

AN ABSTRACT OF THE THESIS OF

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Title: FREE RADICAL HYDROGEN ABSTRACTION FROM  
BENZOCYCLOALKENES

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The relative rates of hydrogen abstraction from o-xylene, o-diethylbenzene and a series of four benzocycloalkenes by trichloromethyl radical were determined at 70°. The strain energies of the hydrocarbons and the corresponding radicals were calculated. A good correlation between the log of the relative rates and the calculated changes in strain energy, with a coefficient of -0.974, was obtained. The results showed that in free radical substitutions, benzocycloalkenes are less dependent on strain factors than polycycloalkanes. This is due to the benzylic-type radicals formed in the former series being greatly stabilized by resonance and hence somewhat insensitive to other structural factors.

Free Radical Hydrogen Abstraction from  
Benzocycloalkenes

by

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# FREE RADICAL HYDROGEN ABSTRACTION FROM BENZOCYCLOALKENES

## INTRODUCTION

It would be of interest to examine the effect of strain on the formation of benzylic free radicals. Brown, in 1950, coined the term I-strain to describe the influence of ring size on reactivity (1). According to the definition of I-strain, any change in the preferred bond or coordinate number of an atom in the course of reaction would cause a change in the internal strain (2). Attempts to apply this to free radical substitution reactions are, however, very few. Recent work of Ferguson and Whittle concerning free radical bromination of cycloalkanes indicates a good correlation between relative rates of reaction and estimated changes in strain energy factors (3). Ferguson and Whittle found that the order of the relative rate constants with respect to the ring size is:

$$C_4 < C_5 > C_6 < C_7$$

The corresponding ground state strain energies are reported to be 26.5, 6.2, 0.0, and 6.2 kcal/mole, respectively (4). The lower reactivity of cyclohexane as compared to cyclopentane in free radical hydrogen abstraction using trichloromethyl (5,6), trichloromethylsulfonyl (6) or methyl radicals (3,7) as the abstracting agents has also

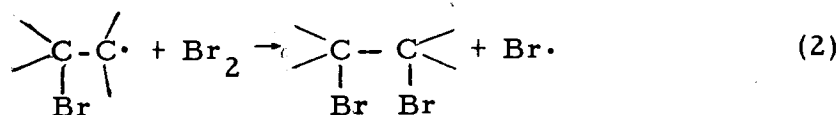
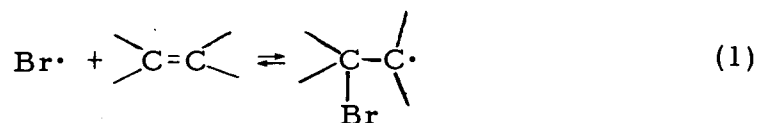
been reported in other works. The changes in strain energy between a cycloalkane and the corresponding radical are more important than the ground-state strain energy (3, 5). It was found that strain in small rings is mainly caused by bent bonds, while the strain of cyclo-pentane, -hexane and -heptane arise from intramolecular H-H interactions and torsional strains (3). The inertness of the apparently strain-free cyclohexane molecules in solvolytic reactions is accounted for by Brown in terms of intermolecular non-bonded interactions and I-strain present (1). When cyclohexane is converted to its radical, a carbon atom will be converted from  $sp^3$  to  $sp^2$  hybridizations. Such a change will increase ring strain and, therefore, free radical formation is disfavored for cyclohexane. Relief of ring strain originally present in cyclopentane and cycloheptane, however, acts as a driving force to form the less strained radicals. Overberger and coworkers suggested that if strain is relieved from the cyclane when the radical is formed, the activation energy is reduced (8).

Studies have also been performed in which cycloalkyl free radicals are generated via an additional reaction. Such free radical additions to cycloalkenes are stereoselective. Abell and Chiao observed that variations in ring size affect the rate of radical addition (9). They attributed this to an inhibition of the approach of the radical to the cycloalkene due to intermolecular steric effects. Free radical



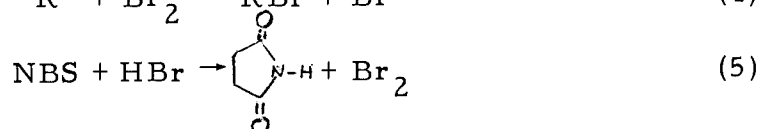
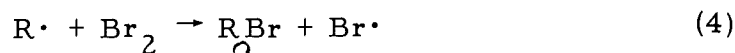
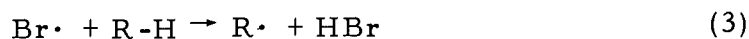
addition of hydrogen bromide to a series of 1-bromoalkenes give predominantly the cis product (9).

One problem encountered in the kinetic studies of free radical addition is the occurrence of allylic substitution simultaneously in the reaction process. In the photobromination of cyclenes using NBS, the order of reactivities of the cyclenes reported by Russell and Desmond is: cycloheptene > cyclopentene > cyclohexene (10). This order is similar to that obtained by Ferguson and Whittle for the reactivities of cyclanes toward bromine atoms (3), even though it is found that the range of the relative rates of bromination for the former series is much larger. Furthermore, during the process of free radical bromination, the cyclenes have been observed to disappear faster than aralkyl hydrocarbons containing benzylic hydrogens! The result is interpreted by Russell and Desmond to be due to the addition of bromine atoms to the double bonds of the compounds in the former



series (as shown in Equations 1 and 2) simultaneous with allylic substitution (10). Such substitution is greater especially when the concentration of bromine molecules present is low (11). The mechanism

of substitution is given in the following equations:



In the reaction with methyl radicals, cyclohexene is found to be less than one-fifth as reactive as cyclopentene (12). The lower reactivity of cyclohexene is in good agreement with data obtained from the addition of methyl radical (13) and trichloromethyl radical to olefins (14). Similarly, complications in kinetic studies due to competitive addition and substitution also arise in two other cases. Walling and McGuinness chlorinated a variety of olefins with *t*-butylhypochlorite (15). They found that with most olefins, allylic substitution rather than addition is preferred by *t*-butoxy radicals. Walling and Thaler, however, later showed that a portion of the olefinic substrate disappeared by reaction with chlorine atom in an addition process (16). Also, in the study of the reactivities of carbon-hydrogen bonds in allylic systems toward phenyl radicals, Bridger and Russell discovered that an appreciable fraction of phenyl radicals was consumed by addition reaction (17).

Strain energies of cyclanes and cycloenes are difficult to compute due to the flexibilities of cyclic compounds (12, 30, 31, 32, 33, 34). To ameliorate this problem, benzocycloalkenes might be used in

place of cyclenes in the present study. One of the advantages of using benzocycloalkenes is that the benzylic carbon-hydrogen bond has a low dissociation energy due to resonance stabilization of the resulted radical. Thus only the benzylic hydrogens are abstracted (18, 19). Russell and DeBoer illustrated this result in the bromination of hydrocarbons where they found that primary benzylic hydrogens are abstracted 60,000 times faster than hydrogens in ethane and secondary benzylic hydrogen atoms are abstracted 5,000 times faster than the secondary hydrogens in propane (18). This effect is even exhibited by less selective radical sources. Williams and coworkers have investigated the rates of hydrogen abstraction by t-butoxy radical (20). The relative rates of hydrogen abstraction is expressed by the ratio  $k_h/k_d$ , where  $k_h$  is the rate of hydrogen abstraction from the substrate and  $k_d$  is the rate of the decomposition of the t-butoxy radical to acetone. The results obtained are presented in Table 1. Reaction of t-butoxy radical with alkanes gives the sequence: primary, 1; secondary, 7; tertiary, 28. Hydrogen atoms activated by a benzene ring are more reactive but preserve the same ordering: primary, 12; secondary, 32; tertiary, 51. Secondary hydrogen atoms of tetralin activated by the benzene ring, as well as the alicyclic ring, are the most reactive types found here.

In addition to the favorable benzylic site for radical formation in benzocycloalkenes, benz-annellated molecules are less flexible than

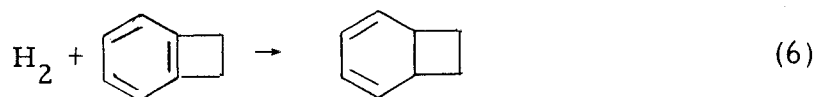
cyclanes and cyclenes and thus are less likely to rotate to the conformations of higher energy. Hence computational problems are greatly simplified.

Table 1. Relative rates of hydrogen abstraction by t-butoxy radical (20).

H Atom Type	Calculated From	Relative Rates $k_h/k_d$
Benzene	benzene	0.3
Primary, unactivated	t-butylbenzene	1.0
Secondary, unactivated	cyclohexane	3.2
Secondary, activated	ethylbenzene	32.0
Secondary, cyclohexyl, activated	tetralin	76.0
Tertiary, unactivated	1,2-dimethylcyclopentane	28.0
Tertiary, activated	isopropylbenzene	51.0

The reactivities of carbon-hydrogen bonds toward free radicals can be determined by examining the various structural factors, namely, resonance, steric, entropy and polar effects (21). However, since the present study is restricted to homologous compounds with similar structural type, it is possible that the above effects should be so small as not to cause significant problems. This reduces our problem in studying the reactivities of benzocycloalkenes to strictly strain energy terms which are most important particularly in the formation and stability of the radical.

In 1971, Gleicher and Koch carried out strain energy calculations for a series of polycyclic aliphatic hydrocarbons. The good correlation of the relative rates with calculated strain energies is compatible with the assumption of a planar transition state (22). The strain energies of benzocycloalkenes are hitherto unknown. However, the heat of hydrogenation of benzocyclopentene has been reported by Dolliver to be  $-45.800$  kcal/mole at  $355^\circ\text{K}$  and  $-45.987$  kcal/mole at  $373^\circ\text{K}$  (23). Attention should be called to the result obtained by Turner and coworkers in the catalytic hydrogenation of benzocyclobutene and related compounds at  $25^\circ\text{C}$  (24). The heat of hydrogenation is directly proportional to the strain energy of the compound and any large degree of strain might interfere with electron delocalization in the benzene ring. The heat of hydrogenation of benzocyclobutene is  $-50.3$  kcal/mole. This value is close to that obtained for *o*-xylene ( $-47.3$  kcal/mole) and may be compared with the heat of hydrogenation of 2,4-bicyclo[4.2.0]-octadiene. From the heats of hydrogenation of benzocyclobutene and 2,4-bicyclo[4.2.0]-octadiene, the heat of hydrogenation of the following reaction,

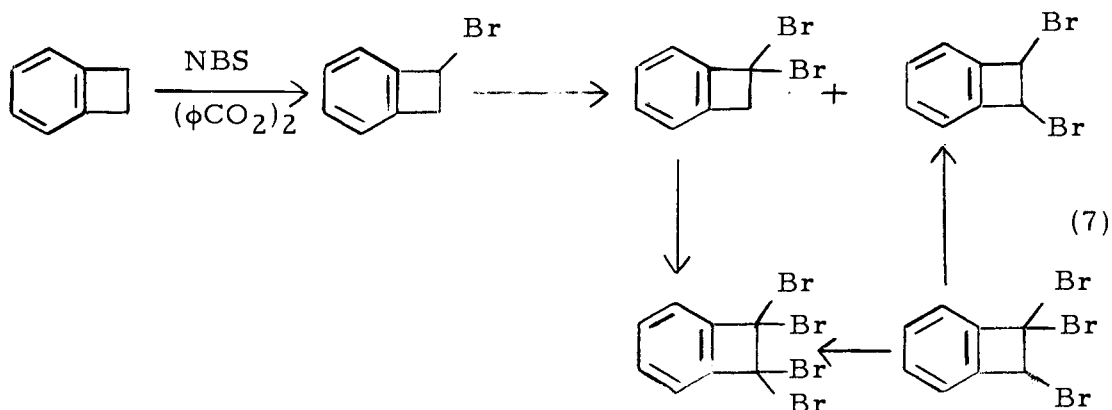


is found to be  $1.4$  kcal/mole. The corresponding system for the heat of hydrogenation of benzene to 1,3-cyclohexadiene is  $5.6$  kcal/mole.

These results emphasize the smallness of the effect of the strain in benzocyclobutene on aromatic resonance. It is interesting to point out that non-strained systems such as 1-phenylalkanes react with both bromine atoms and trichloromethyl radical with rates which are independent of the length of the alkyl chain and that simple n-alkyl groups have negligible steric hindrance associated with them (25).

The mechanism of benzylic hydrogen abstraction using trichloromethyl radical is well documented (18, 26, 27, 39). Although hydrogen abstraction from some benzocycloalkenes had been previously studied by other groups using bromine atom as the abstracting agent (28, 29), trichloromethyl radical is preferred in this work because of its anticipated selectivity and the advantage of operating in a homogeneous medium (25).

Prolonged bromination of benzocyclobutene utilizing NBS has been reported to produce various halogenated products the ultimate of which is tetrabrominated benzocyclobutene (28):



Fortunately, the monobrominated product has been isolated after two and one-half hours of reaction. Dibromides are formed only on further bromination.

The relative reactivities of indan and tetralin in the bromination reactions toward bromine atoms generated by photolytic decomposition of NBS at 40° C are much smaller than those of cyclenes. Even cyclohexene, the least reactive among the cycloalkenes, is more than four times as reactive as indan and tetralin as shown in Table 2. The greater reactivities of cyclenes are interpreted before to be due to competitive addition and substitution reactions (10). The relative reactivity of indan to tetralin, however is not consistent with data obtained from hydrogen abstraction from the two compounds by radicals other than bromine atom. With methyl radical (37), phenyl radical, trichloromethyl radical (21) and t-butoxy radical (36) as the abstracting agents, tetralin always reacts faster than indan. One exception is chlorine atom. As in the case of bromine atom, indan is observed to be more reactive than tetralin towards chlorine atom (38). The differences in reactivity between the two compounds, however, are always small. Table 3 compares the relative rates of the free radical formation when different common radicals and atoms are used as the abstracting agents in solution.

Table 2. Relative reactivities of cyclenes and benzocycloalkenes toward NBS bromination at 40° C (10).

Compound	Relative Rates
Indan	49
Tetralin	47
Cyclopentene	780
Cyclohexene	160
Cycloheptene	1100

Table 3. Comparison of the relative rates of indan and tetralin toward free radicals.

Compounds	Br. <sup>a</sup>	Phenyl radical <sup>b</sup>	CCl <sub>3</sub> · <sup>c</sup>	t-BuO· <sup>d</sup>	CH <sub>3</sub> · <sup>e</sup>	Cl· <sup>f</sup>
Indan	49	8.0	0.85	2.08	8.3	4.4
Tetralin	47	12.3	1.10	3.27	11.5	4.1

<sup>a</sup>Ref. 10; bromine atoms are generated from NBS. Rates were measured relative to toluene at 40° C.

<sup>b</sup>Ref. 17; rates measured at 60° C.

<sup>c</sup>Ref. 21; given data are log<sub>10</sub> of the relative rates measured at 91° C. CCl<sub>3</sub>· was generated from CCl<sub>4</sub>.

<sup>d</sup>Ref. 36; rates measured at 135° C.

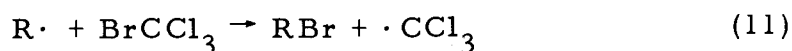
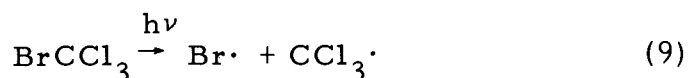
<sup>e</sup>Ref. 35.

<sup>f</sup>Ref. 38; rates measured at 40° C.



Statement of the Problem

This work is undertaken in order to study the formation of radicals directly from the parent hydrocarbons such that the results can be easily correlated with calculated strain energy differences between the starting material and the transition state. Kinetic data are acquired in this study by considering a series of benzocycloalkenes in competition with fluorene for trichloromethyl radical as the abstracting agent. The reaction sequence is as follows:



Due to the unreactive character of *t*-butylbenzene towards trichloromethyl radical, *t*-butylbenzene is used as the internal standard in the reaction (26). Fluorene, on the other hand, is moderately reactive towards the abstracting agent and in the present work, hydrogen abstractions were run relative to fluorene (19). Ortho-diethylbenzene and *o*-xylene are non-strained alkylbenzenes. They should provide relatively strain-free radical intermediates after the abstraction of the benzylic hydrogens. Strain energies calculated

for this system with respect to the relative rates of hydrogen abstraction were compared to those of benzocycloalkenes.

Strain energies for the ground-state hydrocarbons and the free radical intermediates were calculated using a computer program similar to the one used by Gleicher and Schleyer in their study of bridgehead carbonium ion (40). The input data are based upon the initial geometry and consist of bond lengths, force constants, torsional potentials and angles determined from the original hydrocarbons. A strain energy was calculated with respect to the geometry and the coordinates of each atom were altered iteratively until an energy minimum was approached. Since the abstraction of the benzylic hydrogen is endothermic, it follows by the Hammond postulate that intermediate radical resembles the transition state. In the present work, the energies of the free radical intermediates themselves have been calculated, it being assumed that the transition state energies are proportional thereto. The free radical center in the intermediate produced preferred to be planar, therefore, the transition state should also be essentially planar.

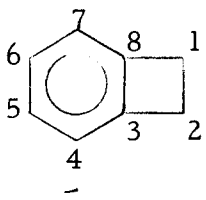
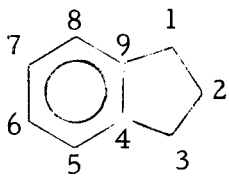
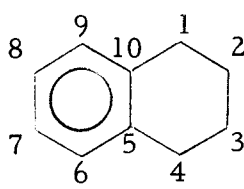
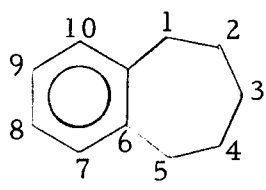
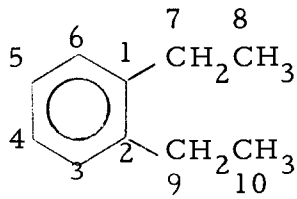
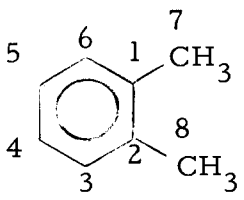
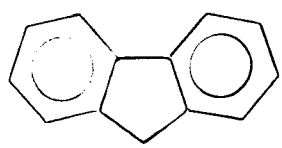
The series of compounds studied is presented in Table 4. Benzocycloalkenes are used here because of their inflexibilities and their incapability to undergo addition reaction. Furthermore, other than o-xylene all the hydrocarbons considered have equivalent number of secondary benzylic hydrogen atoms in the same electronic

environment.

The calculated energy differences between the hydrocarbons and the corresponding free radicals are to be compared with experimentally determined rates of hydrogen abstraction.

The following report includes: preparations of the compounds; kinetic studies of benzocycloalkenes and o-dialkylbenzenes run in competition with fluorene for trichloromethyl radical and the correlation of relative rates of reaction with the calculated changes in strain energies.

Table 4. Benzocycloalkenes and alkylbenzenes.<sup>a</sup>

Benzocyclobutene		$C_8H_8$
Benzocyclopentene (Indan)		$C_9H_{10}$
Benzocyclohexene (Tetralin)		$C_{10}H_{12}$
Benzocycloheptene		$C_{11}H_{14}$
o-Diethylbenzene		$C_{10}H_{14}$
o-Xylene		$C_8H_{10}$
Fluorene		$C_{13}H_{10}$

<sup>a</sup>The numbering system shown above for the benzocycloalkenes is utilized in all further discussion of calculated energies and geometries reported herein.

## RESULTS AND DISCUSSION

### Preparations of Compounds

With the exception of benzocyclobutene and benzocycloheptene, all the utilized compounds are commercially available. Benzocyclobutene was kindly donated by Professor P. Radlick of the University of California at Riverside. The reduction of benzosuberone by the Minlon-Huang modification of the Wolf-Kishner reaction gave benzocycloheptene (49). Procedures for the preparations and purifications of the compounds may be found in the experimental section.

### Product Studies

Product studies only for benzocyclopentene and benzocyclohexene were carried out. In the course of reaction, nmr spectra of the reaction mixtures showed that bromination utilizing bromotrichloromethane occurred exclusively at the benzylic positions. Such a result is also obtained by Russell and Desmond in their work where NBS is used as the radical source (10). Attempts had been made to analyze the reaction mixtures by gas-liquid chromatography. In each case only one product peak was found. As the products were eluted from the glc column, they were collected. The nmr spectra showed those to be the respective olefins instead of the bromides. This indicates that  $\alpha$ -bromobenzocyclopentene and -hexene were

dehydrohalogenated on the glc column to form indene and 1,2-dihydronaphthalene, respectively. In view of the above, an alternate method other than glc was employed for the quantitative analysis of the reaction mixture. NMR spectroscopy was used in this work. As an experimental tool, nmr should provide a fairly accurate means of analysis. Details of determining the precision of nmr may be found in the experimental section.

No product studies were performed on benzocyclo-butene and -heptene. From Cava and coworkers' extensive study on the free radical bromination of benzocyclobutene using NBS as the bromine atom source, it is reported that  $\alpha$ -bromobenzocyclobutene is the only product (28). In view of these findings, it is also assumed that only benzylic hydrogen atoms are abstracted from benzocycloheptene and that only  $\alpha$ -bromobenzocycloheptene is formed. The nmr spectrum of benzocycloheptene reaction mixture shows that this assumption is correct.

The amount of bromotrichloromethane consumed in the reaction is not in good agreement with the hydrocarbons consumed thus showing that side reaction occurs, such as the photolytic decomposition of bromotrichloromethane. This is caused by the attack of bromotrichloromethane molecule by the bromine atom that is generated and as the result bromine molecules and trichloromethyl radical are produced.

A material balance of ca. 95% was found for the total hydrocarbon.

### Kinetic Studies

Solutions of benzocycloalkenes, fluorene, t-butylbenzene and bromotrichloromethane were prepared in the approximate ratio of 1:0.5:0.25:5. Small samples were reserved for analysis as a starting material. The remainders were irradiated with ultraviolet light at 70° until about 30% to 60% of the total hydrocarbons had reacted. A five-fold excess of bromotrichloromethane ensures that trichloromethyl radical is the only abstracting agent of benzylic hydrogens.

Within experimental error, the internal standard, t-butylbenzene was not observed to participate in the reaction.

The results of the relative rates of the disappearance of benzocycloalkenes to fluorene are presented in Table 5.

Table 5. Relative rates of disappearance of benzocycloalkenes and o-dialkylbenzenes to fluorene with trichloromethyl radical as the abstracting agent at 70° C. <sup>a</sup>

Compounds	$k_x/k_F$	Number of Kinetic Runs
Benzocyclobutene	0.08 ± 0.01	4
Benzocyclopentene	1.39 ± 0.08	5
Benzocyclohexene	1.41 ± 0.08	7
Benzocycloheptene	0.42 ± 0.03	5
o-Xylene	0.60 ± 0.05	8
o-Diethylbenzene	0.84 ± 0.06	9

<sup>a</sup> Complete data for the kinetic studies may be found in the Appendix, Tables 9 to 14.

### Determination of Strain Energies

The strain energies of both the ground-state hydrocarbon and the free radical intermediate were calculated utilizing a program developed by Gleicher and Schleyer (40). Calculations were performed on a CDC 3300 computer at the Oregon State University. The coordinates of the atoms in each system served as input data and from this an initial strain energy was evaluated. The coordinates of each atom were altered repeatedly along the Cartesian coordinates until an energy minimum was reached. That is, the total energy calculated was constant to about 0.01 kcal/mole. In order to be economical in computational time and to accelerate the minimization process for the series of benzocycloalkenes, geometry of the non-aromatic, cyclic part of each benzocycloalkene at energy minimum was calculated first with the benzene ring detached from the structure. The benzene ring was then attached to this geometry and calculations are repeated to obtain the final energy minimum of the entire molecule.

In the calculations, the values of the bond length for  $sp^3-sp^3$  carbon-carbon and  $sp^3$  carbon-hydrogen bonds were taken as 1.533 and 1.108 Å respectively;  $sp^2-sp^2$  carbon-carbon bond lengths were set at 1.1515 Å;  $sp^2$  carbon-hydrogen bond lengths were taken to be 1.075 Å. The aromatic carbon-carbon bonds were assumed to be 1.40 Å. Preferred values for the angles were a function of



hybridization with  $sp^3$  centers essentially tetrahedral and  $sp^2$  centers trigonal (22). The bending force constants for the radical and the ground state hydrocarbon were assumed to be the same. Stretching force constants for all bonds were fitted to the Tractrix equation and are a function of the bond length (41). Standard functions for determining non-bonded interactions and torsional strain were employed.

The results of the strain energy calculations are given in Table 6.

Table 6. Calculated strain energies for benzocycloalkenes and o-dialkylbenzenes in kcal/mole.

Hydrocarbons	Ground State Strain ( $H_1$ )	Transition State Strain ( $H_2$ )	$\Delta H (=H_2 - H_1)$
Benzocyclobutene	116.547	128.637	12.110
Benzocyclopentene	24.797	24.328	-0.469
Benzocyclohexene	17.238	14.195	-3.043
Benzocycloheptene	21.941	27.037	5.096
o-Xylene	13.562	12.489	-1.073
o-Diethylbenzene	22.627	21.341	-1.286

Table 7 presents the comparison of the relative rates of reaction with the calculated strain energy differences.

Table 7. Relative rates of reactions and corresponding changes in strain energy.

Hydrocarbons	$k_x/k_F$	$\Delta H$ kcal/mole
Benzocyclobutene	0.08	12.110
Benzocyclopentene	1.39	-0.469
Benzocyclohexene	1.41	-3.043
Benzocycloheptene	0.42	5.096
o-Xylene	0.60	-1.073
o-Diethylbenzene	0.84	-1.286

#### Correlation of Kinetic Data with Strain Energies

Within the series of benzocycloalkenes, the relative rate of hydrogen abstraction is greatest when the energy of the free radical intermediate is smaller than that of the parent compound such that energy is released in reaching the transition state.

The low rate of reaction observed for benzocyclobutene is due to the increase of strain in going from the ground state to the free radical intermediate. Torsional strain actually decreases somewhat (2.28 kcal/mole) when the planar intermediate is formed. However, this small loss in torsional strain is compensated by a large increase in the angle strain. This is most important at the site of radical formation. The  $C_8-C_1-C_2$  angle strain already present in the ground state is increased in the free radical intermediate. In an attempt to partially alleviate this angle strain, bond strain is somewhat reduced. In spite of this compensating factor, the resultant radical is highly strained.

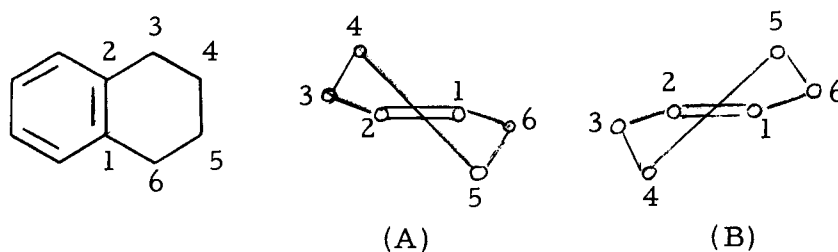
From the electron diffraction study of Goldish, Hedberg and Schomaker, the molecular structure of cyclobutene has been determined to be planar (42). In the present work, it is therefore not unreasonable to consider the structures of benzocyclobutene and the corresponding radical also as essentially planar.

Inspection of the data in Table 7 indicates that indan and tetralin have very close values of relative rates of reactions. This agrees with data on the relative rates of hydrogen abstraction from these two compounds obtained by other authors when other common radicals are used as the abstracting agents (Table 3). However, it must be emphasized that indan and tetralin are 20 times more reactive than benzocyclobutene. The high reactivities may be due to the similarities of the strain energy changes between the ground and the transition states of the individual systems. In both cases, removal of benzylic hydrogens seems to diminish interactions between atoms such that stretching energies, non-bonded interactions and torsional strains are reduced to some extent.

The main difference in the calculated energy differences between the indan and tetralin systems dwells primarily in the energy caused by angle strain. The greater negative strain energy difference calculated for the latter system arises from the release of angle strain in approaching the transition state. The benzylic carbon is changed from  $sp^3$  to  $sp^2$  hybridization in going from the tetrahedral ground

state to the trigonal center. This necessitates the expansion of bond angles from  $109.5^\circ$  to  $120^\circ$  ideally. The calculated bond angles about the free radical center in tetralin are found to be:  $119.85^\circ$ ,  $120.08^\circ$  and  $120.09^\circ$ . Such arrangement at the reaction site produces a stable free radical. The increase in  $C_2-C_1-C_9$  angle of the indan system from  $97.90^\circ$  in the ground state to  $105.26^\circ$  in the transition state, and further increasing angle strain at sites adjacent to the reaction site, cause the angle strain of the free radical intermediate to be 3.13 kcal/mole larger than that of the parent hydrocarbon.

Structural determinations have been carried out for indan and tetralin by nmr (43), X-ray (44,45) and UV techniques (46,47). Moore and coworkers obtained near UV spectra for the series of benzo-cycloalkenes. They favor a non-planar six-membered ring in the ground state of tetralin which is represented by conformations A and B:

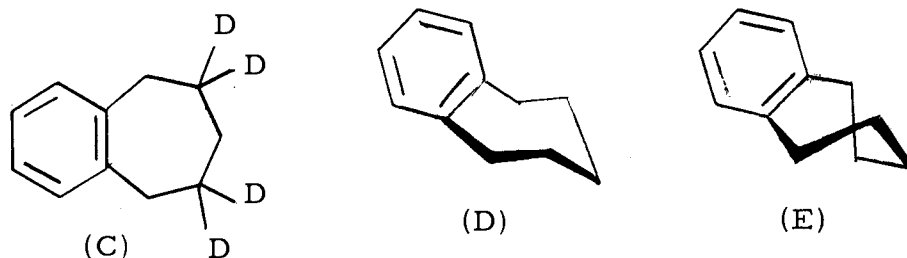


Because of this zig-zag structure, tetralin has stable conformations (A and B) such that  $C_4$  and  $C_5$  are alternately above and below the plane of the benzene ring and  $C_3$  and  $C_6$  are assumed to be slightly

above or below the plane of the ring, depending on the positions of  $C_4$  and  $C_5$ . This structure is in accord with our calculated ground-state geometry of tetralin. Also, the conformations A and B confirm the results obtained previously via X-ray measurements by Ganapathi (44) and Mills and Nixon (45). The dimensions for the six-membered ring proposed by Mills and Nixon are:  $C_1-C_2 = 1.42$ ,  $C_2-C_3 = C_1-C_6 = 1.48$  and  $C_3-C_4 = C_4-C_5 = C_5-C_6 = 1.54 \text{ \AA}$ . This is not a critical example, however, since no precise knowledge of the bond angles for tetralin was then available.

Although Moore's group found that indan is not a completely planar molecule, they believed that the difference in the out-of-plane vibrations in ground state and the excited state is much smaller than that in tetralin. Our calculated planar geometry of indan in this work should introduce no serious error.

No detailed structure determinations have been calculated on benzocycloheptene. However, nmr analysis of 4,4,6,6-tetradeutero-1,2-benzocycloheptene (C), has shown that 95% of the hydrocarbon exists in the chair conformation (D) and 5% exists in the twisted



form (48, 49). The structure of benzocycloheptene utilized in the present work is calculated from a molecular model similar to the one (D) proposed by Allinger and Sprague (48).

The magnitude of the ground- and transition-state energies in benzocycloheptene are found in the same neighborhood as those of indan. However, the energy difference between the ground and the transition state of the former system is 5.56 kcal/mole greater than that of the indan system. Hence, benzocycloheptene is only one-third as reactive as indan and tetralin. Again, this change in strain energy is mainly due to the increase in angle strain in forming the intermediate. All the angles in the seven-membered ring of benzocycloheptene are found to have increased in magnitude going from the ground to the transition state. For example,  $C_2-C_1-C_7$  angle is enlarged from  $109.49^\circ$  to  $124.11^\circ$ ; angles  $C_4-C_3-C_2$  and  $C_5-C_4-C_3$  are respectively  $4.9^\circ$  and  $4.5^\circ$  larger. Therefore, as the result, some bond deformation is created in the free radical intermediate and the stretching energy is slightly increased in order to accommodate this angle distortion. It has been mentioned before that benzocycloheptene principally exists in chair form seven-membered rings. Hence, when the groups attached to the trigonal center approach planarity an increase in torsional strain also results. The above effects, therefore, account quantitatively for the observed reactivity of benzocycloheptene towards free radical substitution.

Both o-xylene and o-diethylbenzene are assumed to be planar in structures. As expected, the calculated angle strain in the ground and transition states of these two systems are of a small value as compared to the torsional strain and non-bonded interactions present. From the differences in strain energies between the ground and the transition states, o-xylene and o-diethylbenzene should be more reactive than indan. However, examination of the relative rates showed that o-diethylbenzene is only slightly more than one-half as reactive as indan and the reactivity of o-xylene is similar to that of benzocycloheptene. The reactivity of o-xylene is easily explained by the fact that the benzylic hydrogen atom abstracted from this system is located on a primary rather than a secondary center as in the other cases. According to Russell and DeBoer, abstraction of benzylic hydrogen atom from a secondary position should occur 16 times as fast as abstraction from a primary position (18).

It should be noted here that strain differences are enthalpy effects while rates are determined by both enthalpy and entropy influences. For o-diethylbenzene, the magnitude of the strain difference is insufficient to explain the observed rate of reaction. Kooyman and Strang have pointed out that steric effects decrease the reactivity of alpha methylenic groups in alkylbenzenes (53). The effects are attributed to steric interference with an energetically favorable orientation of the alkyl group attacked. Although the calculated

geometries of *o*-diethylbenzene and its radical did not present any non-bonded distance much smaller than the Van der Waals radius, viz.  $2.0 \text{ \AA}$ , it is very likely that the proximity of the two ortho-substituted alkyl groups may interfere with the approach of the attacking trichlormethyl radical (25, 27). A complete breakdown of strain energy terms accompanying the reactions is given in Table 8.

Figure 1 presents the log of the relative rates of reaction plotted against the calculated changes in strain energy. A correlation was made using the least-squares method. The slope for the benzocycloalkenes series and *o*-diethylbenzene is  $-0.082$  with a correlation coefficient equal to  $-0.974$ .

It is of particular interest to compare these results with those obtained by Koch and Gleicher for hydrogen abstraction from polycycloalkanes by the same radical (22). The corresponding slopes for correlating bridgehead and bridge hydrogen atom abstractions were  $-0.327$  and  $-0.537$ . The greater dependence on strain factors in the latter case is in keeping with the lessened stability of secondary alkyl radicals relative to their tertiary counterparts. The systems presently studied all form benzylic type radicals. The inherently high stability of such systems should make them somewhat insensitive to changes in strain factors. This appears to be the case.

In conclusion, the small slope of  $-0.082$  obtained in the plot demonstrates that the influence of internal strain on the rate of



Table 8. Strain energy terms in kcal/mole.

System	Bond Strain	Angle Strain	Torsional Strain	Non-bonded Interactions	Total	$\Delta$
Benzocyclobutene	4.510	101.769	8.952	1.316	116.547	12.110
Benzocyclobutene radical	3.158	118.352	6.668	0.439	128.637	
Benzocyclopentene	1.001	10.788	11.989	1.019	24.797	-0.469
Benzocyclopentene radical	0.499	13.911	9.662	0.256	24.328	
Benzocyclohexene	0.193	2.057	6.912	8.076	17.238	-3.043
Benzocyclohexene radical	0.154	0.809	6.853	6.378	14.195	
Benzocycloheptene	0.242	0.728	9.371	11.600	21.941	5.096
Benzocycloheptene radical	0.512	4.988	11.016	10.521	27.037	
o-Diethylbenzene	0.062	0.116	6.004	16.445	22.627	-1.286
o-Diethylbenzene radical	0.237	0.049	6.669	14.386	21.341	
o-Xylene	0.089	0.032	6.001	7.440	13.562	-1.073
o-Xylene radical	0.050	0.545	5.668	6.226	12.489	

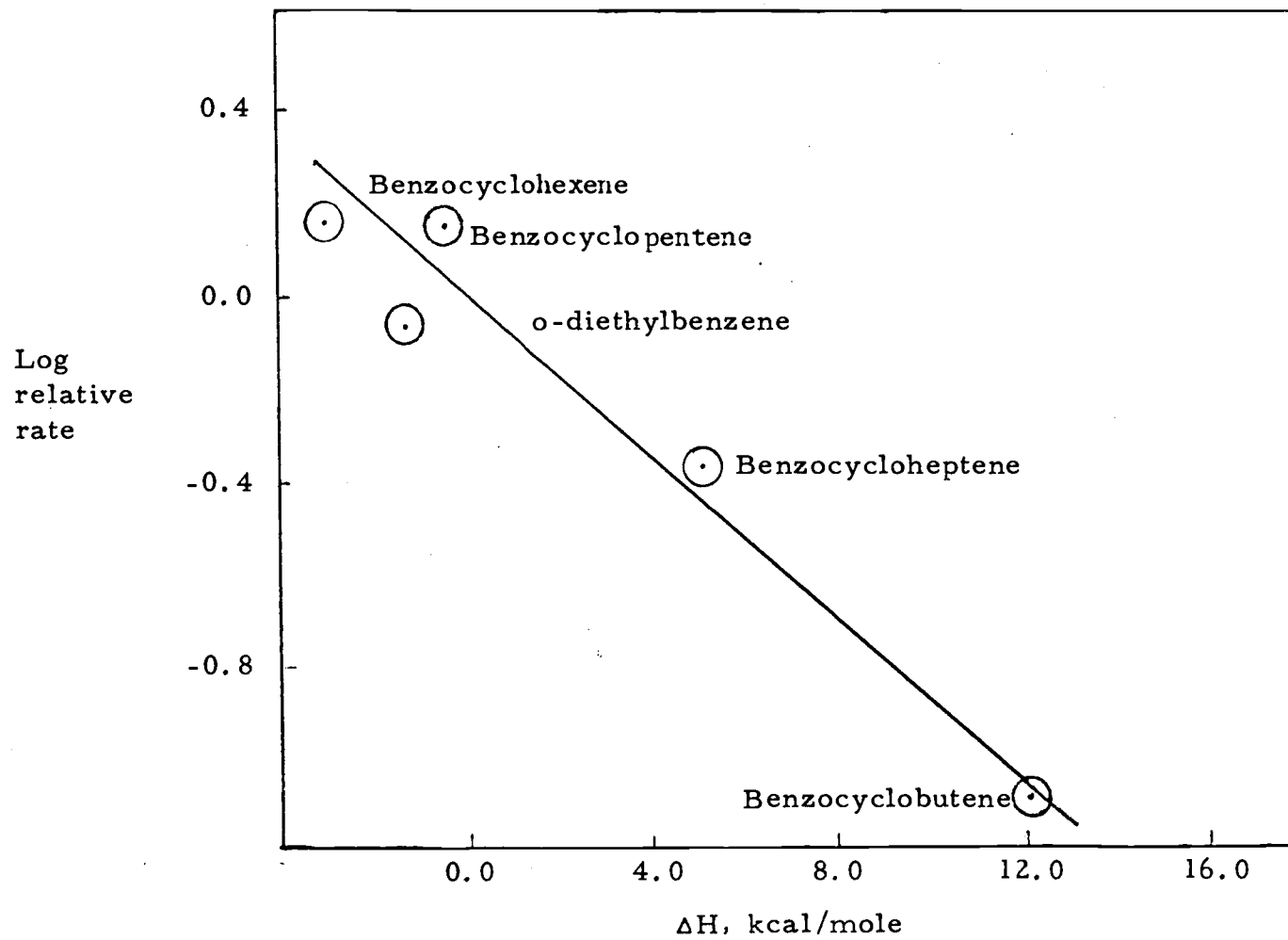


Figure 1. Correlation of relative rates with changes in strain energy.

hydrogen abstraction from benzocycloalkenes and o-dialkylbenzenes, unlike the effects of strain on cyclanes and cyclenes, is very small. This is, indeed, due to the stability exhibited by the benzylic type radicals formed by benzocycloalkenes and o-dialkylbenzenes.

## EXPERIMENTAL

Melting points were taken in sealed capillary tubes with a Buechi melting point apparatus. Melting and boiling points are uncorrected. NMR spectra were taken on HA-100 instrument with tetramethylsilane as the internal standard. Both preparative and analytic gas-liquid chromatograph was carried out using a Varian Aerograph 202B gas chromatograph equipped with a Sargent recorder with disc integration. A 12' x 1/4" column of 5% SE-30 on chromosorb W was used at column temperatures varying from 140-200°C. Thermal conductivity detectors and helium gas were used in the gas chromatograph.

Purifications of Reagents

Commercial o-diethylbenzene (Aldrich), b.p. 183.5° and indan (Aldrich), b.p. 70° at 20 mm., were used without further purification. No impurities were detected on the gas-liquid chromatography.

Benzocyclobutene was kindly supplied by Professor P. Radlick of the University of California at Riverside. The compound was used without further purification. Gas-liquid chromatography showed no impurities present.

### Purification of Bromotrichloromethane

Commercial bromotrichloromethane (Matheson, Coleman and Bell) was distilled and the portion boiling over the range 102.5° -104° was collected. Gas-liquid chromatography showed no detectable impurities.

### Purification of t-Butylbenzene

Commercial t-butylbenzene (Aldrich) was distilled and collected over the range of 167-168°. Gas-liquid chromatography showed the presence of a single impurity which amounted to less than 0.5% of the mixture.

### Purification of Fluorene

Commercial fluorene (Eastman Organic Chemicals) was recrystallized from hot ethanol; white crystals with m.p. 113-114° were obtained. No impurities were detected by gas-liquid chromatography.

### Purification of o-Xylene

Commercial o-xylene (Aldrich) was distilled and the portion boiling at 143-144.5° was collected.

### Purification of Tetralin

Commercial tetralin (Matheson, Coleman and Bell) was distilled, b.p. 32°, 0.3 mm.; and dried over magnesium sulfate. No impurities were detected by gas-liquid chromatography.

### Preparation of Benzocycloheptene

Benzocycloheptene was prepared by reduction of benzosuberone (Aldrich, 99% pure) according to the procedure of Huang-Minlon modification of the Wolf-Kishner reduction (50). To a solution of 80 ml. of diethylglycol 10.5 g. of potassium hydroxide pellets were added. The mixture was refluxed till all the pellets were dissolved. To the cooled solution, 9.4 g. of hydrazine hydrate and 10.0 g. of benzosuberone were added. The mixture was allowed to reflux for 1 hour and ca. 50 ml. of hydrazine hydrate and water were distilled off. The remaining solution was refluxed again for 5 1/2 hours. After the refluxing, the reaction mixture was poured into 100 ml. of water. The aqueous layer was separated and washed with two 40 ml. portions of ether. The combined organic layers were washed with water and dried over magnesium sulfate. Ether was removed from the solution by evaporation under reduced pressure. A clear, colorless liquid was collected at 39° C at 0.5 mm.; lit. 217°, 764 mm. (51). A yield of 83% (7.6 g. of product) was obtained. No impurities were

detected in the product by gas-liquid chromatography.

### Product Studies

Product studies for indan and tetralin were carried out. NMR spectra of the reaction mixtures showed that only benzylic brominations have occurred.

Material balance for tetralin was satisfactory. A mixture of 4.232 g. of tetralin (32.186 mmoles) and 36.60 g. of bromotrichloromethane (184.64 mmoles) were reacted under nitrogen for 18 hours at 70° with irradiation by our standard source. After reaction, the reaction mixture was analyzed by gas-liquid chromatography on a 5% SE-30 column. It was shown that about 40% of the tetralin had reacted and one product with a longer retention time than tetralin was formed. Sample of this product was collected as it was eluted from the glc column. NMR spectrum identified the product as 1,2-dihydronaphthalene by the two peaks at  $\delta$ 5.93 and  $\delta$ 6.4 with the ratio of the areas equal to 1:1. Material balance was evaluated assuming that the entire quantity of tetralin injected into the glc column had all been converted to the olefin. The peak area of 1,2-dihydronaphthalene in the glc chromatography of the reaction mixture was taken as being equivalent to the actual quantities present. The unreacted starting material amounts to 19.311 mmoles (2.51 g.) and the product weighed 1.49 g. (11.620 mmoles). The material balance thus found is 96.1%.

Material balance for indan has also been carried out as for tetralin. A mixture of 4.913 g. of indan (41.574 mmoles) and 39.89 g. (20.092 mmoles) of bromotrichloromethane was reacted for 15 hours. Gas-liquid chromatography showed the presence of only one product which was identified as the olefin by nmr spectroscopy, as in the case of tetralin. From the glc chromatograph, analysis of the peak areas indicated that unreacted starting material weighed 3.189 g. (37.024 mmoles) and the olefinic product weighed 1.406 g. (12.138 mmoles). A material balance of 94.2% is obtained.

### Kinetic Studies

#### Procedure for Kinetic Runs

Solutions of fluorene, the hydrocarbon, bromotrichloromethane and t-butylbenzene were prepared in the approximate molar ratio of 0.5:1; 5.0:0.25. Approximately 0.75 ml. of the solution was placed in each of the several ampoules. The ampoules were cooled to dry ice-isopropyl alcohol temperature until the solutions solidified. The ampoules were evacuated at 0.5-1.0 mm. and flushed with nitrogen several times with three intermediate thawings. The ampoules were sealed under vacuum and one was reserved for the analysis of the unreacted starting materials. The remainder were placed horizontally just below the surface of a mineral oil constant temperature bath



maintained at  $70.0 \pm 0.5^\circ$ . The solution was irradiated with ultra-violet light provided by a Sylvania 275-W sun lamp placed 20 cm, above the surface of the oil. Reaction times varied from 20 to 40 hours, by which 30 to 70% of the total hydrocarbons had reacted. The ampoules were then cooled and opened. Analysis of the mixtures, both before and after the reaction was carried out via nmr spectroscopy. All determinations were run in replicate. Kinetic data were determined by having the hydrocarbon compete directly with fluorene for the trichloromethyl radical.

Determination of  $k_x/k_F$

The kinetic expressions for the determinations of these relative rates

$$\frac{k_x}{k_F} = \frac{\log(X_i)/(X_f)}{\log(F_i)/(F_f)} \quad (13)$$

constants have been previously reported (26, 27, 52). The relative rates of disappearance of the hydrocarbon to fluorene is given by Equation 13, where  $X_i$  and  $F_i$  are the initial number of mmoles of the hydrocarbon and fluorene;  $X_f$  and  $F_f$  are the final number of mmoles of the hydrocarbon and fluorene. The above ratios may be directly obtained from spectrometric analysis using the following equation:

$$\frac{X_i}{X_f} = \frac{\left( \frac{\text{area under X peak}}{\text{area under standard peak}} \right)_{\text{initial}}}{\left( \frac{\text{area under X peak}}{\text{area under standard peak}} \right)_{\text{final}}} \quad (14)$$

For benzocycloalkenes and o-dialkylbenzenes, since more than one type of hydrogen atoms are present in each molecule, several peaks will appear on the nmr spectrum. In these cases, it is only necessary to consider the area of the benzylic hydrogens in each system.

In certain cases, dibrominated products were formed in addition to the monobrominated product. Errors in evaluating the peak areas, however, are avoided by incorporating the area of the benzylic hydrogens in the former system with that of the latter one.

Detailed kinetic data may be found in the Appendix, Tables 9 to 14.

#### Determination of the Precision of NMR Integration

Solutions of fluorene and t-butylbenzene were weighed out precisely and prepared in approximate molar ratios varying from 1:4 to 4:1 of each compound. The prepared solutions were analyzed by nmr spectroscopy and the molar ratio of each solution was determined from the integration. A correlation of the weight ratios to the area ratios was obtained by the least-square method. A correlation coefficient of 1.000 points out that nmr spectroscopy may be used as an accurate mean of analyzing reaction mixtures.

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## APPENDIX

Data from Kinetic Runs

Table 9. Relative rates of disappearance of benzocyclobutene to fluorene.

Rxn No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% Rxn	$\frac{k_{\text{benzocyclobutene}}}{k_{\text{F}}}$
Conditions: 37 hours at 70° C						
	Mmoles t-butylbenzene	1.46				
1.	Benzocyclobutene	6.16	5.88	0.28	4.7	0.07
	Fluorene	4.56	2.32	2.24	49.2	
	BrCCl <sub>3</sub>	31.94				
2.	Benzocyclobutene	6.16	5.80	0.30	5.8	0.08
	Fluorene	4.56	2.14	2.42	53.2	
	BrCCl <sub>3</sub>	31.94				
3.	Benzocyclobutene	6.16	5.11	1.05	17.1	0.08
	Fluorene	4.56	0.46	4.10	89.9	
	BrCCl <sub>3</sub>	31.94				
4.	Benzocyclobutene	6.16	5.20	0.96	15.6	0.08
	Fluorene	4.56	0.48	4.08	89.4	
	BrCCl <sub>3</sub>	31.94				
Average $\frac{k_{\text{benzocyclobutene}}}{k_{\text{F}}} = 0.08 \pm 0.00$						



Table 10. Relative rates of disappearance of benzocyclopentene to fluorene.

Rxn No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% Rxn	$\frac{k_{\text{benzocyclopentene}}}{k_F}$
Conditions: 20 hours at 70°C						
	Mmoles t-butylbenzene	1.82				
1.	Benzocyclopentene	7.02	3.45	3.57	50.9	1.35
	Fluorene	3.50	2.06	1.44	41.0	
	BrCCl <sub>3</sub>	35.09				
2.	Benzocyclopentene	7.02	3.78	3.24	46.2	1.36
	Fluorene	3.50	2.22	1.28	36.5	
	BrCCl <sub>3</sub>	35.09				
3.	Benzocyclopentene	7.02	3.77	3.25	46.3	1.60
	Fluorene	3.50	2.37	1.13	32.2	
	BrCCl <sub>3</sub>	35.09				
4.	Benzocyclopentene	7.02	3.57	3.45	49.1	1.27
	Fluorene	3.50	2.07	1.43	40.9	
	BrCCl <sub>3</sub>	35.09				
5.	Benzocyclopentene	7.02	3.51	3.51	50.0	1.40
	Fluorene	3.50	2.13	1.37	39.1	
	BrCCl <sub>3</sub>	35.09				

Average  $\frac{k_{\text{benzocyclopentene}}}{k_F} = 1.39 \pm 0.08$

Table 11. Relative rate of disappearance of benzocyclohexene to fluorene.

Rxn No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% Rxn	$\frac{k_{\text{benzocyclohexene}}}{k_{\text{F}}}$
Conditions: 20 hours at 70°C						
	Mmoles t-butylbenzene	3.51				
1.	Benzocyclohexene	7.00	4.42	2.58	36.9	1.49
	Fluorene	3.50	2.57	0.93	26.7	
	BrCCl <sub>3</sub>	35.08				
2.	Benzocyclohexene	7.00	3.81	3.19	45.5	1.31
	Fluorene	3.50	2.20	1.30	37.0	
	BrCCl <sub>3</sub>	35.08				
3.	Benzocyclohexene	7.00	4.05	2.95	42.2	1.45
	Fluorene	3.50	2.40	1.10	31.4	
	BrCCl <sub>3</sub>	35.08				
4.	Benzocyclohexene	7.00	4.31	2.69	38.4	1.44
	Fluorene	3.50	2.50	1.00	28.6	
	BrCCl <sub>3</sub>	35.08				

(continued)

Table 11. Continued.

Rxn No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% Rxn	$\frac{k_{\text{benzocyclohexene}}}{k_F}$
Conditions: 20 hours at 70°C						
	Mmoles t-butylbenzene	1.76				
5.	Benzocyclohexene	7.17	4.08	3.09	43.1	1.31
	Fluorene	3.52	2.29	1.23	35.0	
	BrCCl <sub>3</sub>	35.08				
6.	Benzocyclohexene	7.17	4.73	2.44	34.0	1.54
	Fluorene	3.52	2.69	0.83	23.7	
	BrCCl <sub>3</sub>	35.08				
7.	Benzocyclohexene	7.17	4.05	3.12	43.5	1.35
	Fluorene	3.52	2.31	1.21	34.5	
	BrCCl <sub>3</sub>	35.08				
Average		$\frac{k_{\text{benzocyclohexene}}}{k_F} = 1.41 \pm 0.08$				

Table 12. Relative rates of disappearance of benzocycloheptene to fluorene.

Rxn No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% Rxn	$\frac{k_{\text{benzocycloheptene}}}{k_{\text{F}}}$
Conditions: 33 hours at 70° C						
	Mmoles t-butylbenzene	1.34				
1.	Benzocycloheptene	5.47	3.60	1.87	34.2	0.35
	Fluorene	2.70	0.81	1.89	70.0	
	BrCCl <sub>3</sub>	26.99				
2.	Benzocycloheptene	5.47	3.71	1.76	32.2	0.46
	Fluorene	2.70	1.17	1.53	56.8	
	BrCCl <sub>3</sub>	26.99				
3.	Benzocycloheptene	5.47	3.70	1.77	32.4	0.43
	Fluorene	2.70	1.09	1.61	59.7	
	BrCCl <sub>3</sub>	26.99				
4.	Benzocycloheptene	5.47	3.33	2.14	39.2	0.45
	Fluorene	2.70	0.90	1.80	66.6	
	BrCCl <sub>3</sub>	26.99				
5.	Benzocycloheptene	5.47	3.33	1.70	31.0	0.42
	Fluorene	2.70	1.11	1.59	58.8	
	BrCCl <sub>3</sub>	26.99				
Average $\frac{k_{\text{benzocycloheptene}}}{k_{\text{F}}} = 0.42 \pm 0.03$						

Table 13. Relative rates of disappearance of o-xylene to fluorene.

Rxn No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% Rxn	$\frac{k_{o\text{-xylene}}}{k_F}$
Conditions: 33 hours at 70°C						
	Mmoles t-butylbenzene	1.70				
1.	o-Xylene	6.85	3.25	3.60	52.6	0.62
	Fluorene	5.08	1.52	3.56	70.0	
	BrCCl <sub>3</sub>	34.18				
2.	o-Xylene	6.85	3.55	3.30	48.2	0.69
	Fluorene	5.08	1.96	3.12	61.5	
	BrCCl <sub>3</sub>	34.18				
3.	o-Xylene	6.85	4.27	2.58	37.7	0.52
	Fluorene	5.08	2.05	3.03	59.7	
	BrCCl <sub>3</sub>	34.18				
4.	o-Xylene	6.85	3.97	2.88	42.0	0.47
	Fluorene	5.08	1.62	3.46	68.2	
	BrCCl <sub>3</sub>	34.18				
						(continued)

Table 13. Continued.

Rxn No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% Rxn	$\frac{k_{o\text{-xylene}}}{k_V}$
Conditions: 32 hours at 70°C						
	Mmoles t-butylbenzene	1.73				
5.	o-Xylene	6.92	4.51	2.41	34.9	0.69
	Fluorene	3.40	1.82	1.58	46.4	
	BrCCl <sub>3</sub>	34.14				
6.	o-Xylene	6.91	3.70	3.22	46.5	0.60
	Fluorene	3.40	1.20	2.20	64.7	
	BrCCl <sub>3</sub>	34.14				
7.	o-Xylene	6.92	4.50	2.42	34.9	0.63
	Fluorene	3.40	1.72	1.68	49.3	
	BrCCl <sub>3</sub>	34.14				
8.	o-Xylene	6.92	4.06	2.86	41.3	0.62
	Fluorene	3.40	1.43	1.97	58.0	
	BrCCl <sub>3</sub>	34.14				

$$\text{Average } \frac{k_{o\text{-xylene}}}{k_F} = 0.62 \pm 0.05$$

Table 14. Relative rates of disappearance of o-diethylbenzene to fluorene.

Rxn No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% Rxn	$\frac{k_{\text{o-diethylbenzene}}}{k_{\text{F}}}$
Conditions: 23 hours at 70° C						
	Mmoles t-butylbenzene	1.07				
1.	o-Diethylbenzene	6.24	3.42	2.82	45.2	0.88
	Fluorene	3.03	1.53	1.50	49.6	
	BrCCl <sub>3</sub>	30.00				
2.	o-Diethylbenzene	6.24	3.28	2.96	47.5	0.88
	Fluorene	3.03	1.45	1.58	52.1	
	BrCCl <sub>3</sub>	30.00				
3.	o-Diethylbenzene	6.24	4.23	2.01	32.2	0.92
	Fluorene	3.03	1.99	1.04	34.4	
	BrCCl <sub>3</sub>	30.00				
4.	o-Diethylbenzene	6.24	3.38	2.86	45.8	0.86
	Fluorene	3.03	1.49	1.54	50.8	
	BrCCl <sub>3</sub>	30.00				

(continued)

Table 14. Continued.

Rxn No.	Compound	Initial (mmoles)	Final (mmoles)	Amount Reacted (mmoles)	% Rxn	$\frac{k_{\text{o-diethylbenzene}}}{k_{\text{F}}}$
Conditions: 24 hours at 70°C						
	Mmoles t-butylbenzene	1.48				
5.	o-Diethylbenzene	5.93	4.25	1.68	28.3	0.90
	Fluorene	4.49	3.10	1.39	31.0	
	BrCCl <sub>3</sub>	30.28				
6.	o-Diethylbenzene	5.93	4.23	1.70	28.7	0.82
	Fluorene	4.49	2.96	1.53	34.0	
	BrCCl <sub>3</sub>	30.28				
7.	o-Diethylbenzene	5.93	3.91	2.02	34.0	0.88
	Fluorene	4.49	2.79	1.70	37.8	
	BrCCl <sub>3</sub>	30.28				
8.	o-Diethylbenzene	5.93	4.29	1.64	27.6	0.79
	Fluorene	4.49	2.97	1.52	33.8	
	BrCCl <sub>3</sub>	30.28				
9.	-Diethylbenzene	5.93	4.11	1.82	30.7	0.67
	Fluorene	4.49	2.59	1.90	42.4	
	BrCCl <sub>3</sub>	30.28				
Average $\frac{k_{\text{o-diethylbenzene}}}{k_{\text{F}}} = 0.84 \pm 0.06$						