bond dissociation energies³⁷ are shown in Table V. The corrected rates $(k_{Br}/k_{CCl_4})_{corr}$ were then plotted versus $D(C-H)$ as shown in Fig. 4, which gave a line fit by equation 10 with a correlation coefficient $r = 0.988$.

$$D(R-H) = (-7.407) (\log k_{Br}/k_{CCl_4})_{corr} + 89.48 \quad (10)$$

From this equation the $D(R-H)$ for CH_2BrCH_2-H was calculated giving 96.1 kcal/mole. When compared to the bond dissociation energy of ethane this method gives ca. 1.9 kcal/mole stabilizing influence.

This value of ca. 1.9 kcal/mole from bromine abstraction data and the

TABLE IV

POLAR SUBSTITUENT CONSTANTS AND THE RELATIVE RATES
OF ABSTRACTION OF BROMINE FROM SUBSTITUTED ALKYL BROMIDES

Substrate	$k_{\text{Br}}/k_{\text{CCl}_4}$	σ^* ⁴⁰
$\text{CH}_3\text{CH}_2\text{-Br}$	0.076 ----	0.00
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-Br}$	0.083 ± 0.006	-0.115
$\text{N}\equiv\text{CCH}_2\text{CH}_2\text{-Br}$	0.144 ± 0.021	1.05
$\text{CF}_3\text{CH}_2\text{-Br}$	0.200 ± 0.002	2.62

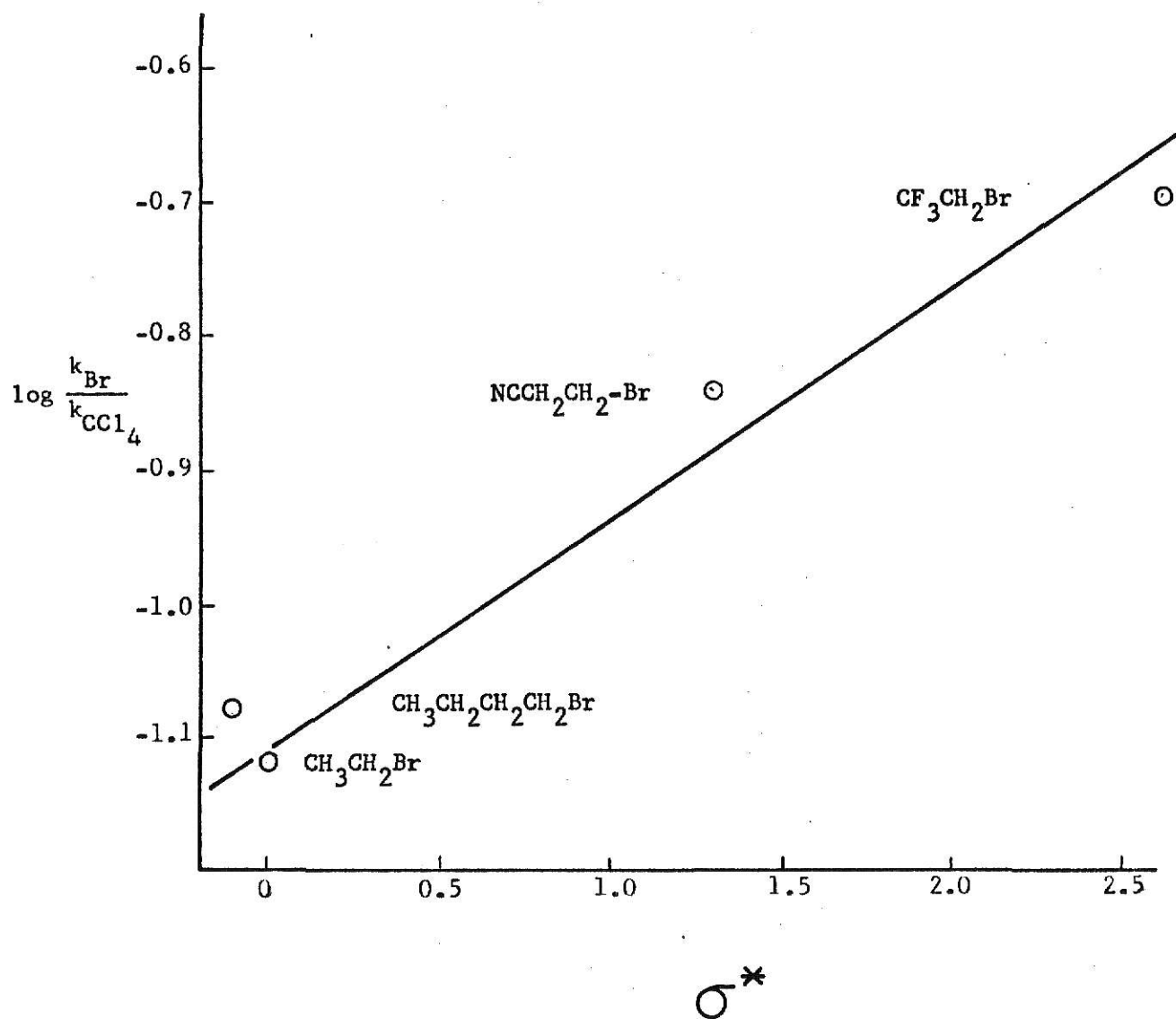


Figure 3. Plot of $\log k_{\text{Br}}/k_{\text{CCl}_4}$ for the primary iodides RCH_2Br versus the Taft polar substituent constant σ^* . Values of σ^* were obtained from ref 40.

TABLE V

RELATIVE RATES OF BROMINE ABSTRACTION CORRECTED
FOR INDUCTIVE EFFECTS AND THE RESPECTIVE C-H BOND
DISSOCIATION ENERGIES FOR SOME ALKYL BROMIDES

Substrate	$k_{\text{Br}}/k_{\text{CCl}_4}$	$(k_{\text{Br}}/k_{\text{CCl}_4})_{\text{corr}}$	$\Sigma \sigma^*$	$D(\text{R-H})^{37}$
$\text{CH}_3\text{-Br}$	0.021 ± 0.001	0.0087	1.47	104
$\text{CH}_3\text{CH}_2\text{-Br}$	0.076 ----	0.0419	0.98	98
$i\text{-C}_3\text{H}_7\text{-Br}$	0.256 ----	0.1901	0.49	94.5
$\text{sec-C}_4\text{H}_9\text{-Br}$	0.238 ± 0.006	0.1878	0.39	94.6
$t\text{-C}_4\text{H}_9\text{-Br}$	0.692 ----	0.692	0.00	91
$\text{CH}_2\text{BrCH}_2\text{-Br}$	0.37 ----	0.1110	1.98	96.1^a
$\text{CH}_2=\text{CHCH}_2\text{-Br}$	2.43 ± 0.02	0.9005	1.633	90.0^a

^a Obtained by extrapolation from Fig. 4.

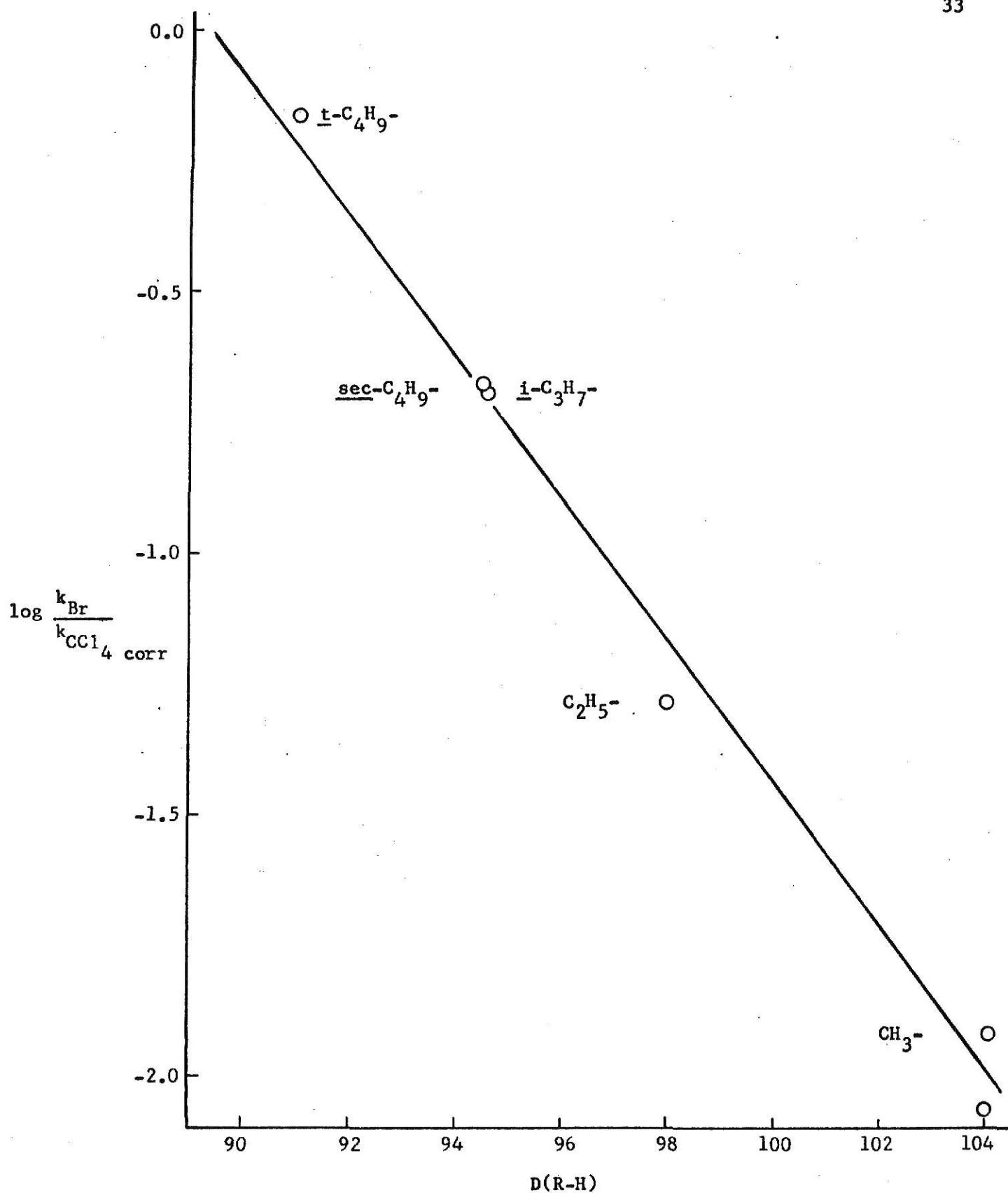


Figure 4. Plot of log of relative rate corrected for inductive effects for $R-Br$ vs the respective C-H bond dissociation energies. Values of $D(R-H)$ were obtained from ref 37.

previously discussed value of 2.1 kcal/mole from iodine abstraction data are probably underestimated due to assuming a constant ΔS^\ddagger for these reactions. Skell and Shea¹¹ reported a $\Delta\Delta H^\ddagger = -3.0$ kcal/mole and a $\Delta\Delta S^\ddagger = -6$ eu for the β position of 1-bromobutane relative to the secondary hydrogens of propane.

The same treatment was applied to allyl bromide as a check on the validity of these calculations. If this treatment can give an allylic resonance energy of correct magnitude, then the Evans-Polanyi relationship holds true and the calculations for the β bromine stabilization are realistic.

From equation 10 the $D(R-H)$ for $CH_2=CHCH_2-H$ was calculated to be 90.0 kcal/mole. From the bond dissociation energy for a primary hydrogen of propane (98 kcal/mole) a resonance energy of ca. 8.0 kcal/mole was calculated. This was a little lower than other values, but in view of assuming a constant ΔS^\ddagger it was expected to be a little underestimated. The generally accepted value for the allylic resonance energy is 12-13 kcal/mole,⁴¹ although Benson and co-workers reported a value of 10.2⁴² which they later refined to 9.6 kcal/mole.⁴³ Other values for $D(R-H)$ for the allyl hydrogen are 85,³⁷ 87.5,⁴⁴ and 89 kcal/mole.⁴⁵ Thus, it appeared that the method employed here was reasonably reliable for obtaining the stabilizing influence of a β bromine on the transition state, although the method might underestimate the stabilization somewhat.

CONCLUSIONS

From this study we demonstrated that the abstraction of a bromine by the phenyl radical was a reasonably sensitive method for obtaining information concerning the stabilizing effects of a neighboring bromine on an alkyl

radical and for determining the effects of polar substituents on the transition state. When the rates of abstraction of bromine from cycloalkyl bromides were compared with the rates of formation of cycloalkyl carbonium ions, the same trends in rate vs. ring size were observed. According to the arguments of Ruchardt this indicated that the transition state is far enough along the reaction coordinate to allow ring strain effects to affect the rates of reaction.

The same trend observed in the rates for the cyclic monobromides and dibromides for the C-3, C-5, and C-6 rings was taken as evidence that bromine abstraction does not involve a concerted $E_{\text{H}}2$ elimination but rather occurs by a two-step process with a radical intermediate. The similarity in the rates of abstraction from meso- and dl-2,3-dibromobutane suggested that both isomers have a high percentage of the conformation having the bromines anti in the ground state.

A reasonable correlation between the log of the abstraction rate and the polar substituent constant σ^* was obtained, giving $\rho = +0.16$. This falls in line with positive ρ values obtained from the abstraction of iodine from phenyl iodides and alkyl iodides. The rates of a series of alkyl bromides corrected for the inductive effects of substituents correlated very well with the bond dissociation energies of the respective C-H bonds. From this correlation the stabilizing influence of bromine in the β -bromoethyl radical was calculated to be ca. 2.0 kcal/mole. The resonance stabilization of the allyl radical was also calculated, giving ca. 8.0 kcal/mole which approximated the value obtained by Benson and co-workers of 9.4 kcal/mole. Thus it was felt that this method of calculating the stabilization of radical intermediates was quite reliable although the resulting values are underestimated somewhat.

EXPERIMENTAL

General

All glc was performed using a Hewlett-Packard F & M Model 700-231 dual column gas chromatograph equipped with dual flame ionization detectors. The kinetic analyses were conducted utilizing 6 ft. x 1/4 in. columns with liquid phase packing of SE-30, Carbowax 20-M, or FFAP on Chromasorb W, 60-80 mesh, and a 12 ft x 1/8 in. column packed with Carbowax 20-M. Areas under the peaks were determined by tracing with a planimeter and corrected for differences in detector response.

Nuclear magnetic resonance spectra were obtained using a Varian T-60 nmr at ambient temperatures using TMS as reference. Liquids were run neat and solids were run in CCl_4 solution. Infrared spectra were obtained using a Perkin Elmer 137 infrared spectrometer. Solids were run in KBr pellets and liquids were run as neat films between NaCl plates. A Fisher-Johns melting point apparatus was used for melting point determinations. All melting points and boiling points are uncorrected.

Syntheses

meso- and dl-2,3-Dibromobutane. These isomers were prepared from trans- and cis-2-butene respectively by bubbling the butene through a 0.1 mole solution of Br_2 in CCl_4 into a closed system with a balloon attached. The progress of the reaction was monitored by watching the rate at which the balloon deflated. The exothermic reaction occurred quite fast and the bromine color was discharged in fifteen minutes. The CCl_4 was removed on a rotary evaporator

and the product distilled at 29-30°C at 5 mm pressure. Analysis by glc showed each isomer >99% pure, the only detectable impurity being the other diastereomer.

trans-1,2-Dibromocyclopropane. This was prepared by addition of Br₂ to cyclopropene in CH₂Cl₂. The cyclopropene was generated by the method of Closs and Krantz⁴⁶ using 33 ml (0.4 mole) of allyl bromide and 16 g (0.4 mole) of sodium amide rather than allyl chloride as reported. The higher boiling allyl bromide gave better results with less allyl bromide contaminate in the product. The cyclopropene generated escaped through the condenser as it was formed and was bubbled into 5.8 g (0.4 mole) Br₂ in CH₂Cl₂. The CH₂Cl₂ was removed by fractional distillation and the product collected by glc and identified by nmr spectroscopy.⁴⁷

trans-1,2-Dibromocyclobutane. The same procedure as used by Abell⁴⁸ in the Hunsdieker reaction to form dibromocyclohexane was used to make the dibromocyclobutane. Starting with 12.5 g (0.087 moles) of trans-1,2-cyclobutanedicarboxylic acid, the silver salt was prepared and dried in a vacuum oven over P₂O₅ for 48 hours at 110°C. This was then added to a slight stoichiometric excess of bromine in CCl₄ which was dried by passing it through a bed of P₂O₅ as it was added to the flask. The silver salt was placed in a dried Erlenmeyer flask and connected to the top of a reflux condenser by a short length of polyvinylchloride tubing, and was added as rapidly as safety permitted to the refluxing CCl₄ by inverting the Erlenmeyer flask. The salt reacted instantly at reflux temperature giving off CO₂ which was bubbled through a trap containing bromine in CCl₄. This

was used to determine if any cyclobutene had been formed and had escaped with the CO_2 . Analysis of the contents of the trap after the reaction was complete revealed no dibromocyclobutane. A problem with this method of adding the silver salt was that it stuck to the inside of the condenser at the point where the CCl_4 was refluxing and eventually plugged the condenser. The condenser had to be opened at the top periodically and the salt forced into the reaction flask with a glass rod. The addition required about one hour after which the mixture was left at reflux for two hours. After removing the silver bromide precipitate by filtration, the CCl_4 and Br_2 were removed by fractional distillation leaving a dark residue which was vacuum distilled at 10 mm. The fraction which boiled at $58-60^\circ\text{C}$ was collected and was shown to be about 90% pure trans-1,2-dibromocyclobutane by glc. A second fraction from $60-75^\circ\text{C}$ was also collected which contained about 60% product by glc. The combined weight of these two fractions (0.8 ml each) was 2.67 g, giving approximately 10.8% yield from the dicarboxylic acid. The first fraction was further purified by preparative glc as the material was needed. Earlier attempts to synthesize dibromocyclobutane using the Cristol modification with HgO following the procedure of Meek and Osuga⁴⁹ led to very poor yields and a product apparently not suitable for kinetic analyses giving conflicting results. No literature reports of attempts to use the HgO modification on vicinal diacids could be found, although the reaction works well for monoacids.

trans-1,2-Dibromocyclopentane, -cyclohexane, -cycloheptane, and -cyclooctane. The trans vicinal cyclic dibromides of C-5 through C-8 were prepared by the slow addition of the respective cycloalkene to a solution of bromine (ca. 0.3 mole) 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. The dibromides were distilled as follows:

Dibromocyclopentane	b.p.	53-56°C (4.5 mm)
Dibromocyclohexane	b.p.	55-57°C (0.4 mm)
Dibromocycloheptane	b.p.	42-46°C (0.1 mm)
Dibromocyclooctane	b.p.	71-73°C (0.1 mm)

All products were determined to be >99% pure by glc. The cycloalkenes were all obtained commercially⁵⁰ and, with the exception of cyclopentene, were fractionally distilled prior to using.

The first dibromide to be prepared was trans-1,2-dibromocyclohexane. It was first distilled by spinning band at reduced pressure, resulting in an apparently less pure product than before distillation, as analyzed by glc. This at first was quite puzzling, until a literature search uncovered the same problem experienced by Skell and Readio⁵¹ in which they found that the problem was thermal decomposition in the glc injection port. Indeed there was found to be a direct relationship between injection port temperature and the amount of impurities appearing on the glc chart, with a decomposition threshold of about 150°C. Thus with an injection port temperature of 105°C, the product was found to be quite pure. All of the dibromides were shown to be sensitive to injection port temperature, especially the dibromocyclobutane which decomposed at temperatures above 100°C. Also bromocyclooctane and bromocycloheptane decomposed at temperatures above 90°C, making purification and subsequent kinetic analyses extremely difficult.

Bromocyclopropane. This reagent was obtained from Aldrich and was found to be ca. 98% pure by glc analysis on SE-30 and Carbowax 20-M columns, and was used without further purification.

Bromocyclobutane. This reagent was purchased from P.C.R. Inc. and contained ca. 5% impurity by glc analysis. This impurity could not be separated sufficiently on either SE-30 or Carbowax 20-M to be efficiently purified by glc, and since only 1 g of the substance was available it was used as obtained. A satisfactory nmr spectrum was obtained.

Bromocyclopentane. This was prepared in high yield by adding dry HBr to cyclopentanol following the method outlined by Fieser and Fieser.⁵² A reflux condenser with a balloon attached at the upper end was placed in one neck of a 250 ml three-neck flask, a distillation head with condenser was placed on the middle neck, and dry HBr from a gas cylinder was bubbled into 0.3 mole of cyclopentanol. A 100 ml round bottom flask was fitted to the lower end of the distillation condenser, making a closed system. The progress of the reaction was monitored by watching the rate of deflation of the balloon after addition of HBr. The reaction was kept at 100°C to distill off the H₂O as it was formed in the reaction, thus driving the reaction to completion. When it appeared that no more HBr was being consumed and no more water was coming off, the product was isolated and found to contain about 5% of the unreacted cyclopentanol by glc. This was removed by taking advantage of its slight solubility in water by repeated extractions with water. It was then distilled at 137-139°C and found to be about 95% pure by glc.

Bromocyclohexane. The commercially obtained compound contained two sizeable impurities. Several washings with H_2O removed most of the impurity suspected to be cyclohexanol. The other peak was found to be cyclohexene. It was removed by saturation with Br_2 , followed by washing with 10% NaHSO_3 and water, drying, then distilling to remove the resulting dibromocyclohexane. The bromocyclohexane fraction boiling at $64\text{--}65^\circ\text{C}$ (21 mm) was collected and determined >99% pure by glc.

Bromocycloheptane. By following the procedure of Mozingo and Patterson⁵³ this compound was obtained in 57% yield. To a solution of 0.2 mole cycloheptene in anhydrous ether in a round bottom flask wrapped in tin foil⁵⁴ was added a slight excess of dry HBr from a gas cylinder, keeping the temperature below 5°C . The reaction was allowed to stir for twenty hours. 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, dried, and the bromocycloheptane obtained by distillation at $26\text{--}26.5^\circ\text{C}$ (0.3 mm), yielding a product >99% pure by glc and containing no detectable dibromide. This compound was very sensitive to thermal decomposition, and injection port temperature and distillation pot temperatures were kept below 80°C . Commercially obtained bromocycloheptane was found to contain ca. 10% lower boiling impurities, and was initially fractionated by spinning band distillation. Even at reduced pressures the product contained more impurities than before distillation. Realizing that the problem was thermal decomposition attempts to purify by distillation were abandoned.

Bromocyclooctane. The same procedure was used for bromocyclooctane except for the work-up. 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°C following the procedure of Cope, Brown, and Woo.⁵⁵ Other low boiling components of the mixture were removed by distillation at 50°C (0.3 mm), leaving bromocyclooctane that was >99% pure by glc.

2-Bromobutane. This was prepared the same way as bromocyclopentane by reacting HBr with 2-butanol. The alcohol which remained in the product was removed by water extraction. The product was purified by spinning band distillation at $91\text{--}92^\circ\text{C}$ and determined >99% pure by glc.

1-Bromobutane, allyl bromide, and methyl bromide⁵⁶ were obtained commercially and it was necessary for only the allyl bromide to be redistilled to increase purity to >99%.

Kinetic Analyses

The relative rate of abstraction of bromine from an alkyl bromide versus the rate of abstraction of chlorine from CCl_4 by the phenyl radical gave the rate ratio $k_{\text{Br}}/k_{\text{CCl}_4}$ and was calculated as shown in equation 6 in the Results section. The ratio of bromobenzene and chlorobenzene in the reaction product was determined by glc peak analysis and the amounts of CCl_4 and R-Br were determined gravimetrically as they were added to the reaction ampoule. The phenyl radicals were generated by thermal decomposition of

phenylazotriphenylmethane (PAT) at $60.0 \pm 0.1^\circ\text{C}$. The ratio of CCl_4 to R-Br was adjusted to give approximately equal yields of chloro- and bromobenzene. The amount of PAT ranged from 1 to 2% of the lesser of the two reagents for the faster abstractions and up to 5% for the slower ones. In previous studies it was determined that variation of the PAT concentration over a tenfold range and the ArI/CCl_4 ratio from 0.059 to 0.41 has a negligible effect on the $k_{\text{I}}/k_{\text{CCl}_4}$ values for the abstraction of iodine by the phenyl radical from substituted iodobenzenes. By addition of an internal standard immediately after opening the ampoule the yield of chloro- and bromobenzene was calculated. Typical yields for the dibromides ranged from 70 to 85% and for the slower monobromides were 20 to 30% based on PAT. The relative glc response to chloro- and bromobenzene and the internal standard had to be determined from weighed mixtures of the compounds dissolved in CCl_4 for different columns, column temperatures, carrier gases, carrier gas flow rates, and for different detectors. Thus, all rate values reported are corrected for relative detector response. All glc peak measurements were made by planimeter with the exception of bromocyclooctane which was measured by peak heights using carefully controlled glc conditions. This method was shown to be quite reliable as long as the retention times were constant.

The reactions were run in sealed, degassed Pyrex ampoules which initially were made from 13 x 100 mm test tubes by heating them in the middle and drawing them out to give an outside diameter of about 5 mm. The ampoules were then dried, weighed, and the reagents were added using a very narrow "V" shaped spatula for solids and by syringe for liquids in such a way that all reagents entered the ampoule below the constricted portion. The liquid with the higher vapor pressure (usually CCl_4) was added

last followed by quick weighing, stoppering with a rubber septum, and freezing in liquid nitrogen to minimize loss by evaporation. Later, due to limited amounts of reagents it became necessary to run the reactions on a smaller scale and five inch lengths of 8 mm glass tubing sealed at one end and constricted to 4 mm outside diameter one inch from the open end were used. These proved much less fragile than the test tube ampoules and were very satisfactory.

The ampoules were degassed by the freeze-thaw technique at 0.1 to 0.5 mm pressure using liquid nitrogen for freezing the solutions. The samples were thawed and refrozen repeatedly until no more bubbles were seen to escape on thawing (usually 3 to 4 thawings were required). The ampoules were then sealed with a flame and incubated at $60.0 \pm 0.1^\circ\text{C}$ in an oil bath covered to omit light for 4 hours (ca. ten half-lives), and quenched in liquid nitrogen. Periodically the two halves of the sealed ampoules were reweighed but never was there a significant loss of volatile components during degassing.

At least two samples of each compound were run and the products were analyzed in triplicate. In cases where there was a variance between values more samples were run. The values for the dibromides are statistically corrected and reported as per bromine atom per CCl_4 molecule. The values obtained are reported in Table I. The relative average deviation between samples was less than 6% for all compounds except bromocycloheptane for which the relative average deviation was 8.2% for three samples.

Part II: Lack of Iodine and Sulfur Anchimeric Assistance in the Formation of Selected Aryl Radicals.

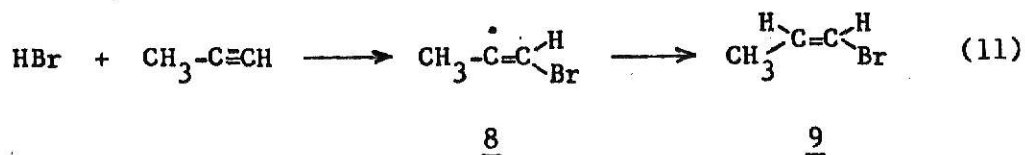
INTRODUCTION

In the preceding part we were concerned with the possibility of anchimeric assistance by a neighboring halogen in homolytic abstraction processes resulting in the formation of 2-bromo substituted alkyl radicals. Now let us turn to a consideration of similar phenomena in the formation of aryl radicals. The object of this study is twofold: (a) to determine the configurational stability of the 2-iodo-4-methylphenyl radical to see if the iodine can migrate to the adjacent position and (b) to determine if a neighboring sulfide can provide anchimeric assistance in the abstraction of aromatic iodine from 2-iodo-2'-methylthiobiphenyl. These two topics will be treated individually as Section A and Section B respectively.

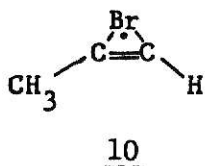
Section A: Lack of Iodine Migration in Thermal Decomposition of 2-Iodo-4-Methylphenylazotriphenylmethane.

BACKGROUND

Skell and Allen⁵⁷ have shown that in the homolytic addition of HBr to propyne the addition is stereospecifically trans in both the liquid and gas phases to give 100% cis-1-bromopropene (9) (equation 11).

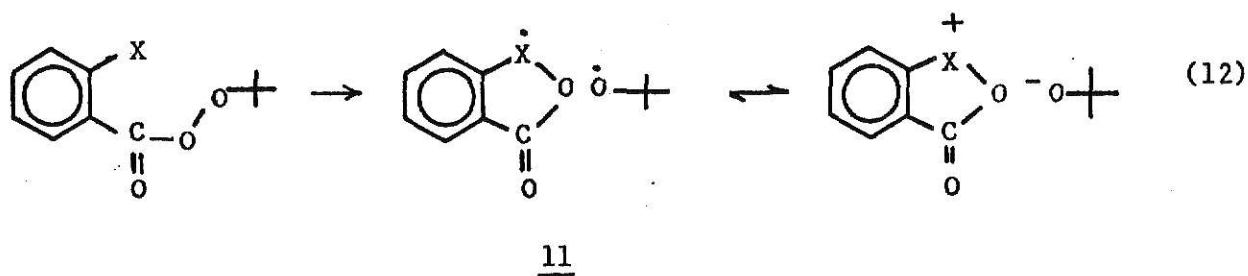


The vinyl radical formed by the addition of a bromine atom to propyne is analogous to aryl radicals in that the bond angles and carbon hybridizations are somewhat similar. Skell and Allen suggest that this stereospecificity may be due to a slow interconversion of the vinyl radical 8, allowing the hydrogen atom time to attack from the side opposite the bromine, or that it may be an example of a bridged bromine radical intermediate 10, forcing



the hydrogen to attack only from the side opposite the bridging bromine. If indeed bridging does occur in this vinyl case, then it might be expected to occur in ortho-haloaryl radicals and migration of the halogen atom from its original position to the adjacent carbon might also be expected.

Evidence for an ortho-halo substituent providing anchimeric assistance in an aromatic system was found by Bentrude and Martin.⁵⁸ The rate of decomposition of ortho-substituted-tert-butylperbenzoates (equation 12) was enhanced by a factor of 54 when the ortho substituent was iodine and by a factor 10^4 when the substituent was S-CH₃ or S-C₆H₅. The authors' rationale for this marked increase in rate was that the substituent could expand its valence shell to accept the unpaired electron from the oxygen and thus facilitate bond cleavage as illustrated by structure 11.



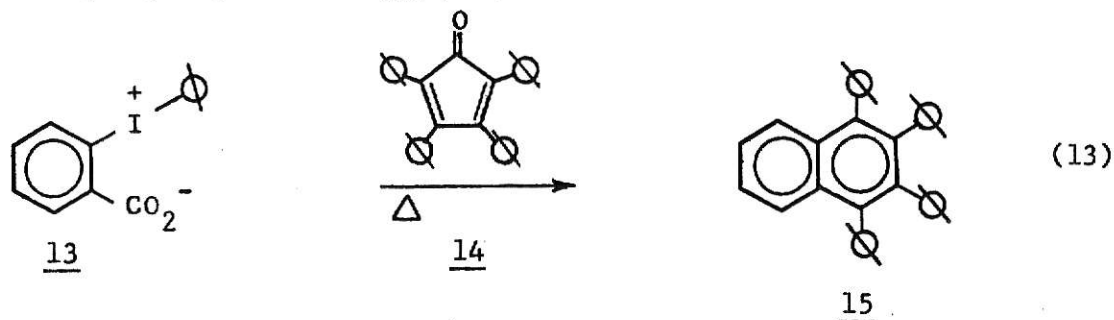
In the abstraction of iodine by the phenyl radical from various meta- and para-substituted iodobenzenes Danen and Saunders¹⁸ found there was a quite good correlation between the relative rates of abstraction (k_I/k_{Cl}) and the Hammett σ constants, and that the abstraction exhibited a positive ρ value ($\rho = +0.57$). A series of ortho-substituted iodobenzenes was also studied,⁵⁹ and a Hammett correlation with ortho constants specifically designed for such compounds⁶⁰ gave wide divergence, although treatment by the extended Hammett relationship as proposed by Charton⁶¹ gave somewhat better correlation. However, an important feature of the ortho series is that the rate for ortho-diiodobenzene is somewhat faster than that predicted from a consideration of electronic and steric factors. This acceleration is thought to be due to the severe steric interaction (over and above that predicted by the extended Hammett treatment) between two adjacent atoms as evidenced by the distorted geometries observed for ortho-diiodobenzene and even for ortho-dibromobenzene,⁶² but could possibly be due to stabilization of the phenyl radical by an ortho-iodine through a bridged radical intermediate (12). An intermediate of



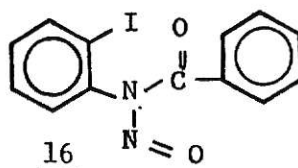
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this type could abstract a hydrogen from solvent to either position on the ring (they are equivalent in this case) yielding iodobenzene. If the bridging is symmetrical, one would expect ca. 50% of the resulting iodobenzene to have this iodine on a carbon adjacent to the carbon to which it was originally attached, thus effecting iodine migration.

Another possible mechanism for iodine migration is through a benzyne intermediate and ortho-iodoaryl radicals have been suggested to be benzyne precursors. E. L. LeGoff⁶³ reported evidence that there is a benzyne intermediate in the thermal decomposition of diphenyliodonium-2-carboxylate (13). Refluxing 13 with tetraphenylcyclopentadienone (14) gave 1,2,3,4-tetraphenylnaphthalene (15), equation 13.



Kampmeier and Hoffmeister⁶⁴ also suggest a benzyne intermediate in the photolysis of 1,2-diiodobenzene in dilute solutions of cyclohexane, furan, benzene, and benzene containing 14. In the first three solvents only the normal radical products were observed, but in the benzene solution with 14 there was 10% of the Diels-Alder adduct 15. Kampmeier and Robin⁶⁵ have shown that decomposition of N-(2-iodophenyl)-N-nitrosobenzamide (16) in benzene solution with 14 also gives the Diels-Alder product 15. The authors propose that 16 decomposes to an ortho-iodoaryl radical



which then loses an iodine to give the benzyne intermediate. However later work by Kampmeier and Clark⁶⁶ has shown that the thermal decomposition of 2-iodophenylazotriphenylmethane in benzene with 14 produced none of the Diels-Alder adduct, and under other conditions gave no indication

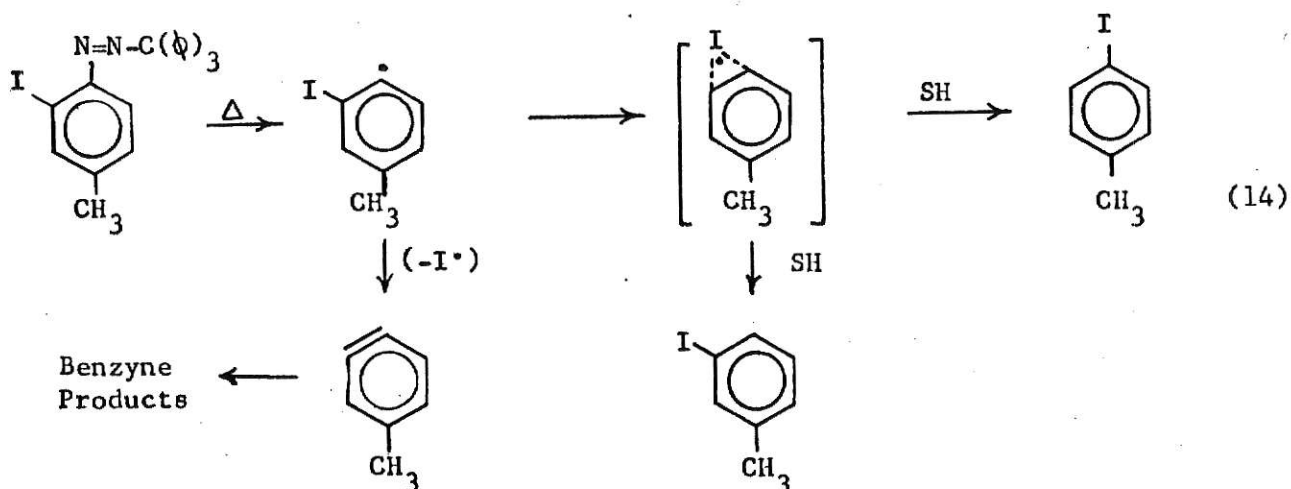
of a benzyne intermediate. The results were discussed in terms of a more "active" radical intermediate being formed in the cases where there is evidence for the benzyne intermediate, i.e., one with sufficient energy to eliminate an iodine atom from the ortho-iodophenyl radical.

If the ortho-iodophenyl radical is a benzyne precursor, one might expect the iodine atom elimination step to be a reversible process in which the iodine could re-add to the adjacent position, thus effecting iodine migration.

These foregoing observations have prompted the study of the configurational stability of ortho-iodoaryl radicals reported here.

RESULTS

In order to establish whether or not a halogen migration can occur in ortho-haloaryl radicals, 2-iodo-4-methylphenylazotriphenylmethane (IMPAT) was thermally decomposed in hydrocarbon solvents to generate the 2-iodo-4-methylphenyl radical. If an iodine migration occurs prior to abstraction of a hydrogen atom from solvent, two products should be obtained, namely m-iodotoluene and p-iodotoluene. Alternatively an iodine atom may be eliminated to give a benzyne intermediate^{64,65,66} as shown in equation 14. It was found that the iodotoluene isomers could not be adequately



separated on any of several glc columns tried, so infrared spectroscopy was chosen as the best method for determining the ratio of these isomers in the product mixture. p-Iodotoluene shows a very strong, sharp absorption at 12.55 microns, whereas m-iodotoluene has a strong absorption at 12.18 microns with very little interference from each other (Fig. 5a). Four calibration solutions of these two isomers were prepared ranging from 0.25% to 2% p-iodotoluene in m-iodotoluene, and their infrared spectra were run as 10% solutions by volume in CS₂. Table VI shows the percent p-iodotoluene by weight in each solution and its relative absorbance.

Three samples of 0.7 mole % IMPAT in cyclohexane were degassed by the routine freeze-thaw technique, sealed in glass ampoules, and thermally decomposed for five hours at 60°C to insure complete decomposition. The ampoules were then opened and analyzed by glc on a 15% SE-30 column to determine the percent of m- and p-iodotoluenes produced. Bromobenzene was added to the opened ampoules as an internal standard. Measuring glc peaks by planimeter gave an average of 81% conversion of IMPAT to the iodotoluenes. The iodotoluene product was collected by glc, mixed 10% in CS₂, and the infrared spectra was run (Fig. 5b), showing virtually none of the p-iodotoluene absorption at 12.55 microns.

The same procedure was run using as solvent tert-butylbenzene which is a much poorer hydrogen atom donator. The rate of abstraction of a hydrogen atom by the phenyl radical from tert-butylbenzene is a factor of ten slower than from cyclohexane.³² The glc analysis of this reaction revealed five peaks similar in size to the iodotoluene peak but no attempt was made to identify these components. Again the iodotoluene peak was collected by glc and the infrared spectra was run in CS₂, and again there

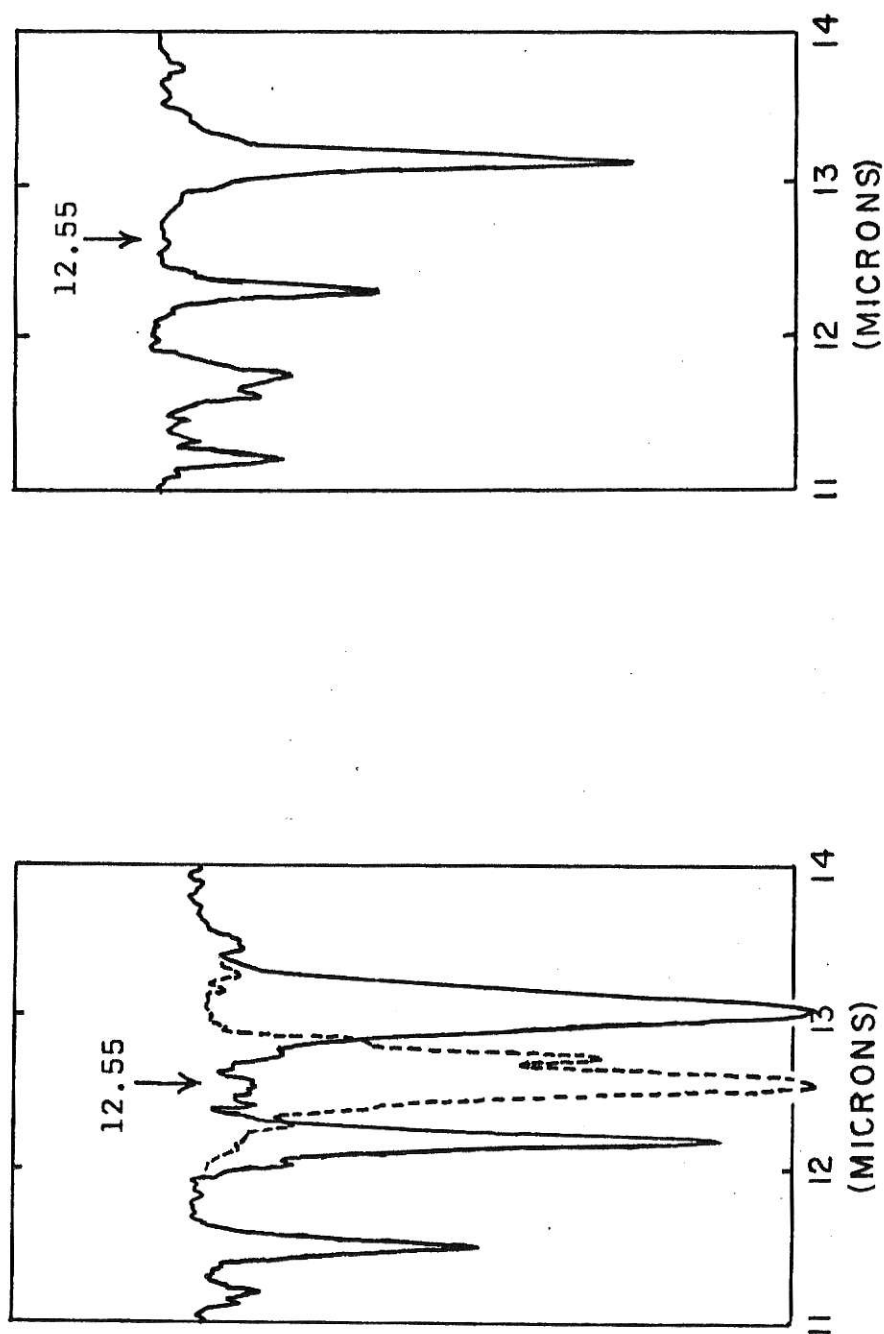


Figure 5a. IR spectra of m- & p- iodotoluene

m-Iodotoluene —

p-Iodotoluene - - - -

Figure 5b. IR spectrum of iodotoluene product from decomposition of IMPAT.

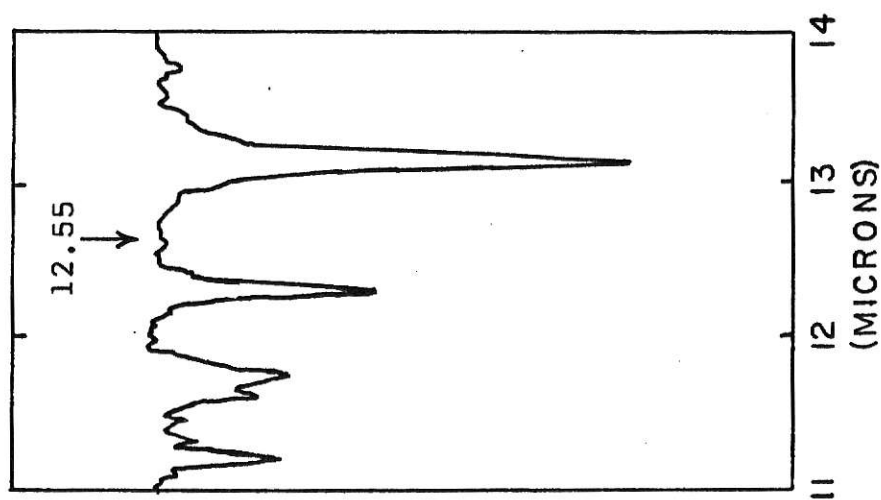


TABLE VI

COMPOSITION AND ABSORBANCE OF STANDARD SOLUTIONS
FOR INFRARED CALIBRATIONS.^a

Solution	% <u>p</u> -Iodotoluene in m-Iodotoluene (w/w)	Relative Absorbance ^b at 12.55 microns
A	2.04	0.038
B	1.15	0.023
C	0.68	0.021
D	0.25	0.008

^a Infrared spectra were run on a Perkin Elmer Model 137 using 0.1 mm NaCl liquid sample cells.

^b Relative to m-iodotoluene absorbance at 12.18 microns.

was no *p*-iodotoluene absorption at 12.55 microns.

Thermal decomposition of a 0.8 mole % solution of IMPAT in CCl_4 resulted in three products by glc analysis whose areas, relative ratios, and retention times appear in Table VII. Two of the products were identified as 4-chloro-3-iodotoluene and iodotoluene. The only sources of hydrogen to form iodotoluene are the benzylic hydrogens of the CH_3 group and cyclohexadienyl radicals formed as intermediates in homolytic substitution processes. Since the ratio between iodotoluene and the unknown peak is 2:1, it is plausible that the unidentified product might be a substituted bibenzyl formed by a dimerization of two substituted tolyl radicals. The retention time of the unknown peak is substantially longer than that of 4-chloro-3-iodotoluene suggesting it may be of considerably higher molecular weight. This product was not observed in the reactions run in cyclohexane and *tert*-butylbenzene. Using bromobenzene as internal standard a 78.5% conversion of IMPAT to products was determined, assuming a constant detector sensitivity for all compounds.

DISCUSSION

The thermal decomposition of IMPAT should be a good system for the investigation of bridged haloaryl radicals or aryl halogen migrations. The methyl group in the 4-position should have very little perturbing influence on the stability of the *ortho*-iodoaryl radicals and thus should not influence the ratio of *meta*- and *para*-iodotoluene products. The phenyl radicals produced in halogen abstraction reactions are σ radicals and hence there is no conjugation with the methyl substituent.

TABLE VIIPRODUCTS OF IMPAT DECOMPOSITION IN CCl_4

Peak	Area	Area Ratio ^a	t _r
Bromobenzene	68	---	0.93 min
Iodotoluene ^b	27	2	2.36
4-Chloro-3-iodotoluene	56	4	5.48
Unknown	14	1	11.48

^a Constant detector sensitivity to each of the components is assumed.

^b Assumed to be meta from above results.

The decompositions run in cyclohexane gave no p-iodotoluene, so t-butylbenzene which is a much poorer hydrogen atom donor was used as solvent. This should extend the lifetime of the radical intermediate, giving the iodine a better chance to bridge or migrate. The infrared spectra of the prepared meta- and para-iodotoluene calibration mixtures gave a detection limit for p-iodotoluene of less than 0.25%. The infrared spectra of the iodotoluene peak for both the cyclohexane and the t-butylbenzene experiments showed certainly less than 0.25% iodine migration to the para-position.

The decomposition of IMPAT was also run in CCl_4 solvent as a check for decomposition of IMPAT prior to thermolysis. Prior decomposition should give iodotoluene in the reaction mixture. The results given in Table VII do show iodotoluene as a product. However there was a high boiling component whose area was exactly twice the area of the iodotoluene peak. Since the benzylic hydrogens of the CH_3 group would be a source of abstractable hydrogen, the high boiling component may be a substituted bibenzyl formed by a dimerization of two substituted tolyl radicals. This explanation would account for the 2:1 ratio between iodotoluene and the unknown and would therefore indicate that no iodotoluene was present in the unreacted IMPAT.

CONCLUSIONS

We found no evidence for an iodine migration from the 2- to the 1-position in the thermal decomposition of 2-iodo-4-methylphenylazotriphenylmethane within the limits of detection. An ortho-iodine may possibly provide anchimeric assistance in the transition state leading to the 2-iodo-4-methyl-

phenyl radical intermediate, but the present results indicate that the intermediate is not symmetrically bridged.

Furthermore we found no evidence for a benzyne intermediate either in the form of an iodine migration or in the form of a biphenylene product in the reaction mixtures. However the possibility of a benzyne intermediate was not rigorously eliminated, nor were other reaction pathways explored. The fact that only ca. 80% of the IMPAT was accounted for in the reaction product leaves open the possibility of other reaction products.

EXPERIMENTAL

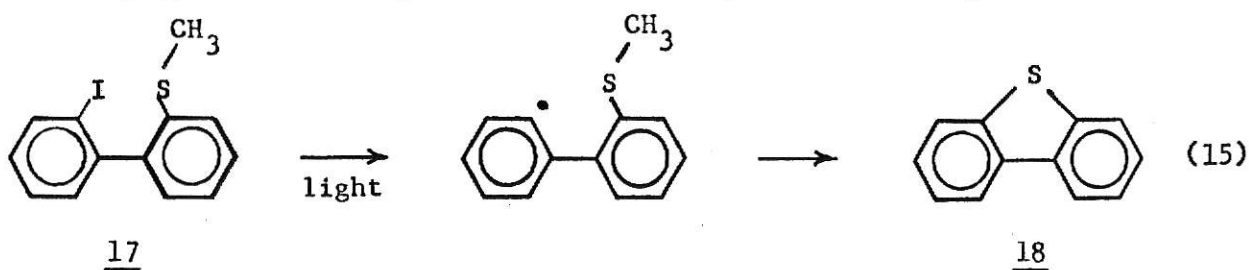
Synthesis of 2-Iodo-4-methylphenylazotriphenylmethane

The title compound, abbreviated herein as IMPAT, used in the study of the configurational stability of ortho-iodoaryl radicals was prepared by A. W. Airey⁶⁷ using the method of Cohen and Wang⁶⁸ in 20% yield, with the modification of using a 200% excess of H_2O_2 for 24 hours in the oxidation step. The product was recrystallized from 95% ethanol, mp 114-116°C with decomposition, and its identity was verified by nmr and ir. Pure samples of m-iodotoluene and p-iodotoluene used for the ir calibration solutions were obtained from Eastman Organic Chemicals and were determined to be >99% pure by glc.

Section B: Lack of Anchimeric Assistance by a Neighboring Sulfide in Iodine Abstraction from 2-Iodo-2'-methylthiobiphenyl.

The anchimeric assistance effect of ortho substituents in the decomposition of tert-butylperbenzoates shown by Bentrude and Martin⁵⁸ and discussed in the background in Section A is a rather long-range 1,4 interaction.

Another case in which rather long-range anchimeric assistance may be playing a role is the reaction studied by Kampmeier and Evans⁶⁹ in which the photolysis of 2-iodo-2'-methylthiobiphenyl (17) resulted in almost quantitative formation of dibenzothiophene (18). The following reaction scheme was proposed. The rapid and efficient capture of the aryl radical



by the neighboring sulfide group may be due to an interaction of the sulfur with the radical site in the transition state.

In an attempt to evaluate the possibility of anchimeric assistance by the sulfide group, we measured the relative rates of abstraction of iodine from 2-iodobiphenyl and 2-iodo-2'-methylthiobiphenyl. If the sulfur provides assistance in the iodine abstraction step, there should be a large difference in their relative abstraction rates.

RESULTS

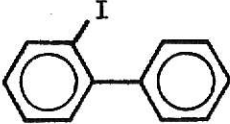
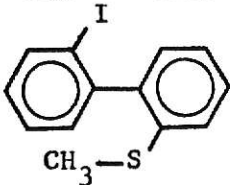
The rates of abstraction of iodine from 2-iodo- and 2-iodo-2'-methylthiobiphenyl versus the rate of abstraction of chlorine from carbon tetrachloride were determined using the competitive technique described in the Experimental - Kinetic Analysis section of Part I with the exception of using five inch lengths of 8 mm Pyrex tubing sealed at one end for ampoules. These smaller ampoules facilitated running the reactions on a smaller scale due to the small amount of iodobiphenyls available. These Pyrex tubing ampoules proved much less susceptible to breakage than the test tube ampoules first used. Four samples made up of weighed amounts of CCl_4 , the iodobiphenyl and PAT in molar ratios of 100:10:1 respectively were degassed and incubated for four hours at 60°C . The $k_{\text{I}}/k_{\text{CCl}_4}$ ratios were determined from glc product analysis and the percent yield of iodobenzene and chlorobenzene was calculated using bromobenzene as internal standard. The results obtained are shown in Table VIII.

DISCUSSION

The $k_{\text{I}}/k_{\text{CCl}_4}$ values obtained for the abstraction of iodine from 2-iodo- and 2-iodo-2'-methylthiobiphenyl (35.7 and 25.6 respectively) indicate no substantial anchimeric assistance by the sulfide group. Indeed the rate for the 2-iodo-2'-methylthiobiphenyl is slightly slower. The lack of anchimeric assistance in the transition state is perhaps not surprising in view of the fact that in disubstituted biphenyls the two substituents tend to lie as far apart as possible due to steric non-bonding interactions.

TABLE VIII

THE RATES OF ABSTRACTION OF IODINE FROM 2-iodo- AND
2-iodo-2'-methylthiobiphenyl BY THE PHENYL RADICAL.^a

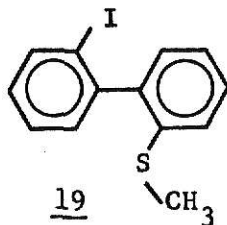
Reactant	Ave k_I/k_{CCl_4} ^b	% Yield ^c
	35.7	80.5%
	25.6	82.2%

^a Rate values are on a per molecule basis.

^b Average of four runs, each analyzed in triplicate by glc.

^c Yield of chlorobenzene and bromobenzene based on PAT.

Dipole-dipole interactions are also acting to keep these polar substituents as far apart as possible (19). There would have to be a rotation about the



bond joining the aromatic rings in order to expect appreciable assistance from the sulfide group in the transition state. The approach of the phenyl radical to the iodine in the transition state causes even more steric interactions with the methylthio substituent. Thus no anchimeric assistance was observed.

EXPERIMENTAL

2-Iodobiphenyl:

2-Iodobiphenyl was obtained from K & K Laboratories and fractionally vacuum distilled to give a liquid >99% pure by glc.

Synthesis of 2-Iodo-2'-methylthiobiphenyl:

The synthesis of this compound was performed following the procedure of Kampmeier and Evans.⁶⁹ To a 20-fold excess of dimethyl disulfide in benzene was added 1.6 g of biphenyleneiodonium-tert-butylmercaptide and the solution was refluxed for 12 hours. Removal of the benzene left a brown oil which would not dissolve in hot ethanol. The oil was removed from the ethanol, placed on a watch glass and after about one hour had crystallized.

This was then further purified by two recrystallizations from a 3:1 benzene-ethanol mixture using an ice-saltwater cooling bath and seed crystals to effect crystallization, resulting in 0.48 g (32% yield) of a yellow solid, mp 88-89°C.

Synthesis of Biphenyleneiodonium-tert-butylmercaptide

The biphenyleneiodonium-tert-butylmercaptide was prepared from biphenyleneiodonium chloride⁷⁰ by the procedure of Greidanus, et al.⁷¹ To 1.44 g of biphenyleneiodonium chloride in 100 ml H₂O degassed with nitrogen was rapidly added a slightly less than stoichiometric amount of tert-butylmercaptan in 10% NaOH solution. The fluffy yellow precipitate which formed within minutes was immediately filtered and air dried. No attempt at recrystallization was made due to thermal decomposition of the trivalent iodine compound. The biphenyleneiodonium-tert-butylmercaptide had a sharp mp of 126°C and satisfactory ir and nmr spectra were obtained.

Kinetic Analysis: The kinetic analyses were performed in the same manner as described in the Experimental - Kinetic Analysis section of Part I.

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VITA

Kenneth Allen Rose was born in Elkhart, Kansas, on August 6, 1946. He was reared on his parents farm near Keyes, Oklahoma, where he attended school for twelve years. He graduated from Keyes High School as salutatorian of his Senior Class in 1964.

In 1964 he entered Bethany Nazarene College where he majored in chemistry. The Bachelor of Science degree in chemistry was awarded him in 1968.

Shortly after graduation he was inscripted into the U. S. Army, where he served for nineteen months. During this time he spent a year in Viet Nam where he worked as a medical lab technologist.

Upon his release from active duty in 1970, he entered the Graduate School at Kansas State University to work on a Master's Degree in chemistry. While at Kansas State University he became a member of Phi Lambda Upsilon fraternity.

On December 26, 1970, he married the former Norma Barnett of Guymon, Oklahoma.

RELATIVE RATES OF ABSTRACTION OF HALOGEN BY PHENYL RADICALS FROM
CYCLOALKYL BROMIDES, CYCLOALKYL TRANS-1,2-DIBROMIDES,
AND SELECTED AROMATIC IODIDES

by

KENNETH ALLEN ROSE

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ABSTRACT

Part I: Rate Acceleration Due to β -Bromine in Halogen Abstraction Reactions of Alkyl Dibromides

The relative rates of abstraction of bromine from a series of cycloalkyl monobromides and dibromides by the phenyl radical were determined. Also the rates of abstraction from substituted alkyl bromides with substituents varying over a wide range of polarity were determined to show the effect of polarity on the transition state.

The rate of abstraction of an atom β to a bromine substituent is known to be especially rapid. Proposed explanations for this accelerated abstraction have invoked bridged bromine radical intermediates and alignment of the C-Br bond with the p orbital of the radical intermediate through homoconjugation and hyperconjugation mechanisms. The actual mechanism of stabilization was not revealed by these studies, although the bromine abstraction data did provide a method for calculating the stabilizing influence of a β bromine on the transition state leading to a radical intermediate. The calculations gave the stabilizing influence of bromine in the β -bromoethyl radical as ca. 2 kcal/mole. Similar calculations for allyl bromide gave the resonance stabilization of the allylic radical as ca. 8 kcal/mole, which approximates the value of 9.4 kcal/mole obtained by Benson and co-workers. This agreement lent validity to the approximations made in these calculations.

It was found the rates of bromine abstraction from alkyl bromides substituted with polar groups correlated well with the respective Taft polar substituent constants σ^* , giving a positive ρ value ($\rho = +0.158$).

This agreed in sign with ρ values obtained from other halogen abstraction reactions, but was opposite in sign to hydrogen abstraction reactions.

This indicated a reversal of polarity in the transition state.

The abstraction of bromine from a series of cycloalkyl trans-dibromides gave evidence that the acceleration in rate for these dibromides was not due to an E_H2 concerted elimination, but that a radical intermediate was involved. The abstraction of bromine from a series of cycloalkyl bromides was shown to correlate with the rate of formation of cycloalkyl carbonium ions for which ring strain effects are thought to influence the rates of reaction. This indicated that the transition state came late enough in the reaction to feel the effects of ring strain, and that considerable radical character had developed on the α -carbon in the transition state.

Part II: Lack of Iodine and Sulfur Anchimeric Assistance in the Formation of Selected Aryl Radicals

In this part of this work the possibility of halogen anchimeric assistance in aromatic compounds was investigated. The thermal decomposition of 2-iodo-4-methylphenylazotriphenylmethane in hydrocarbon solvent produced the 2-iodo-4-methylphenyl radical which abstracted hydrogen from solvent to give iodotoluene. The object of this investigation was to determine if iodine bridging occurs in the radical intermediate. Bridging would result in a mixture of m- and p-iodotoluenes in the product. The infrared spectra of the iodotoluene product revealed only the meta isomer, indicating no bridging in the intermediate.

The rates of abstraction of iodine from 2-iodo- and 2-iodo-2'-methylthiobiphenyl by the phenyl radical were obtained. The object of this experiment was to determine if the neighboring sulfur could provide anchimeric

assistance in the abstraction of the iodine. The relative rates obtained indicated that no anchimeric assistance by the thiomethyl group was being felt in the transition state for this reaction.