IOWA STATE UNIVERSITY
Digital Repository

Retrospective Theses and Dissertations

Iowa State University Capstones, Theses and Dissertations

1963

Directive effects in aliphatic chlorinations

Akihiko Ito
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Organic Chemistry Commons

Recommended Citation

Ito, Akihiko, "Directive effects in aliphatic chlorinations " (1963). *Retrospective Theses and Dissertations*. 2369.
https://lib.dr.iastate.edu/rtd/2369

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Retrospective Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

المنارة للاستشارات

www.manaraa.com

This dissertation has been microfilmed exactly as received 63-6868

ITO, Akihiko, 1928-
DIRECTIVE EFFECTS IN ALIPHATIC CHLORINATIONS.

Iowa State University of Science and Technology
Ph.D., 1963
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

DIRECTIVE EFFECTS IN ALIPHATIC CHLORINATIONS

by

Akihiko Ito

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1963

TABLE OF CONTENTS

LITERATURE SURVEY

The mechanism of the photochemical substitution reaction of hydrocarbons with molecular chlorine (hereafter it is called photochlorination) is well established (1), although the termination steps depend somewhat upon the reaction conditions.

$$Cl_2 \xrightarrow{h\nu} 2Cl$$

$$RH + Cl\cdot \longrightarrow R\cdot + HCl$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$$

Hydrogen abstraction by the chlorine atom is the slowest step of the photochlorination reaction. A primary deuterium-isotope effect has been observed in this step (2). Competitive photochlorination provides a simple method for determining the relative rates of this step. Since the absolute rate constants for reaction between chlorine atoms and the hydrogen molecule have been measured over a wide range of temperature (3), absolute rate constants for chlorine atom attack on simple hydrocarbons and alkyl chlorides are available (4).

In processes involving long kinetic chains, such as the photochlorination reaction, the composition of the product is determined by the relative rates of attack of chlorine atoms on the different carbon-hydrogen bonds. The first extensive work on this point, *i.e.*, the relation between structure and reactivity, was done by H. B. Hass *et al*. (5). They corrected many erroneous data on the boiling points of alkyl chlorides and drew the following important rules:

1) Carbon skeleton rearrangements do not occur during either photochemical or thermal chlorination if pyrolysis temperatures are avoided.
2) The hydrogen atoms are always substituted at rates which are in the order primary $<$ secondary $<$ tertiary.
3) At increasing temperatures there is increasingly close approach to relative rates of 1:1:1.
4) Liquid phase chlorination relative rates are comparable to those obtained at much higher temperatures in vapor phase.
5) Moisture, carbon surface, and light do not affect appreciably these ratios.

In the second rule the sequence in reactivities is in the order of stabilities of the alkyl radical produced. On this basis, one might expect that alkyl chlorides would undergo free radical chlorination preferentially at the α positions, since the following resonance-stabilized radical should be obtained.

$$-\overset{\cdot}{\underset{|}{C}}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}: \longleftrightarrow -\overset{\cdot\ominus}{\underset{|}{C}}-\underset{\cdot\cdot}{\overset{\cdot\oplus}{Cl}}:$$

However, this is not the case. Since chlorine atom is an electron-deficient species, carbon-hydrogen bonds of high electron density are preferentially attacked by chlorine atoms. This tendency was expressed by H. C. Brown as follows (6a): "The attack occurs preferentially at carbon-hydrogen bonds remote from the chlorine substituent." Many data with chlorine gas and sulfuryl chloride are available on this point (6). Sulfuryl chloride is often a more selective reagent than molecular chlorine because of the existence of equilibrium

$$SO_2 + Cl\cdot \rightleftharpoons SO_2Cl\cdot$$

and attack by $SO_2Cl\cdot$ upon carbon-hydrogen bonds should be taken into account (7). Effects of other electron-withdrawing substituents were investigated by other workers and the results summarized by C. Walling (8). Here again the results show that the inductive effect of substituents are very important in free radical chlorinations where chlorine gas or sulfuryl chloride is used as chlorination reagent. H. C. Brown and A. B. Ash (6a) observed the following order of influence in directive effects: $C_6H_5- > CH_3- > H- > ClCH_2- > CH_3CO_2- > Cl_2CH- > Cl_3Si- > HO_2C- > Cl_3C- > ClOC- > Cl_2{=} > Cl_3{\equiv} > F_3C- > F_3{\equiv}$.

An interesting sequence of increasing stability of radicals was observed based on 1,2-chlorine atom migration in free radical addition of hydrogen bromide to polyhaloalkenes (9):

$$R\dot{C}H_2 < R_2\dot{C}H < R_3\dot{C} < R\dot{C}HCl < R_2\dot{C}Cl < R\dot{C}Cl_2$$

where R is the polyhaloalkyl radical. Although the conditions are not strictly comparable, the relative reactivity of carbon-hydrogen bonds in RCH_3, RCH_2Cl and $RCHCl_2$ and the order of stability of the radicals produced by chlorine atom attack on those compounds are completely reverse.

The above mentioned phenomena can be explained in terms of the transition state of the reaction (10).

$$X\cdot + RH \longrightarrow \left[\underset{I}{R{:}H\cdot X} \longleftrightarrow \underset{II}{R^{+}\cdot HX{:}^{-}} \longleftrightarrow \underset{III}{R\cdot H{:}X}\right] \longrightarrow R\cdot + HX$$

In terms of the Hammond postulate (11), when X· is very reactive, the transition state will resemble the reactant but when the reactivity of X· is low, the transition state resembles the products of the reaction and the stability of the products becomes more important. In the case of photochlorination the carbon-hydrogen bond is only partially broken in the transition state (12). The transition state is best represented by structures I and II when I resembles the reactants. The relative reactivities of substituted toluenes toward chlorine atoms are proportional to the *sigma*$^{+}$ constant[*] of the substituent as would be expected for structure II. It would appear that the importance of structure II would depend upon both the extent of bond breaking, the electron affinity of X· and the availability of electrons at the carbon-hydrogen bond being attacked.

Since the contribution of structure II to the transition state is important, this resonance-polar effect should con-

---

[*] Roger Williamson. Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Relative reactivities of substituted toluenes towards chlorine atoms. Private communication to Dr. Glen A. Russell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. 1960.

tribute to the composition of the chlorination product. However, it seems to be difficult to separate this resonance-inductive effect from a polar-inductive effect in the photochlorination reaction.

An example of a primary steric effect in hydrogen abstraction by free radicals was observed in the photochlorination of 2,3,4,5,6-pentachloroethylbenzene (13). The result together with results of photobromination (14) were summarized by E. L. Eliel (15). Photochlorination of 2,3,4,5,6-pentachloroethylbenzene at 75°C. gave a ratio of β-chloride to α-chloride of 1.6 while at 180°C. the ratio was 4.6. Photobromination of the pentachloroethylbenzene gave exclusively the α-bromide. In spite of the fact that bromine has an electron affinity fairly close to chlorine and bond-breaking of the transition state in hydrogen abstraction step by bromine atom would be considerable (10b), the inductive effect of the chlorine substituents and the resonance inhibition in incipient radicals by <u>ortho</u> substituents as postulated by M. Szwarc <u>et al</u>. (16) appear to be not large enough to prevent the α attack. The discrepancy between the β-chloride to α-chloride ratio of 0.74 which was observed in hydrogen abstraction of ethylbenzene by free chlorine atoms at 40°C.* and the

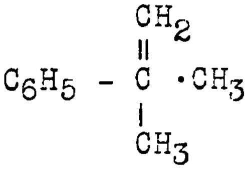
---

*H. D. McBride. Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Relative reactivity of ethylbenzene toward chlorine atoms. Private communication to Dr. Glen A. Russell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. 1960.

β to α ratio of 1.6 observed at 75°C. for pentachlorobenzene can be largely ascribed to the screening of the α-hydrogen atoms by *ortho* chlorine substituents. At higher temperature where the product ratio depends to a greater extent on the frequency factor the proportion of β attack is enhanced (15). The above mentioned example is one of a few examples of the primary steric effect in free radical substitution reactions.

Secondary steric effects in free radical substitution reactions are more frequent. The following sequence of relative reactivities of carbon-hydrogen bonds of cyclopentane, cyclohexane, cycloheptane and cyclooctane toward free chlorine atoms were observed in photochlorination (10a): 2.8:2.7:3.0:4.3. In 12*M* carbon disulfide solution the reactivity ratios were 23:20:40:70. This order is in agreement with the prediction by H. C. Brown *et al*. on the basis of I strain (17-18) and with the order of thermolysis of azo-*bis*-nitriles (19). Low reactivity of cyclopropane was observed in photochlorination (20) as well as in the reaction with methyl radicals (21). No appreciable B strain effects were observed in the photochlorination of branched hydrocarbons (7) when attacked by free chlorine atoms, whereas steric acceleration seems to occur in the thermolysis of *trans*-azo-*bis*-nitriles (22). This difference can be ascribed to the difference of the transition states, *i*.*e*., the amount of bond breaking.

The effect of hyperconjugation in photochlorinations was emphasized by J. M. Tedder *et al.* (6i, 6j, 6k). They compared the reactivity of primary hydrogens of cumene and *tertiary*-butylbenzene (10e) and concluded the reactivity ratio of 1.4 to be due to hyperconjugation. The lower reactivity of primary hydrogen of *tertiary*-butylbenzene than that of cumene was recently confirmed in this laboratory (10a, 23). However, a little lower reactivity of primary hydrogen of ethylbenzene than that of cumene was observed in this laboratory.[*] The same trend was observed when *tertiary*-butyl hypochlorite was used as a chlorinating reagent by Walling *et al.* (25). Therefore, it is doubtful if the low reactivity of *tertiary*-butylbenzene should be ascribed to lack of hyperconjugation. Further, hyperconjugation of the type



$$C_6H_5 - \underset{CH_3}{\overset{CH_2}{\overset{\|}{\underset{|}{C}}}} \cdot CH_3$$

could also contribute to stabilize the incipient radical. The absolute rate constant of primary hydrogen of propane, isobutane and neopentane in photochlorinations at 40°C. calculated from the work of J. H. Knox *et al.* (4c) are 3.4×10^9, 3.5×10^9 and 3.2×10^9 l/mole sec. respectively. In this

---

[*] H. D. McBride. Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Relative reactivity of ethylbenzene toward chlorine atoms. Private communication to Dr. Glen A. Russell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. 1960.

case only small differences are observed and the trend is not consistent. Photochlorinations of halocycloalkanes in this study are of interest from the point of view that most of the derived alkyl radicals have the same number of hyperconjugative resonance structures.

The influence of a substituent in the attack of molecular chlorine upon hydrocarbon radicals has been studied only by P. S. Fredericks and J. M. Tedder (6j). In order to study this point the present work concerning the chlorination of halocycloalkanes was undertaken.

It has generally been assumed that polarity of solvents has little effect upon course and rate of free radical reactions (8, 25). The absence of solvent effects on the over-all rate of polymerization of styrene (26), and the copolymer structure in vinyl copolymerization (27) was observed. The conclusion that the rate of decomposition of various azo compounds is independent of the solvent (28) was drawn by some workers, while Leffler _et al_. (29) observed a small variation in rate with change in solvent with relatively large but compensating changes in the entropy and enthalpy of activation. However, these latter effects have been questioned, and they appear to be more a consequence of experimental error than actual phenomena, since the entropy and enthalpy of activation calculated can not be independently measured (30).

Recently Dr. D. G. Hendry (23) in this laboratory studied the effect of solvents in the autoxidation of cumene. He found a correlation between log(rate-$R_i/2$) + 2 and (D-1)/(2D+1), where R_i is the rate of initiation and D is the dielectric constant of the solvent. This correlation is based on the theory of Laidler and Eyring (31) who obtained the expression

$$\ln k' = \ln k_o' - (U_A^2/a_A^3 + U_B^2/a_B^3 - U_{M^*}^2/a_{M^*}^3)$$
$$(D - 1)/(2D + 1)kT + (\Phi_A + \Phi_B - \Phi_{M^*})kT$$

for effect of solvents on the rate of chemical reactions, where k' is the rate constant in solution, k_o' is the rate constant in dilute gas phase. The second term in the right hand side of the equation represents the electrostatic effect and the third term represents the non-electrostatic effect. Since the rate of reaction of initiator radicals with oxygen molecules is

$$\text{Rate} = -d[O_2]/dt = k_pR_i^{1/2}[RH]/(2k_t)^{1/2} + R_i/2$$

the quantity [rate - $R_i/2$] is proportional to k_p if R_i, [RH] and k_t are constant. In this expression k_p is the rate constant of attack on the hydrocarbon by peroxy radicals and k_t is the rate constant of the termination step.

Dr. Hendry explained the discrepancy between his work and the previous works as follows:

1. In both vinyl copolymerization (10g) and hydrocarbon oxidation, there would be contributions from the structure $R^{+} H \overset{-}{\cdot} X$ to the transition state.

2. In the former case, the nature of the transition state is such that the lines of force between the charged portions of the transition state do not radiate appreciably into the solvent (27).
3. In the latter case, there are variations of solvent effect due to structure of hydrocarbons; the ratios of the rate in nitromethane to that in chlorobenzene are cumene 1.26, bicyclo-(2,2,1)-heptadiene 1.28, cyclohexene 1.91 and cycloheptatriene 2.03.
4. In the former case, the atoms between which the electron transfer occurs would be well shielded from solvent by alkyl and aryl groups. The effect of the alkyl group shielding is reminiscent of the effect of alkyl substitution on the second ionization constant (K_2) of carboxylic acid (32). For example in the case of malonic acid, K_1/K_2 is 734 while this ratio is 121,000 for diethylmalonic acid (33). Consistent with the above is the lack of solvent effect in the copolymerization of vinyl compounds and the small solvent effect observed in the oxidation of cumene and bicyclo-(2,2,1)-heptane (see 3 above).
5. Other factors which contribute to prevent a solvent effect in the copolymerization are the greater degree of charge distribution by resonance and experimental uncertainties in the values of the

relative reactivity of monomers towards radical.

These values are seldom accurate to within ± 10%.

The most striking solvent effect on a free radical reaction was observed in competitive photochlorination of hydrocarbons (2b, 10a, 20, 34). For example, the relative reactivities of the tertiary and primary hydrogen atoms of 2,3-dimethylbutane toward the chlorine atom at 55°C. increase from 3.5:1 in an aliphatic solvent to 32:1 in 8M benzene (2b). It was proven that this increase in reactivity of chlorine atom is due to complexing with the aromatic ring of the solvent since there is a quantitative relationship between the magnitude of the solvent effect and basicity of the solvent as determined by the equilibrium constant for the interaction with hydrogen chloride (35). Certain non-aromatic solvents such as tertiary-butyl alcohol, dioxane, n-butyl ether, dimethylformamide, thionyl chloride, sulfur monochloride, carbon disulfide and various alkyl iodides also show a solvent effect in the photochlorination of 2,3-dimethylbutane. Some of the above might also undergo acid-base interactions with chlorine atoms at the most electron rich site similar to the pi-complex observed for aromatic solvents. Other solvents such as carbon disulfide, alkyl iodides could involve either charge-transfer complexes or complexes with expanded valence shells. Iodobenzene is a more efficient solvent than can be expected from its basicity and it is believed to be due to formation of intermediate radical involving expansion of the valence shell of iodine (2b).

A rule for inductive effects and resonance effects in complexing solvents has been stated as follows: relative reactivities that are determined mainly by the availability of electrons in the carbon-hydrogen bond are not particularly sensitive to solvent effect while relative reactivities that are determined mainly by the stabilities of the incipient free radicals are very sensitive to changes in solvent (10a). Toward the chlorine atom the relative reactivities of the primary hydrogen atoms of tetramethylsilane and trimethylchlorosilane, where the incipient radicals are expected to have the same amounts of resonance stabilization but the carbon-hydrogen bonds have widely different reactivities due to inductive effect, in the absence of a complexing solvent, and in the presence of 4M tertiary-butylbenzene or 12M carbon disulfide were 6.5, 6.9 and 4.8 respectively. It appears that there was little effect of solvent. Similar situations were observed when the reactivities of the primary hydrogen of tertiary-butyl chloride and the primary hydrogen of 2,3-dimethylbutane, the primary hydrogen of acetonitrile and the primary hydrogen of 2,3-dimethylbutane, and the primary hydrogen of tertiary-butylbenzene and the primary hydrogen of 2,3-dimethylbutane are compared (10a). The large solvent effect noted in the chlorination of 2,3-dimethylbutane which was previously mentioned is very likely due to the resonance stabilization of the incipient alkyl radicals. In the photochlorination of 1-chlorobutane in the absence or presence of complexing solvents (20a), the following relative reactivities of the carbon-hydrogen bonds were observed:

CH_3-CH_2-CH_2-CH_2-Cl in aliphatic solvent at 0°C.
1.0 3.1 1.35 0.30

CH_3-CH_2-CH_2-CH_2-Cl in 11.1M benzene at 0°C.
1.0 8.1 2.4 0.5

The ratios of 2- to 1-attack changed from 4.5 to 4.8 and the ratios of 3- to 2-attack changed from 2.3 to 3.3 (an increase of 45 per cent) while the ratios of 3- to 4-attack increased from 3.1 to 8.1 (an increase of 160 per cent). The relative reactivity at the 3- and 4-positions is determined mainly by differences in bond dissociation energies while the relative reactivities at the 1-, 2- and 3-positions are determined mainly by the inductive effect of the chlorine substituent (10c). Here again the above mentioned rule is consistent with the results. An increase in the selectivity of the chlorine atom in the presence of complexing solvents should be due to an increase in the importance of resonance structure III (see page 4) (10a) or due to loss of energy by complex formation (21). These two interpretations lead to the same conclusion when viewed in terms of the Hammond postulate (11).

The *tertiary*-butoxy radical appears to be complexed by aromatic solvents in the same manner. However, the effects so far reported have not been very large (24, 37).

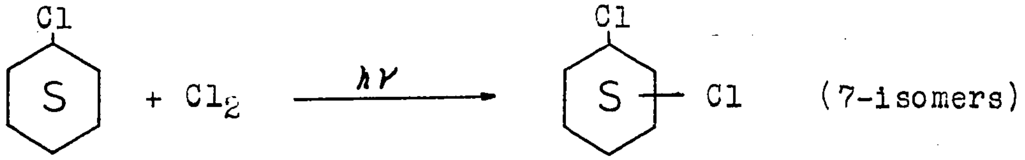
Recently C. Walling and A. Padwa reported a striking change of course in the reaction of the alkoxy radical derived from the hypochlorite of benzyldimethylcarbinol and hydrocarbons in the absence and presence of certain olefins (38).

The formation of a <u>pi</u>-complex from a radical and an aromatic nucleus and the relation between a <u>pi</u>- and a <u>sigma</u>-complex has been discussed (2b, 39). It appears that high electron affinity and a sufficiently high potential energy barrier between <u>pi</u>- and <u>sigma</u>-complex are the most important conditions required to form a stable <u>pi</u>-complex.

Other free radical reactions have been reviewed in connection with changes in either the course or the rate of the reactions (2b). However, few definite conclusions could be drawn because of the incompleteness of the data.

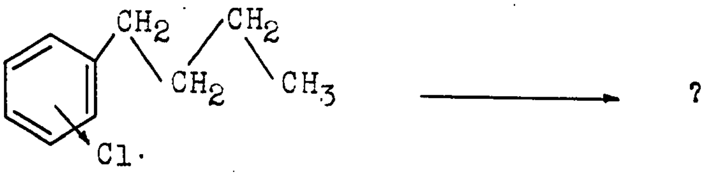
GENERAL INTRODUCTION

Part I of this thesis presents a study of the chlorination, principally by chlorine and light, of chloro and bromocyclopentane and chlorocyclohexane. This work was undertaken to further establish the polar effect of a halogen substituent upon directing the position of attack of a chlorine atom in the substitution reaction.



This model system was chosen because in the 3- and 4-positions the resulting alkyl radicals have the same number of hyperconjugated structures. Since attack at the 2-, 3- or 4-position eventually leads to a mixture of <u>cis</u> and <u>trans</u> isomers this model system provided an opportunity to observe the stereochemistry of the reaction of molecular chlorine and other chlorinating agents with the chlorocyclohexyl radical. Chloro and bromocyclopentane were studied since in these molecules the conformational problems present in cyclohexane derivatives are absent. It was hoped that a comparison of the results in the cyclopentane and cyclohexane series would add significantly to our understanding of the importance of conformational problems both in the attack of a radical on a carbon-hydrogen bond and in the reaction of an alkyl radical with a halogen molecule.

Part II concerns itself with a study of directive effects in the chlorination of aralkyl hydrocarbons. Here, because of the ability of aromatic rings to complex chlorine atoms (2b, 10a, 20, 34), the selectivity of the free chlorine atom in hydrogen atom abstraction reactions can be approached only indirectly. Since only intermolecular reactions of complexed chlorine atoms have been reported in the literature, I thought it of considerable interest to investigate the photochlorination of butylbenzene in a variety of solvents. Here intramolecular reactions of the complexed chlorine atom and the alkyl side-chain can be reasonably formulated to give



preferred attack at the β, γ or ω-positions. No evidence was found for such an intramolecular process.

PART I. CHLORINATION OF HALOCYCLOALKANES

Introduction

Chlorocyclopentane, bromocyclopentane and chlorocyclohexane were employed as halocycloalkanes in this study. Chlorocyclopentane was subjected to the most extensive investigation. This compound was photochlorinated in various solvents and was chlorinated with several chlorinating reagents in carbon tetrachloride solution. The other two compounds. were photochlorinated in carbon tetrachloride. To obtain relative reactivities of those three compounds to their parent cycloalkanes, the compounds were photochlorinated competitively in the presence of a reference cycloalkane. If two hydrocarbons R_1H and R_2H are photochlorinated competitively with rate constant k_1 and k_2 respectively,

$$R_1H + Cl\cdot \xrightarrow{k_1} R_1\cdot + HCl$$

$$R_2H + Cl\cdot \xrightarrow{k_2} R_2\cdot + HCl$$

$$\frac{-d[R_1H]}{dt} = k_1[R_1H][Cl\cdot]$$

$$\frac{-d[R_2H]}{dt} = k_2[R_2H][Cl\cdot]$$

The rate of consumption of hydrocarbons is expressed by the above differential equations. By dividing the first expression by the second, one obtains the following expression.

$$\frac{-\dfrac{d[R_1H]}{[R_1H]}}{-\dfrac{d[R_2H]}{[R_2H]}} = \frac{k_1dt}{k_2dt}$$

Upon integration, the ratio of the two rate constants is obtained by the equation

$$\frac{\log \dfrac{[R_1H]_o}{[R_1H]_f}}{\log \dfrac{[R_2H]_o}{[R_2H]_f}} = \frac{k_1}{k_2}$$

where $[\ \ ]_o$ represents the initial concentration and $[\ \ ]_f$ represents the final concentration.

It had been previously proven that the products of a photochlorination reaction are a true measure of the initial site of attack by the chlorine atom (2). If geometric isomers are formed upon photochlorination, the ratio of the isomers would be controlled by the step

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$$

In this study the dihalocycloalkanes found in the chlorination product were analyzed by gas liquid chromatography. The chlorination mixture was chromatographed alone, and then with an authentic dihalogenocycloalkane. The enlarged peak in the chromatogram was thus identified. In the case of chlorination of chlorocyclopentane and of bromocyclopentane, five isomeric dihalocyclopentanes are possible. In the case of chlorination of chlorocyclohexane, seven isomeric dichlorocyclohexanes are possible. Authentic samples of all the dichloropentanes and hexanes were prepared.

The analysis depends on the assumption that the thermal conductivity of isomeric dihalogenocycloalkanes are identical. This assumption was checked with 1,1-dichlorocyclopentane and trans-1,2-dichlorocyclopentane which were available in a high state of purity. The correction factor, the ratio (mole of trans-1,2-dichlorocyclopentane/mole of 1,1-dichlorocyclopentane) to (area of trans-1,2-dichlorocyclopentane/area of 1,1-dichlorocyclopentane), was 1.029. It appears that this figure is unity within experimental error. Thus, the relative reactivity of carbon-hydrogen bonds in each position of the halocycloalkane were obtained. The combination of this figure and the reactivity of the whole molecule relative to a reference cycloalkane, leads to reactivity of a carbon-hydrogen bond at the certain position of a halocycloalkane relative to a carbon-hydrogen bond of the reference cycloalkane:

Relative reactivity per hydrogen = relative reactivity as the whole molecule x relative reactivity in the molecule (expressed as per cent) x $\frac{n_2}{n_1}$

where n_1 is the number of hydrogen at the certain position of a halocycloalkane and n_2 is the number of hydrogen of the reference cycloalkane.

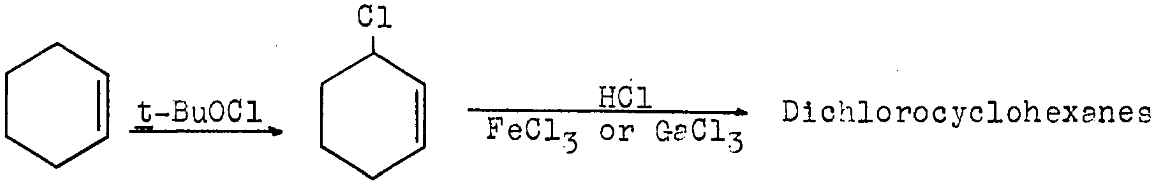
Some 1,2-halogen migrations are reported in the literature (9, 40). However, even if such a migration occurs, there would be no complication in the measurement of the relative reactivities, since for the halocycloalkanes a radical formed after 1,2-halogen migration is identical with the unrearranged radical. Further discussion of this point will be given later.

Synthesis and Identification of Unreported Dihalocycloalkanes

Among the dihalocycloalkanes which have been investigated extensively in the past are the dihalocyclohexanes. Of the seven isomeric dichlorocyclohexanes, all except 1,3-dichlorocyclohexanes are reported in the literature. The reaction of 1,3-cyclohexanediols and concentrated hydrochloric acid has been reported to give 1,4-dichlorocyclohexanes as the main products (41). A few unsuccessful attempts were made to prepare the 1,3-dichlorides from the 1,3-diols, the details of which are given in the experimental part.

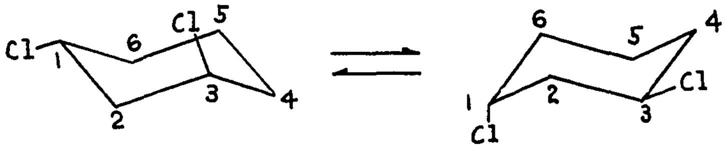
R. Cornubert _et_ _al_. (42) and M. S. Kharasch _et_ _al_. (43) independently obtained _trans_-1,3-dibromocyclohexane by addition of hydrogen bromide to 3-bromocyclohexene. In the latter work the same compound was obtained under both "peroxidic" and "antioxidant" conditions. The assignment of _trans_ configuration, however, does not seem to be certain because there has been considerable confusion on the products of reaction of 1,3-cyclohexanediols and 1,4-cyclohexanediols with hydrogen bromide. A good review on this subject is provided in reference (42).

The reaction of 3-chlorocyclohexene and hydrogen chloride was thus attempted. Anhydrous ferric chloride or gallium (III) chloride was added as the catalyst. When the reaction product of 3-chlorocyclohexene and hydrogen chloride was chromatographed, the two major peaks in the chromatogram did not correspond to any of the reported dichlorocyclohexanes but had retention times identical with the third peak and the fifth peak in the chromatogram of the photochlorination product of chlorocyclohexane. Three other peaks were observed in the chromatogram due to <u>trans</u>-1,2-dichlorocyclohexane, <u>cis</u>-1,4-dichlorocyclohexane and <u>trans</u>-1,4-dichlorocyclohexane. The latter two compounds may result from the presence of 4-chlorocyclohexene as a by-product in the reaction of cyclohexene and <u>tertiary</u>-butyl hypochlorite.



The compound which corresponds to the third peak in the chromatogram of the photochlorination product will be called "compound A" and the compound which corresponds to the fifth peak will be called "compound B" temporarily. The isolation of these compounds by preparative gas-liquid chromatography is described in the experimental section. The n.m.r. spectra of those two compounds are shown in Fig. 1. The trans-1,3-configuration has been assigned to compound A and the cis-1,3-configuration has been assigned to compound B based on the following argument.

1. In the trans compound, the chlorine substituents should be in (1e,3a) or (1a,3e). Since both conformations must be equivalent, there would be an equilibrium:

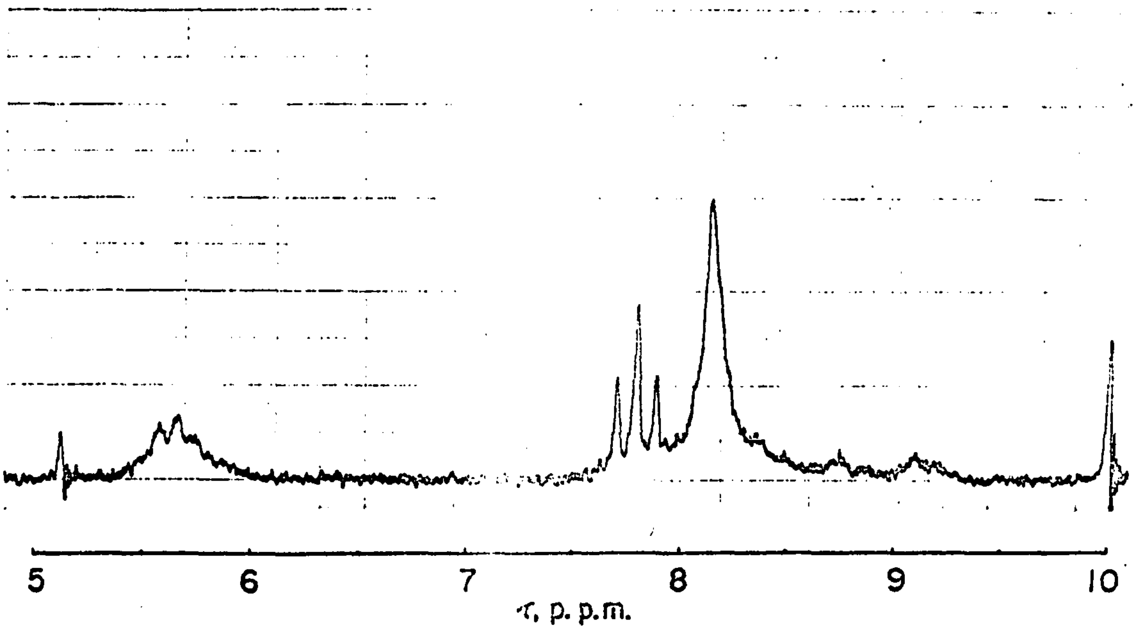


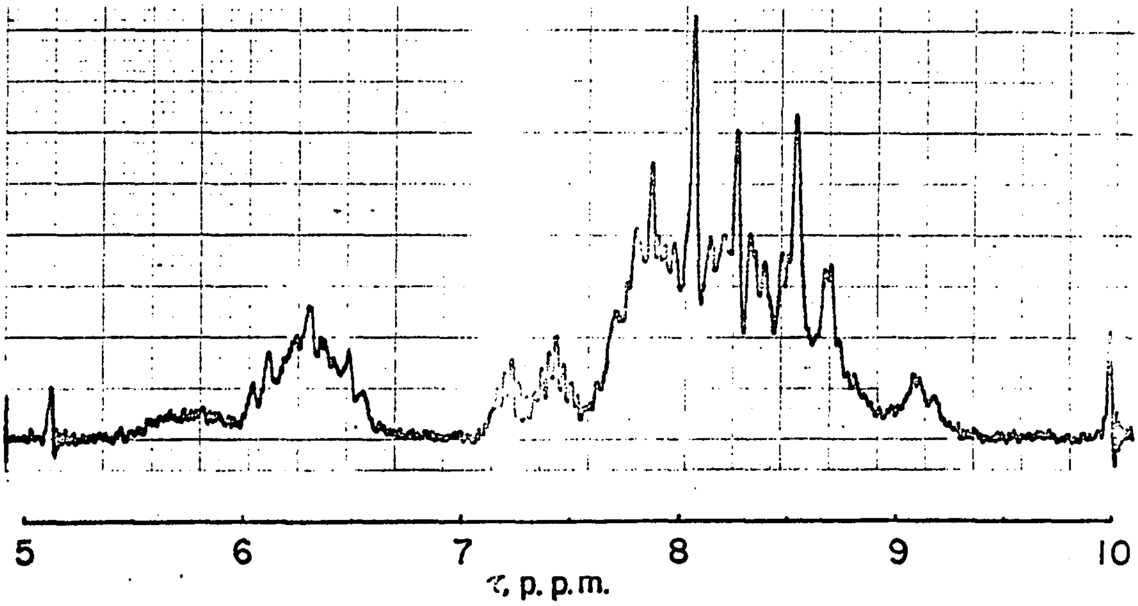
If the rate of the interchange is rapid enough compared with the frequency of the spectrometer, the chemical shift of the methylene protons attached to the 2 and 5 carbon atoms should be equal and spin-spin coupling between these protons would not occur. The protons attached to carbon atoms 4 and 6 are nearly equal and spin-spin coupling would not be expected to be important.

In the cis compound, the possible position of chlorine substituents would be (1e,3e) and (1a,3a). The (1e,3e) conformation may be energetically much more favorable than the (1a,3a) conformation because of 1,3 interaction between the chlorine substituents in the latter conformation. In general diequatorial conformation is thought to be more stable than diaxial conformation (44). However, it is reported that the diaxial conformation of trans-1,4-dichlorocyclohexane is more stable than the diequatorial in carbon tetrachloride solution

Fig. 1a. Proton magnetic resonance spectrum of compound A (*trans*-1,3-dichlorocyclohexane) at 60 Mc./sec. in carbon tetrachloride

Fig. 1b. Proton magnetic resonance spectrum of compound B (*cis*-1,3-dichlorocyclohexane) at 60 Mc./sec. in carbon tetrachloride


5
6
7
8
9
10
τ, p.p.m.


5
6
7
8
9
10
τ, p.p.m.

(45).

Thus, if two methylene protons on the same carbon atom experience different magnetic environment owing to the frozen diequatorial conformation or the existence of equilibrium where one conformation is favored over the other, those two protons can couple and the spectrum of *cis*-1,3-dichlorocyclohexane should be more complicated than that of *trans*-1,3-dichlorocyclohexane.

2. In the *trans* compound the two methylene protons in the 2-position would form an A_2X_2 system with the two methine protons on the 1 and 3 carbon atoms. Therefore, the triplet observed at $\tau = 7.81$ in the spectrum of compound A is consistent with the *trans* isomer.

3. The broad singlet at $\tau = 8.15$ in the spectrum of compound A should be due to the other six methylene protons. The *tau* value of cyclohexane protons is 8.56 (46).

4. The peak at $\tau = 5.68$ in the spectrum of compound A should be due to the two methine protons. The *tau* value of a methine proton of chlorocyclohexane is 6.11 (46). The peak content at $\tau = 5.68$ appears to be approximately a triplet of triplets with the coupling constant 5.3 c/s.

5. The peak at $\tau = 6.30$ in the spectrum of compound B appears to be due to the two methine protons of *cis*-1,3-dichlorocyclohexane, since it is at higher field by 0.62 p.p.m. than that of *trans* compound and axial protons are known

to be more shielded than equatorial protons (46). Theoretically 0.40 p.p.m. for the difference in tau values of the axial and equatorial protons can be expected (46). If the methine protons of trans compound experience the average field of equatorial and axial and the methine protons of cis compound are in axial positions, the difference of 0.20 p.p.m. could be expected. Although the magnitude of the difference does not agree, the difference is in the right direction.

6. The peaks around $\tau = 7.3$ in the spectrum of compound B would be due to the two methylene protons between the methine groups. The half in the higher field is overlapped by peaks of other methylene protons. Those two protons are roughly an AB system and if this is the case, the coupling constant is 12.5 c/s. A similar situation can be found in the spectrum of β-D-xylopyranose tetraacetate (47).

7. Area ratios of peaks in the spectra are consistent with the above descriptions.

It is interesting to compare the n.m.r. spectra of 1,3-dichlorocyclohexanes with other reported dichlorocyclohexanes. The spectra of cis-1,4-dichlorocyclohexane and trans-1,4-dichlorocyclohexane are shown in Fig. 2 and Fig. 3, respectively. For the cis compound equilibrium (1e,4a) $\rightleftharpoons$ (1a,4e) can be expected and both conformations are equivalent. Therefore, an approximate doublet due to the methylene protons are observed. For the trans compound the equilibrium

Fig. 2. Proton magnetic resonance spectrum of _cis_-1,4-dichlorocyclohexane at 60 Mc./sec. in carbon tetrachloride

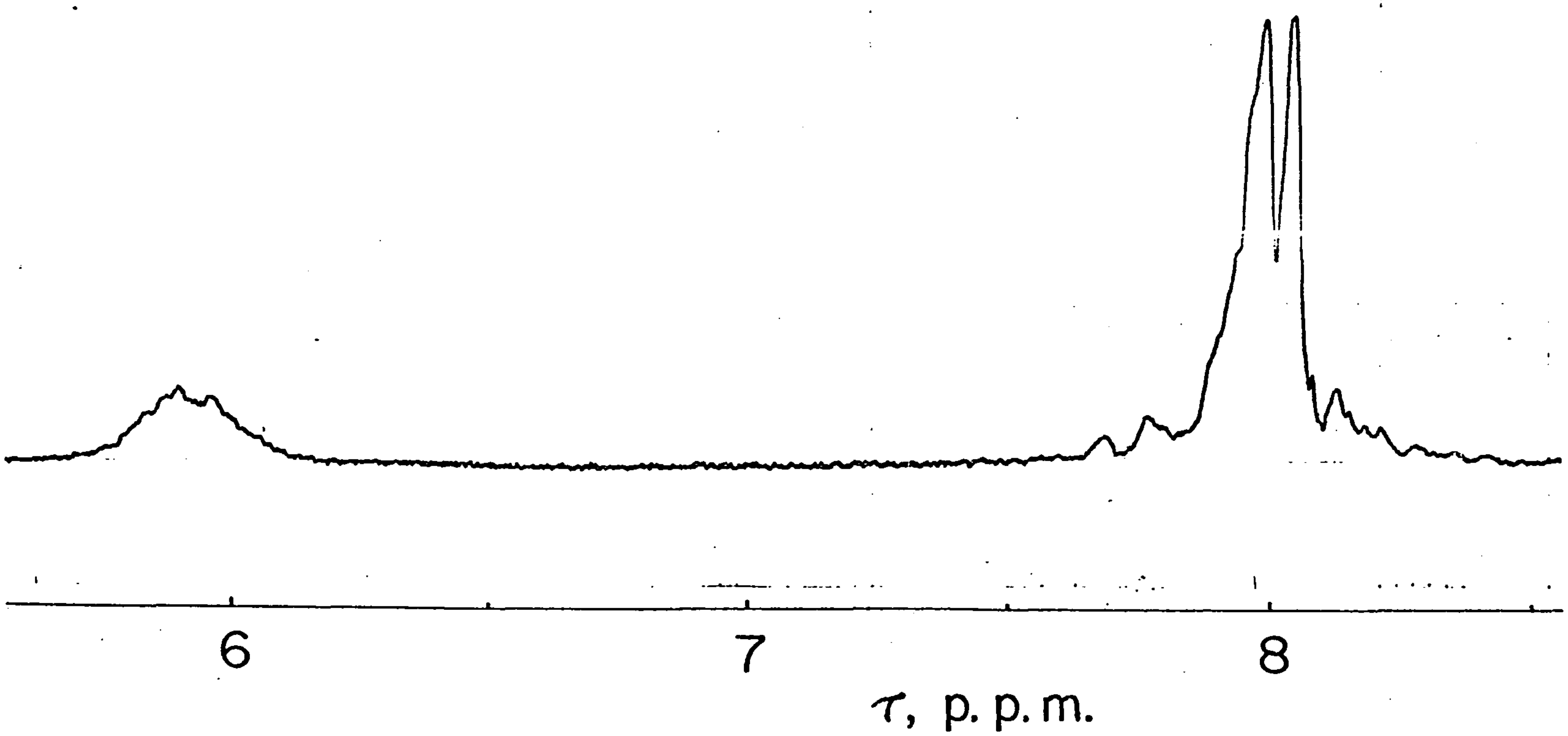
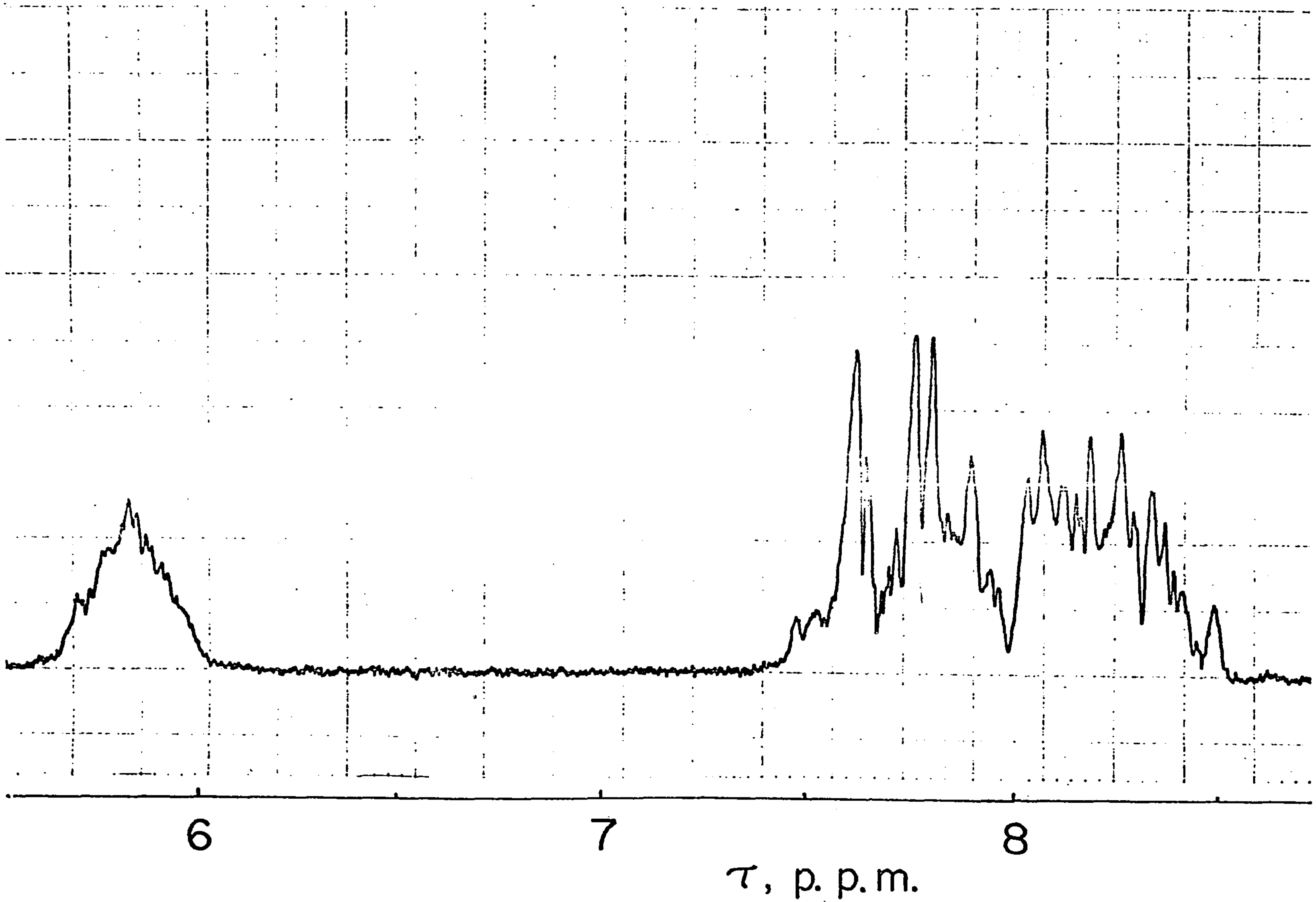

6
7
8
τ, p. p. m.

Fig. 3. Proton magnetic resonance spectrum of <u>trans</u>-1,4-dichlorocyclohexane at 60 Mc./sec. in carbon tetrachloride


6
7
8
τ, p. p. m.

(1e,4e) $\rightleftharpoons$ (1a,4a) in solutions was reported by K. Kozima and T. Yoshino on the basis of its Raman spectra (45) as mentioned before, and mole fraction of the diequatorial conformation calculated from energy difference given is 0.25 in carbon tetrachloride solution, presumably at room temperature. No explanation was given why the diaxial conformation is more stable in solution. It was reported that in vapor phase the two conformations are present in equal amount on the basis of electron diffraction, presumably at room temperature (48). Only the (1e,4e) conformation was reported to exist in solid state based on x-ray (49) and Raman spectra (45). Since the (1a,4a) conformation is predominant, two methylene protons on the same carbon atom are not equivalent and the n.m.r. absorption is complicated. The methine peak of cis compound occurs at slightly higher field than that of trans compound, a fact which supports the predominance of the diaxial conformation in carbon tetrachloride solution.

The n.m.r. spectra of cis-1,2-dichlorocyclohexane and trans-1,2-dichlorocyclohexane are shown in Fig. 4 and Fig. 5, respectively. For the trans compound equilibrium (1e,2e) $\rightleftharpoons$ (1a,2a) in solutions was reported by K. Kozima et al. on the basis of dipole moment and Raman spectra (50), and by E. Havinga et al. on the basis of dipole moment (51). In the solid state only the (1e,2e) conformation was reported to exist on the basis of Raman spectra (50). The mole

Fig. 4. Proton magnetic resonance spectrum of <u>cis</u>-1,2-dichlorocyclohexane at 60 Mc./sec. in carbon tetrachloride

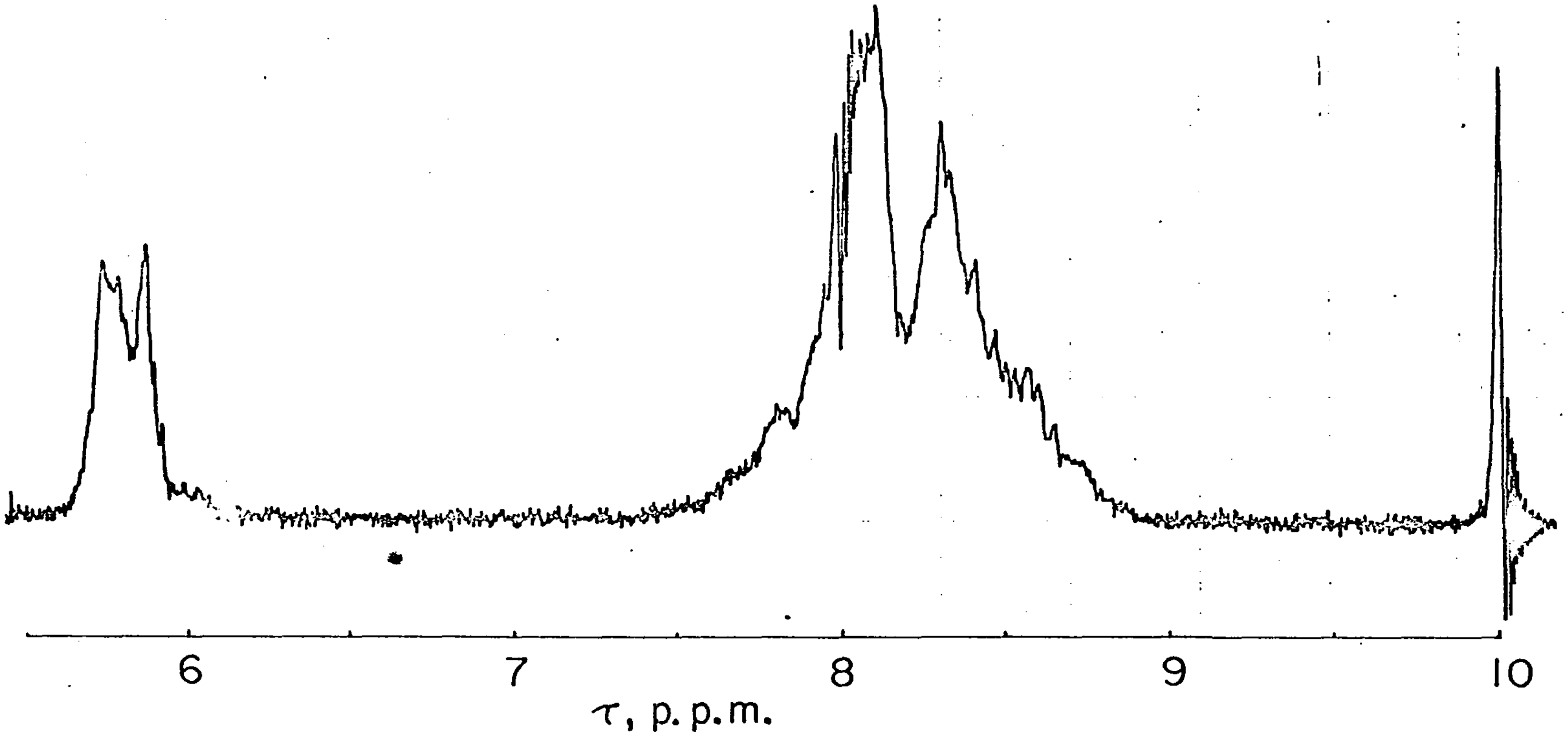
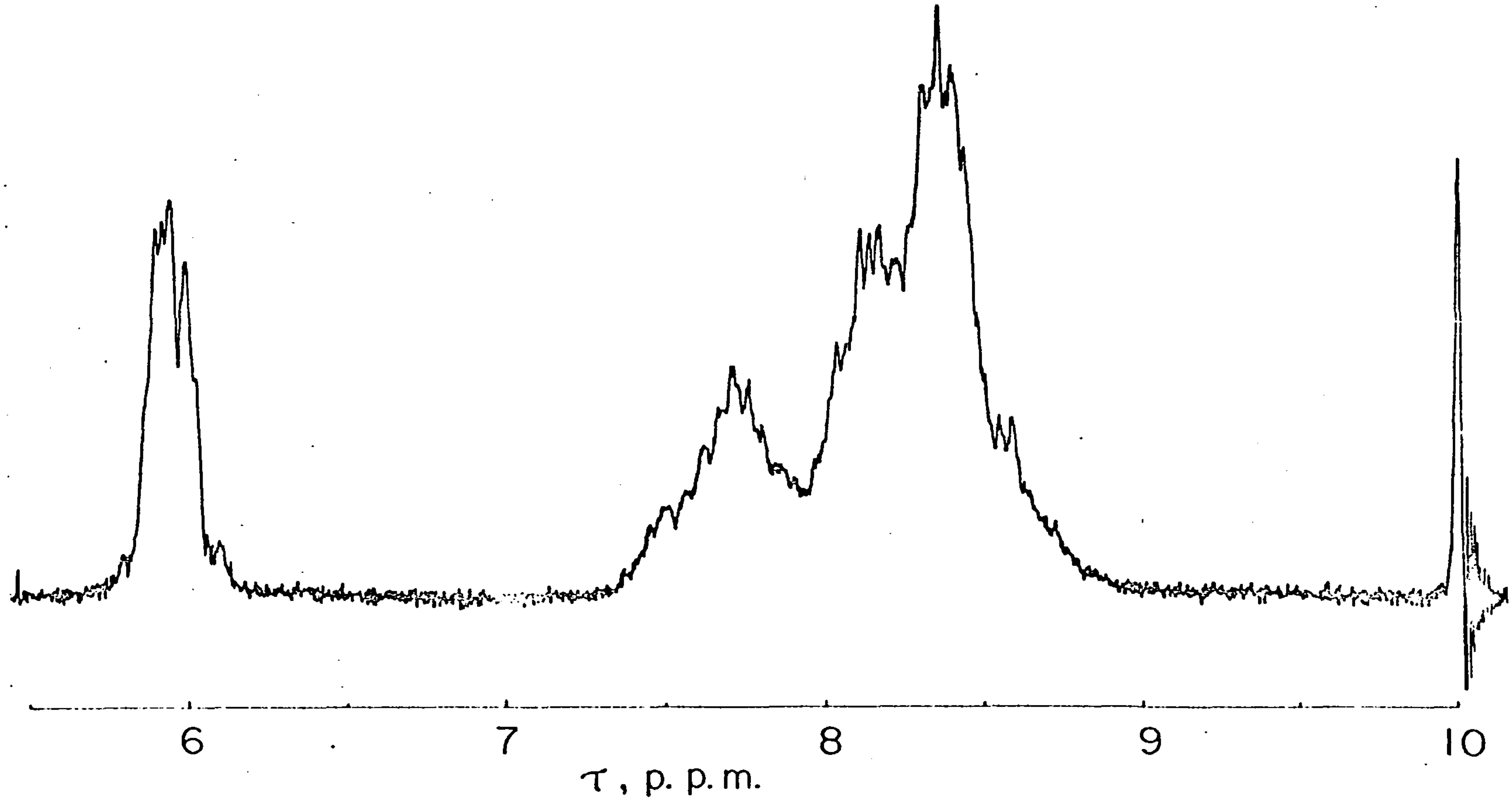
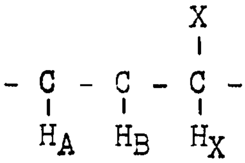

6
7
8
9
10
τ, p.p.m.

Fig. 5. Proton magnetic resonance spectrum of <u>trans</u>-1,4-dichlorocyclohexane at 60 Mc./sec. in carbon tetrachloride


6
7
8
9
10
τ, p. p. m.

fraction of diequatorial conformation of *trans*-1,2-dichlorocyclohexane in carbon tetrachloride was 0.50 (50) and 0.53 (51) presumably at room temperature. The spectrum of *cis*-1,2-dichlorocyclohexane is complicated as well as the spectrum of the *trans* compound. This could be explained by the fact that the absorption by proton H_X becomes complex when the



$$\begin{array}{ccccccc} & & & & & X & \\ & & & & & | & \\ - & C & - & C & - & C & - \\ & | & & | & & | & \\ & H_A & & H_B & & H_X & \end{array}$$

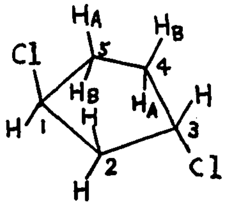
difference of the chemical shift between protons H_A and H_B is smaller than the coupling constant between H_A and H_B even if the coupling constant between H_A and H_X is zero (52) or nearly zero (53). A slightly higher chemical shift of the methine proton of *trans* compound would support the above mentioned equilibrium (1e,2e) $\rightleftharpoons$ (1a,2a) with a preference for the (1e,2e) conformation.

The ratios of dichlorocyclohexanes formed from the addition of hydrogen to 3-chlorocyclohexene are 6% *trans*-1,2-dichlorocyclohexane, 46% *cis*-1,3-dichlorocyclohexane, 32% *trans*-1,3-dichlorocyclohexane, 5% *cis*-1,4-dichlorocyclohexane, and 11% *trans*-1,4-dichlorocyclohexane based on analysis by gas liquid chromatography. The predominance of the *cis*-1,3-dichloride over *trans*-1,3-dichloride is reasonable because the system would be in equilibrium in the presence of the catalyst.

The order of elution of dichlorohexanes with a 2.2 m. polyphenyl ether column (20%) in series with a 1.5 m. diisodecyl phthalate column (10%) is 1,1-dichlorocyclohexane, < *trans*-1,2-dichlorocyclohexane, < *trans*-1,3-dichlorocyclohexane, < *trans*-1,4-dichlorocyclohexane, < *cis*-1,3-dichlorocyclohexane, < *cis*-1,4-dichlorocyclohexane, < *cis*-1,2-dichlorocyclohexane.

Of the dichlorocyclopentanes, *cis*-1,2-dichlorocyclopentane and the two geometric isomers of 1,3-dichlorocyclopentane have not been reported in the literature. Since the reactions of alcohols with thionyl chloride in the presence of pyridine is known to be accompanied with inversion of configuration (54), the dichloride formed from *trans*-2-chlorocyclopentanol and thionyl chloride in the presence of pyridine is undoubtedly *cis*-1,2-dichlorocyclopentane. A similar procedure was used to synthesize *cis*-1,2-dichlorocyclohexane from *trans*-2-chlorocyclohexanol (55).

The compounds which correspond to the third and fourth peaks of the dichlorides were separated from the photochlorination product of chlorocyclopentane by vacuum distillation with a Todd column. The n.m.r. spectrum of the former is shown in Fig. 6 and that of the latter is shown in Fig. 7.



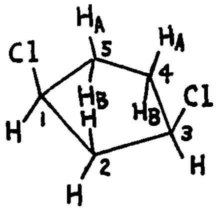


Fig. 6. Proton magnetic resonance spectrum of *trans*-1,3-dichlorocyclopentane at 60 Mc./sec. in carbon tetrachloride

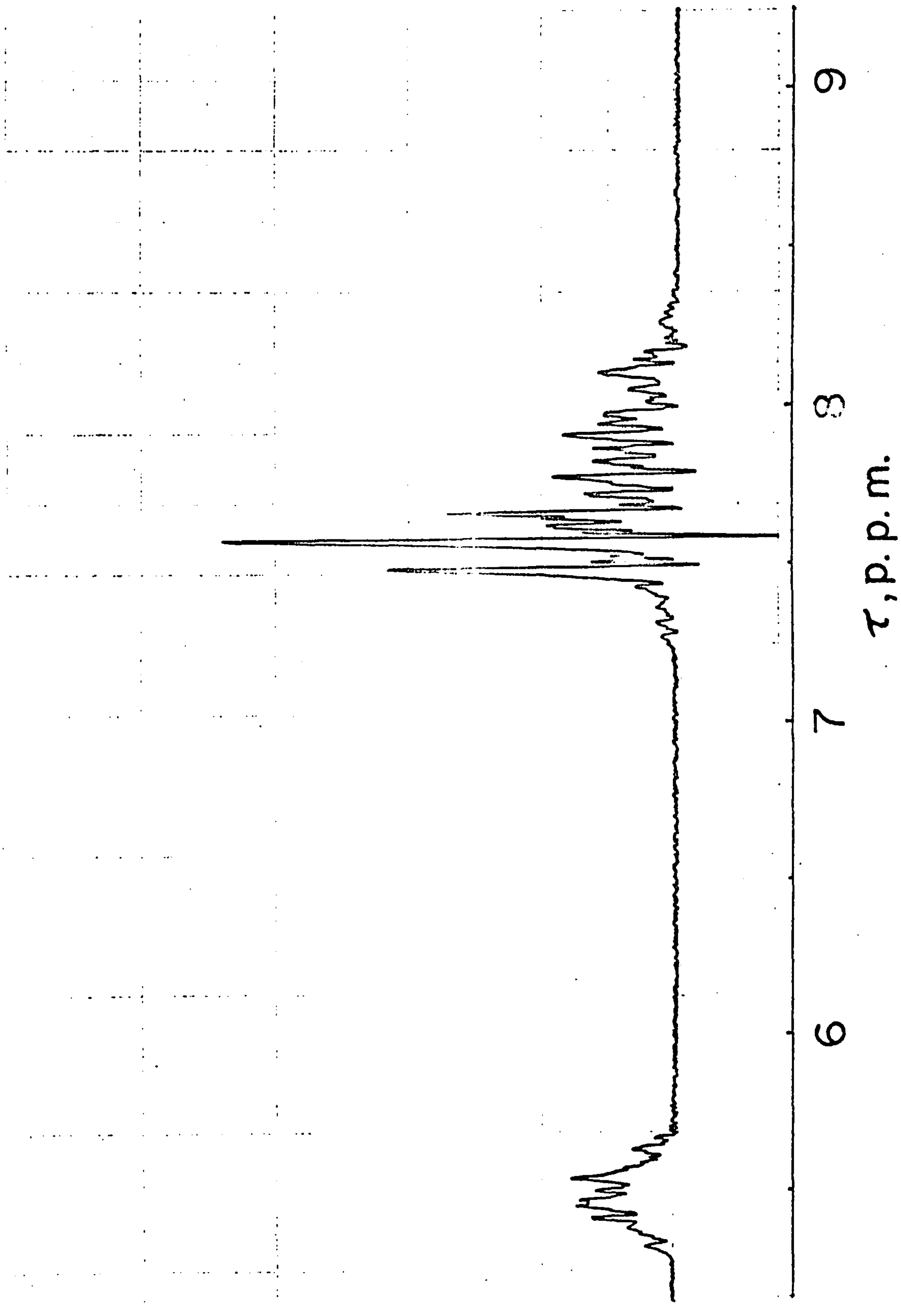
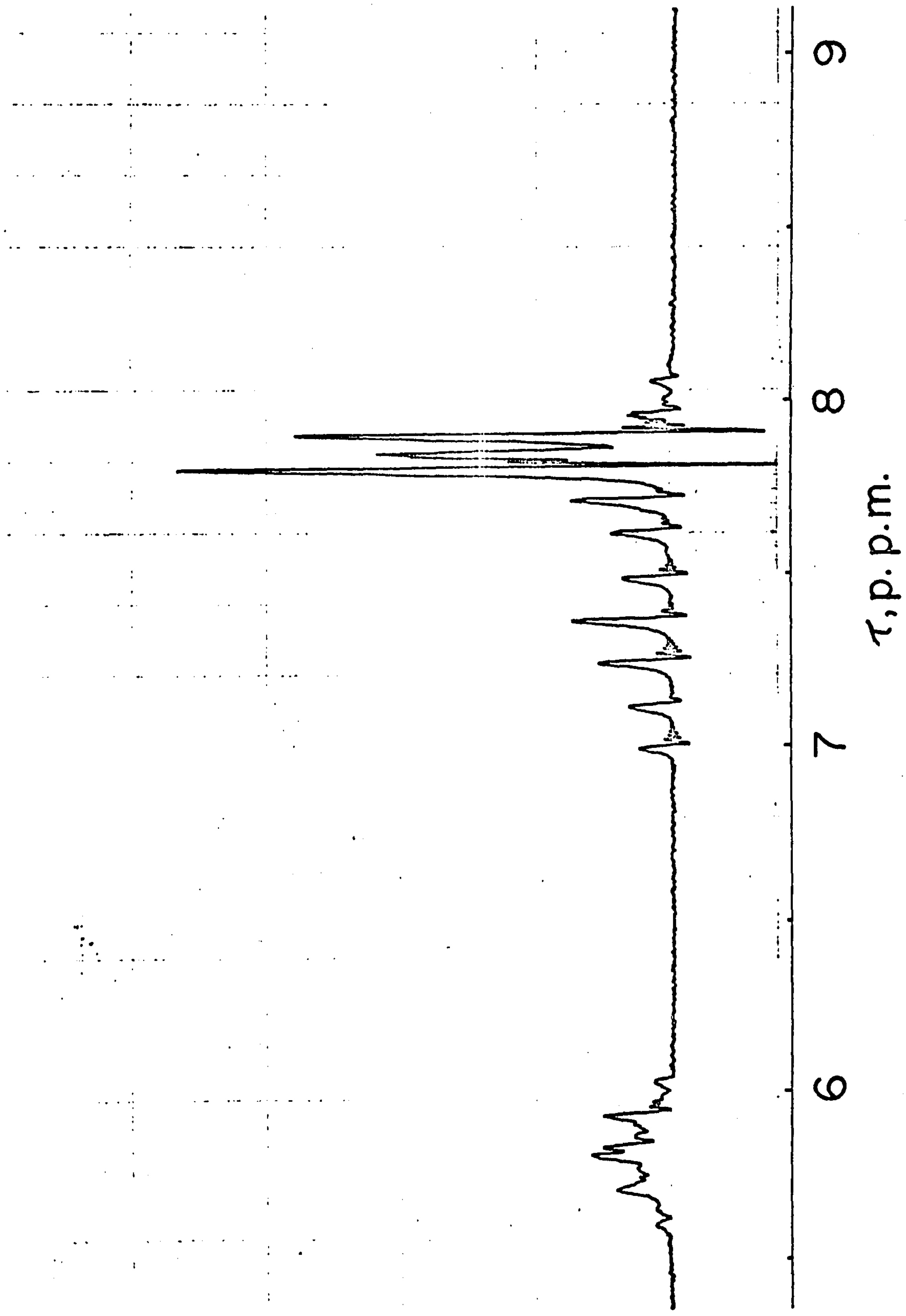

9
8
7
6
τ, p.p.m.

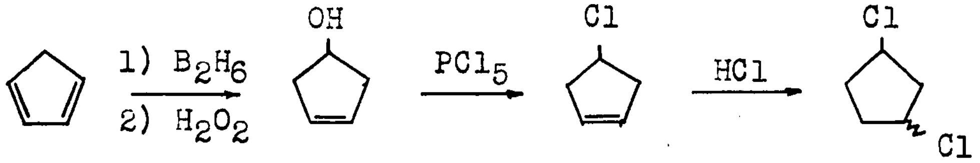
Fig. 7. Proton magnetic resonance spectrum of <u>cis</u>-1,3-dichlorocylopentane at 60 Mc./sec. in carbon tetrachloride


9
8
7
6
τ, p.p.m.

The former compound (Fig. 6) was assigned the trans-1,3 configuration and the latter compound (Fig. 7) was assigned the cis-1,3 configuration based on the following argument.

1. The third and fourth peaks of the chromatogram of the chlorination product do not correspond to the known 1,1-dichlorocyclopentane, trans-1,2-dichlorocyclopentane or cis-1,2-dichlorocyclopentane which correspond to the first, the second, and to the fifth peak, respectively. Dichloride peaks can be easily distinguished from higher chlorinated product since these polychloride peaks became larger when compared with dichloride peaks when a larger ratio of chlorine to chlorocyclopentane was used.

2. Those two compounds which correspond to the third and fourth peaks were synthesized in the following way from cyclopentadiene.



Discussion of the above synthesis will be presented later.

3. Methylene protons between the two chlorine substituents in trans-1,3-dichlorocyclopentane are magnetically equally shielded since both protons are cis to one chlorine substituent and trans to the other. Therefore, a triplet was observed at $\tau = 2.57$ in Fig. 6.

Methylene protons between the two chlorine substituents in cis-1,3-dichlorocyclopentane are not equivalent. Therefore a complex pattern can be expected. Because of the large coupling constant between these two methylene protons, absorption can be expected to be broad.

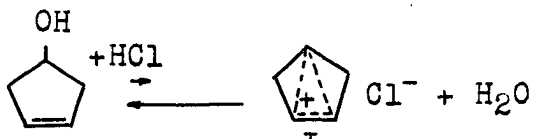
4. In the cis compound H_A and H_B will be weakly coupled and in the trans compound H_A and H_B will be strongly coupled. Therefore, more separation between absorptions due to the high-field methylene protons (on atoms 4 and 5) are expected in the spectrum of the trans compound than in that of the cis compound.

5. Reaction of the ditosylate of cis-1,3-cyclopentanediol with lithium chloride in absolute ethanol gave mainly elimination products as shown by high acidity of the reaction mixture. However, the liquid separated from the reaction mixture, as described in the experimental part, contained as the predominant dichloride the compound which corresponds to the fourth peak in the chromatogram of the dichlorides formed by photochlorination of chlorocyclopentane. The ditosylate used is surely the cis compound because K. A. Saegebarth (56) synthesized a p-nitrobenylideneacetal from the parent 1,3-cyclopentanediol, although there has been some confusion about the configurations of the 1,3-cyclopentanediols (57).

6. The higher boiling point and refractive index of the cis compound than the trans compound agree with the von Auwers-Skita rule (58).

Returning to the reactions described in page 8, the first step was originally described by S. Winstein et al. (59) and modified so that no separate diborane generator was used and no tedious chromatographic separation needed. The yield based on the sodium borohydride used was lower than the original method, the yield based on the cyclopentadiene used was about the same (13%).

To synthesize 4-chlorocyclopentene, the reaction of 3-cyclopenten-1-ol with concentrated hydrochloric acid was attempted. As soon as hydrochloric acid was added to 3-cyclopenten-1-ol a purple color was developed. The color gradually turned brown and 24 hours later the solution became completely dark brown. A purple color also develops when anhydrous aluminum chloride is added to 4-chlorocyclopentene. When concentrated sulfuric acid was added to 3-cyclopenten-1-ol, the mixture turned black immediately. The ultraviolet spectrum of the mixture of 3-cyclopenten-1-ol and concentrated hydrochloric acid in methanol has a large shoulder due to 3-cyclopenten-1-ol and small absorption maxima at 255 and 305 mμ supposedly due to reaction products. A possible interpretation of those phenomena is that carbonium ion I was formed but the equilibrium is unfavorable. The cyclo-



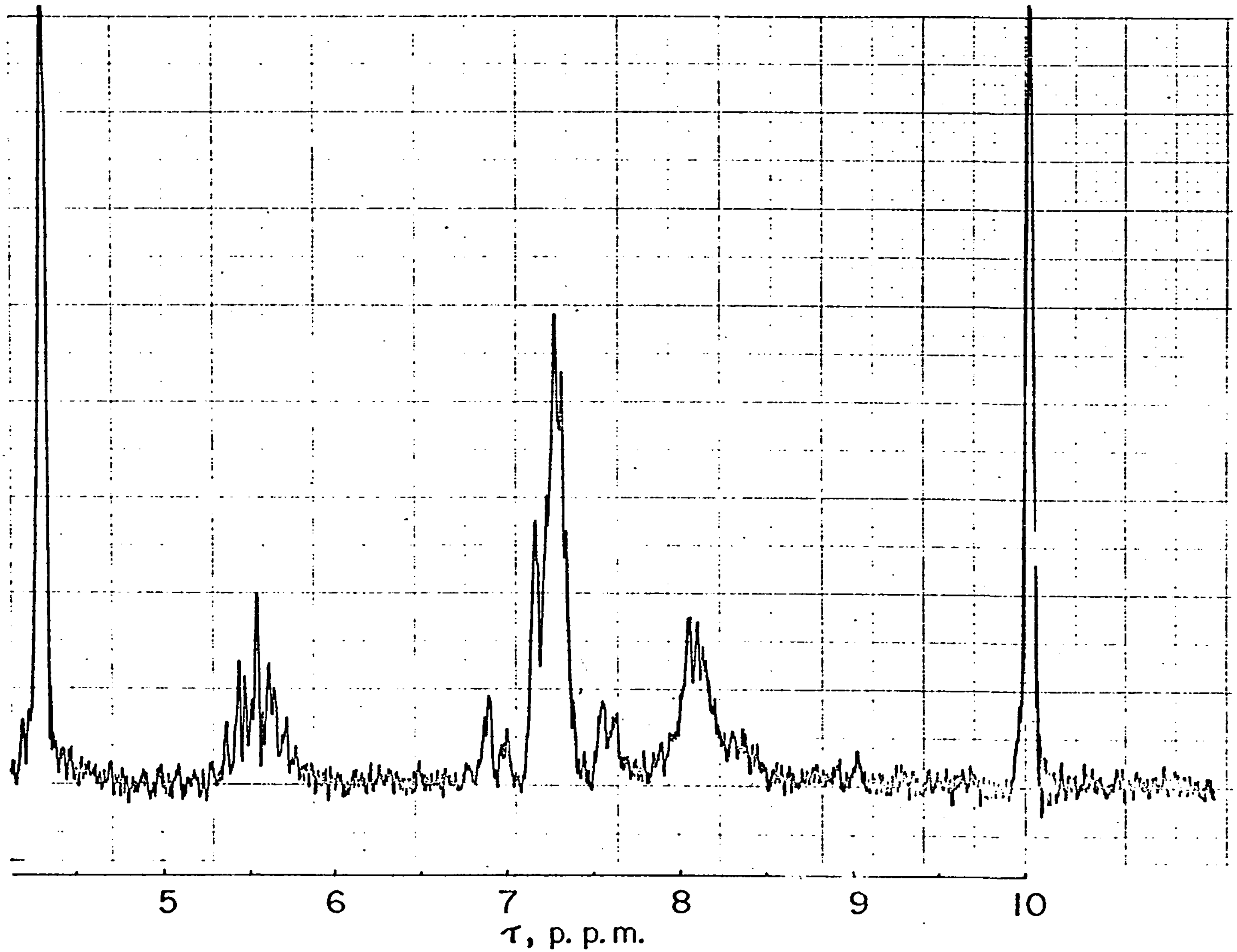
I

hexenyl carbonium ion reported by G. A. Olah and W. S. Tolgyesi (60) has ultraviolet maxima at 307 m μ (ε 234), 242 (ε 1350) and 250 (shoulder ε 1248). N. C. Deno et al. reported that allylic cations have a strong ultraviolet absorption in the range between 310 and 335 m μ (61a) and that tricyclopropylmethyl cation has an ultraviolet absorption at 270 m μ (ε 22,000) (61b).

Reaction of 3-cyclopenten-1-ol with thionyl chloride in the presence of pyridine merely yielded resinous material and reaction of the alcohol with phosphorous pentachloride was successful. Similar observations were reported by W. S. Rapson and R. Robinson for 1-methyl-Δ^2-cyclopentenyl-1-carbinol (62). The n.m.r. spectrum of the product obtained by the reaction of 3-cyclopenten-1-ol with phosphorous pentachloride is shown in Fig. 8 and the spectrum is consistent with the structure 4-chlorocyclopentene. The complex absorption around τ = 7 may be due to four methylene protons. Absorption at τ = 5.54 seems to be a triplet of triplets and due to the methine proton. The singlet at τ = 4.30 may be due to two olefinic protons. Since the two protons should be equivalent, no coupling occurs between them. However, it is interesting that no splitting by the adjacent methylene protons was observed.

The addition of hydrogen chloride to 4-chlorocyclopentene gave a 50:50 mixture of 1,3-dichlorocyclopentanes while

Fig. 8. Proton magnetic resonance spectrum of 4-chlorocyclopentane at 60 Mc./sec. in carbon tetrachloride


5
6
7
8
9
10
τ, p. p. m.

reaction of hydrogen bromide with the chloride gave 41% cis-1-bromo-3-chlorocyclopentane and 59% trans-1-bromo-3-chlorocyclopentane under the same conditions. Although the latter reaction can not be said to proceed through only an ionic mechanism, the reaction occurred in a tube from which air was evacuated and which was allowed to stand in a dark place at 0°C.

The bromochlorocyclopentanes have not been reported in the literature. 1,1-Bromochlorocyclopentane, cis-1-bromo-3-chlorocyclopentane and trans-1-bromo-3-chlorocyclopentane were synthesized in a manner similar to that employed for the cyclohexane analogs (62). Pure 1-bromo-1-chlorocyclopentane could not be isolated because of its instability during distillation. However, it seems to be stable in gas-liquid chromatography, since in the chromatogram of mixture of 1-bromo-1-chlorocyclopentane and trans-1-bromo-2-chlorocyclopentane only two peaks were observed, neither of which corresponds to 1-chlorocyclopentene, the decomposition product formed during distillation.

Radical addition of hydrogen bromide to a double bond is known to proceed by trans addition (63, 64). Therefore, the product of the reaction of 1-chlorocyclopentene and hydrogen bromide in the presence of ultraviolet illumination should give cis-1-bromo-2-chlorocyclopentane.

It appears that N-bromosuccinimide and hydrogen chloride react to give bromine-chloride in a manner similar to N-bromoacetamide and hydrogen chloride (65). Another example of the similar behavior of N-bromosuccinimide and N-bromoacetamide is the observation that both compounds in water react with olefins to give bromohydrins (66). Therefore, reaction of cyclopentene with N-bromosuccinimide and hydrogen chloride presumably gave <u>trans</u>-1-bromo-2-chlorocyclopentane.

Assignment of configurations of the 1-bromo-3-chlorocyclopentanes was made by the same manner as for the 1,3-dichlorocyclopentanes, except for argument no. 5, on the basis that in n.m.r. spectroscopy chlorine and bromine substituent shield protons very similarly (46). The n.m.r. spectra of the bromochlorocyclopentanes are shown in Fig. 9-12, which show a similarity to the corresponding dichlorides.

The ratios of retention times of the corresponding dichlorocyclopentanes and bromochlorocyclopentanes were the same, when a di-2-ethylhexylsebacate column is used for gas-liquid chromatography. The ratios of retention time,

$$\frac{\text{1-bromo-1-chlorocyclopentane}}{\text{1,1-dichlorocyclopentane}} = \frac{\text{trans-1-bromo-2-chlorocyclopentane}}{\underline{\text{trans}}\text{-1,2-dichlorocyclopentane}} = \text{etc.} = 1.55$$

The order of elution is 1,1-dihalocyclopentane < <u>trans</u>-1,2-dihalocyclopentane < <u>trans</u>-1,3-dihalocyclopentane < <u>cis</u>-1,2-dihalocyclopentane.

Fig. 9. Proton magnetic resonance spectrum of _cis_-1-bromo-3-chlorocyclopentane at 60 Mc./sec. in carbon tetrachloride

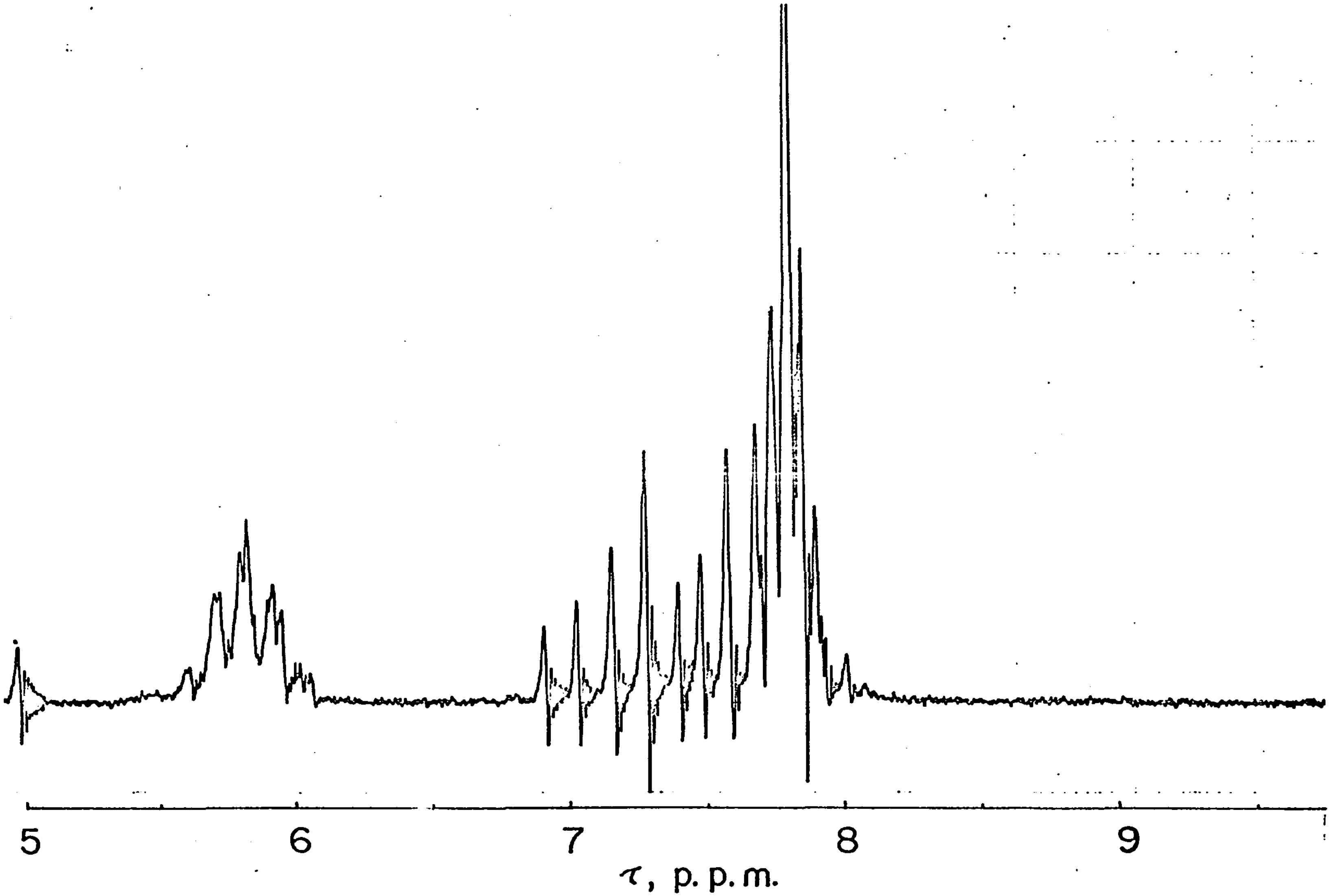

5
6
7
8
9
τ, p.p.m.

Fig. 10. Proton magnetic resonance spectrum of *trans*-1-bromo-3-chlorocyclopentane at 60 Mc./sec. in carbon tetrachloride

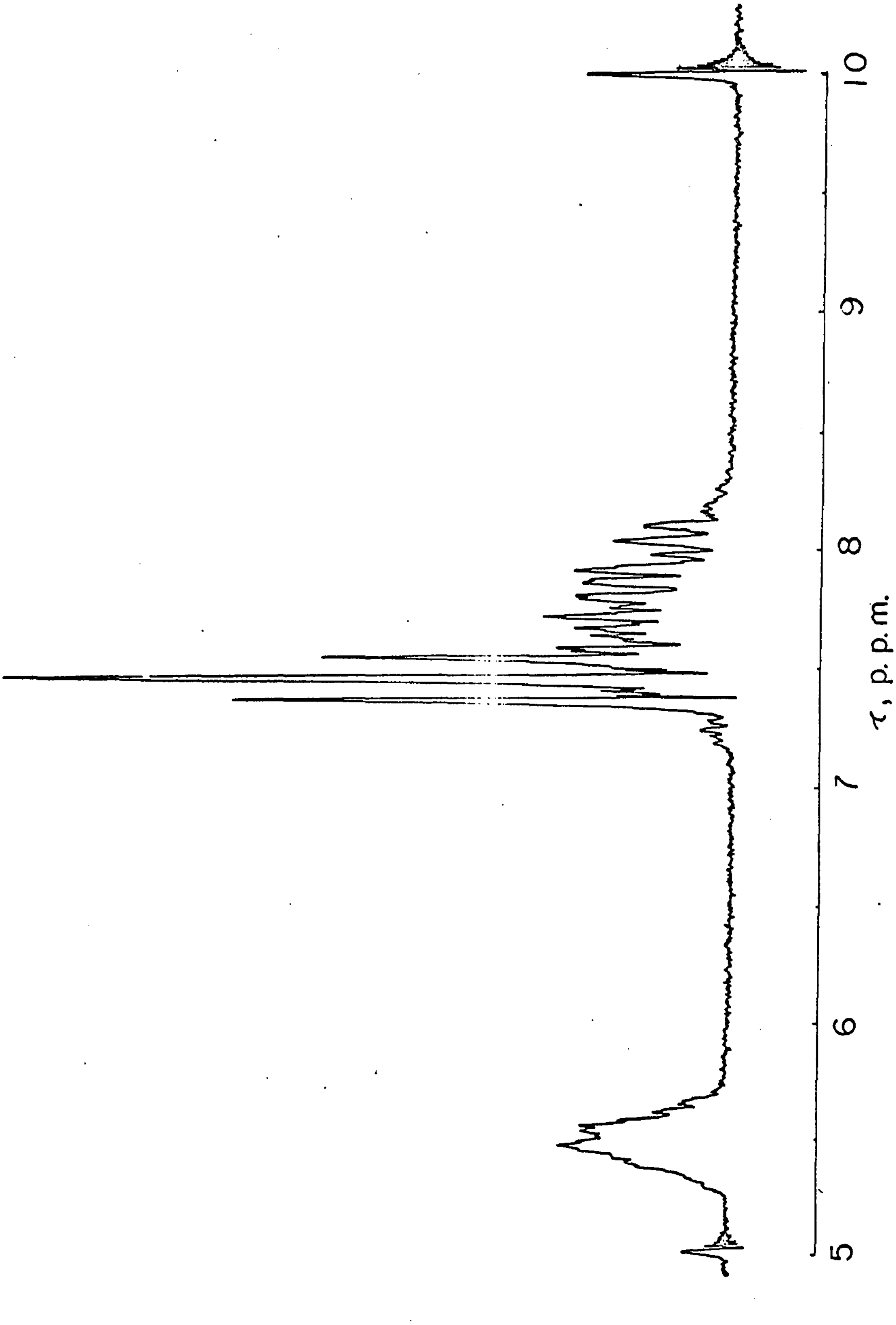
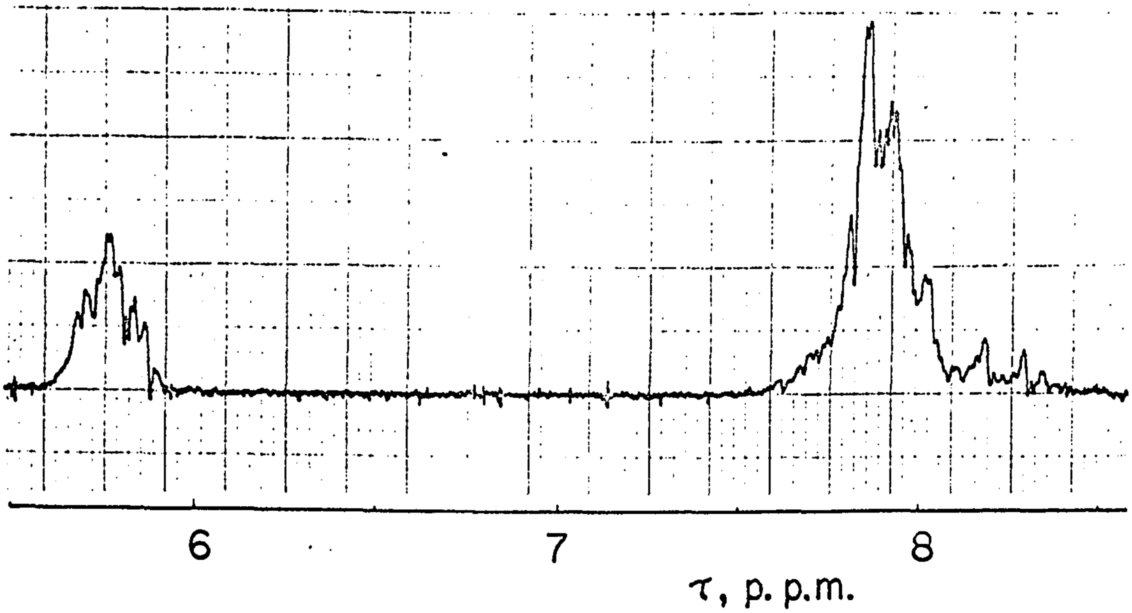

5
6
7
8
9
10
τ, p.p.m.

Fig. 11a. Proton magnetic resonance spectrum of _cis_-1,2-dichlorocyclopentane at 60 Mc./sec. in carbon tetrachloride

Fig. 11b. Proton magnetic resonance spectrum of _cis_-1-bromo-2-chlorocyclopentane at 60 Mc./sec. in carbon tetrachloride


6
7
8
τ, p.p.m.

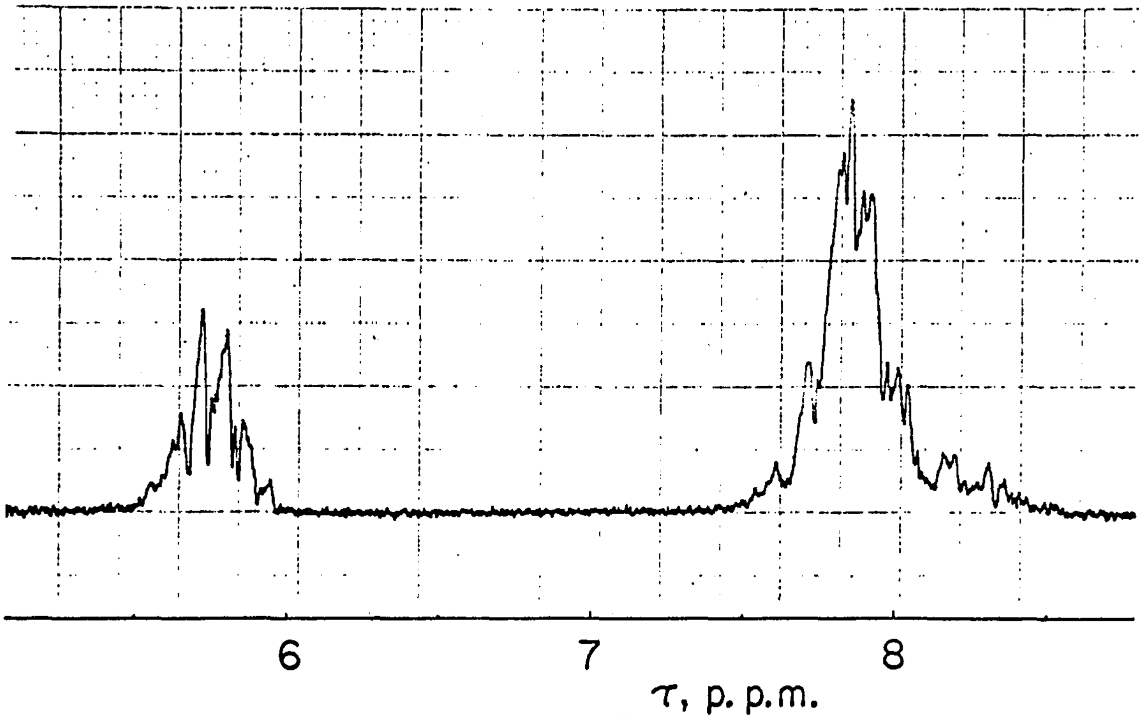
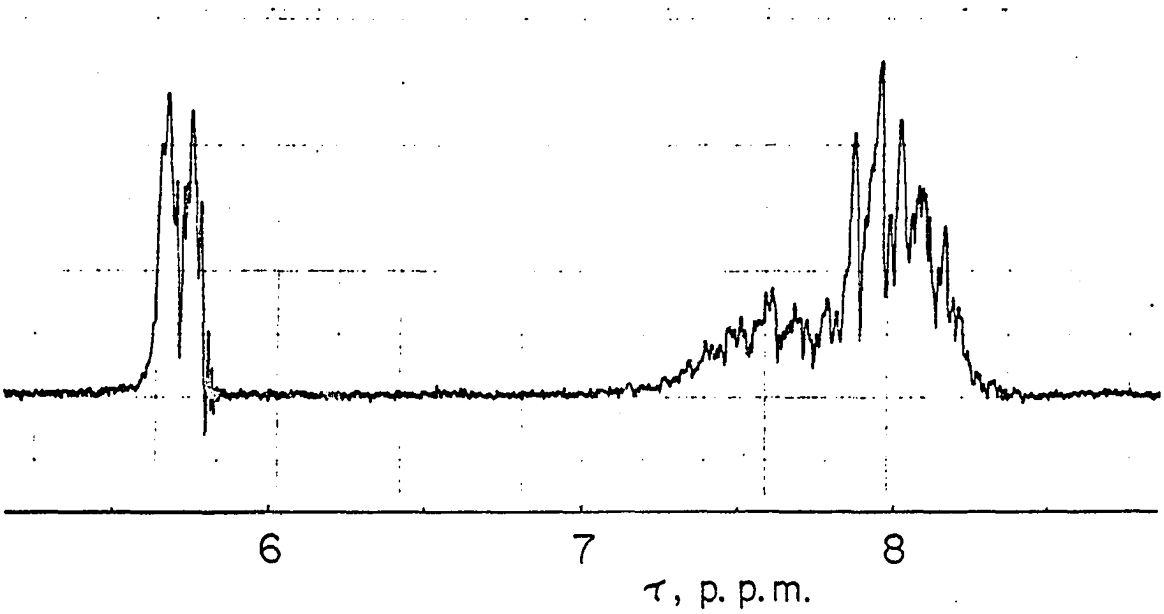
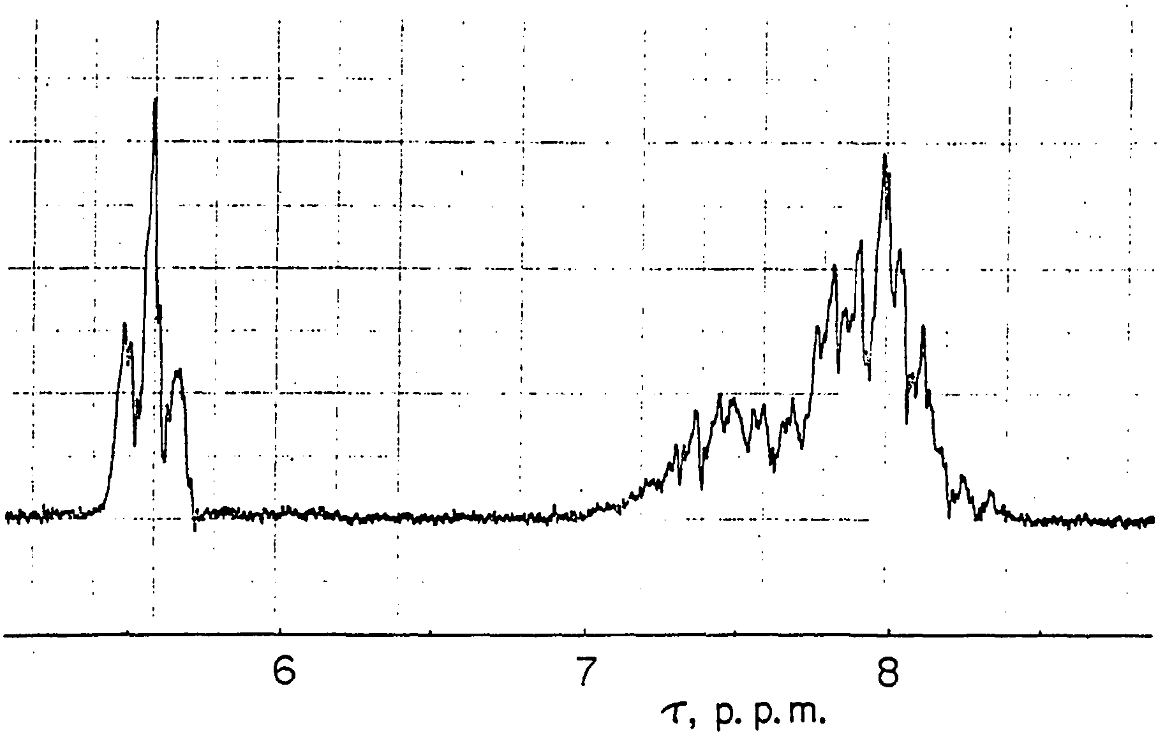

6
7
8
τ, p.p.m.

Fig. 12a. Proton magnetic resonance spectrum of *trans*-1,2-dichlorocyclopentane at 60 Mc./sec. in carbon tetrachloride

Fig. 12b. Proton magnetic resonance spectrum of *trans*-1-bromo-2-chlorocyclopentane at 60 Mc./sec. in carbon tetrachloride


6
7
8
τ, p. p. m.


6
7
8
τ, p. p. m.

Results and Discussion

Photochlorination of halocycloalkanes

Solutions of chlorocyclopentane in carbon tetrachloride were photochlorinated to different extents to ascertain the dependence of the distribution of dichlorocyclopentanes on the ratio of reactants. The results, based on analysis by g.l.c., are listed in Table 1. Variations are so small that they are probably within experimental uncertainty. It seems likely that the relative reactivities of the dichlorocyclopentanes toward chlorination are similar and that polychlorination does not preferentially destroy one of the first formed dichlorides.

To find out if there is any solvent effect, 1 molar solutions of chlorocyclopentane in acetonitrile, nitrobenzene, benzene, and carbon disulfide solutions were photochlorinated. The results are listed in Table 2.

Acetonitrile and nitrobenzene were chosen as solvents which have high dielectric constants. Dielectric constants of those solvents measured at low frequency are 36.7 and 34.8 at 25°C. (67). Dielectric constants of the other solvents used are between 2 and 3. Benzene and carbon disulfide were chosen because of their known ability to complex with chlorine atoms (2b). Nitrobenzene has little complexing ability with chlorine atoms because of its low basicity (2b, 23).

Table 1. Photochlorination of 1*M* chlorocyclopentane in carbon tetrachloride solution at 40°C.

% chlorination	Dichlorocyclopentanes[a] 1,1	*cis*-1,2	*trans*-1,2	*cis*-1,3	*trans*-1,3
15	4.5	--[b]	31.5	25.6	38.4
27	4.7	0.5	31.3	25.6	37.9
47	4.5	0.5	30.9	25.8	38.2
50	4.4	0.5	30.6	26.0	38.4

[a] Percent of dichlorides.

[b] No peak was detected, probably due to low concentration of the compound.

Table 2. Photochlorination of 1M chlorocyclopentane in various solvents at 40°C.

Solvent	Product of 1-attack (%)	Products of 2-attack (%)			Products of 3-attack (%)		
		cis	*trans*	Total	*cis*	*trans*	Total
Carbon tetrachloride[a]	4.6	0.5	31.2	31.7	25.6	38.1	63.7
Acetonitrile[b]	3.1	1.3	28.1	29.4	30.8	36.7	67.5
Nitrobenzene	4.4	1.2	26.9	28.1	30.7	36.7	67.4
Benzene[b]	5.8	0.8	27.4	28.2	27.3	38.7	66.0
Carbon disulfide[c]	9.4	1.0	28.6	29.6	25.2	35.7	60.9

[a] Average of the first three lines of Table 1 assuming 0.5% *cis*-1,2-dichlorocyclopentane was formed in 15 mole per cent chlorination.

[b] Average of two experiments.

[c] 1.15 M C_5H_9Cl.

More attack on the 1-position by complexed chlorine atoms was observed (Table 2, benzene and carbon disulfide solvents) possibly due to resonance stabilization of incipient radicals.

The selectivity of complexed chlorine atoms is known to be more sensitive to such resonance effects than the free chlorine atoms (23). Only small variations were observed in the ratio of 2-attack to 3-attack (see Table 3). Thus, as mentioned in the introduction, the rule,

> Relative reactivities that are determined mainly by the availability of electrons in the carbon-hydrogen bond are not particularly sensitive to solvent effects while reactivities that are determined mainly by the stabilities of the incipient free radicals are very sensitive to changes in solvent. (10a)

applies to the photochlorination of chlorocyclopentane. The increase of reactivity at the 1-position was two-fold in going from carbon tetrachloride to 14<u>M</u> carbon disulfide. However, the increase of reactivity of a secondary carbon-hydrogen bond relative to a primary carbon-hydrogen bond of butane is four-fold at 34°C. (21), when the solvent is changed from an aliphatic solvent to 11.1<u>M</u> carbon disulfide. Stability of an $R_2\dot{C}Cl$ radical is comparable to a *tertiary*-alkyl radical since the bond dissociation energy of chloroform is 90 kcal./mole and that of the *tertiary* carbon-hydrogen bond of isobutane is 89 kcal./mole (68). According to the series given by A. N. Nesmeyanov *et al*. (9), an $R_2\dot{C}Cl$ radical is more

Table 3. Solvent effects in photochlorination of chlorocyclopentane[a]

Solvent	1-Attack/3-Attack	2-Attack/3-Attack	*cis*/*trans* At 3-position
Carbon tetrachloride (8.7*M*)	0.072	0.50	0.67
Acetonitrile (17*M*)	0.046	0.44	0.84
Nitrobenzene (8.6*M*)	0.065	0.42	0.84
Benzene (10*M*)	0.088	0.43	0.71
Carbon disulfide (14*M*)	0.15	0.49	0.71

[a] Calculated from Table 2.

Table 4. Photochlorination of 1*M* chlorocyclohexane in carbon tetrachloride solution at 40°C.

Product of 1-attack (%)	Products of 2-attack (%)			Products of 3-attack (%)				Products of 4-attack (%)			
	cis	*trans*	Total	*cis*	*trans*	Total	*cis*/*trans*	*cis*	*trans*	Total	*cis*/*trans*
3.7	1.3	22.0	23.3	20.2	24.9	45.1	0.81	12.7	15.2	27.9	0.84

stable than a *tertiary*-alkyl radical. Strain in the ring system (I strain) could explain, at least partially, the above discrepancy (17-18).

trans-Substitution is more favorable than *cis*-substitution both at 2- and 3-position presumably because of a steric or electronic effect of the chlorine substituent.

Variation of the *cis*/*trans* ratio at the 3-position is small as the solvent is changed. However, in solvents of high dielectric constant the *cis*/*trans* ratios are larger. It is hard to say definitely that a solvent effect due to a difference of dielectric constant exists. This solvent effect, if any, can be explained by an argument advanced by Dr. D. G. Hendry (23). The electric charge on structure II may interact

$$\underset{\mathrm{I}}{\mathrm{R\cdot\ Cl\text{-}Cl}} \longleftrightarrow \underset{\mathrm{II}}{\mathrm{R^{+}\ Cl\text{-}Cl^{\bar{\cdot}}}} \longleftrightarrow \underset{\mathrm{III}}{\mathrm{RCl + Cl\cdot}}$$

with the dipole caused by the chlorine substituent and make *trans* substitution more favorable in solvents of low dielectric constant. Because of the small amounts of *cis*-1,2-dichlorocyclopentane formed it is probably not fair to discuss the *cis*-*trans* ratio for attack at the 2-position. However, again the highest ratios (more *cis*) were found in the solvents of highest dielectric constant.

The results of the photochlorination of chlorocyclohexane are listed in Table 4. Again, *trans* compounds are more favored than the corresponding *cis* compounds, even though *cis*-1,3-dichlorocyclohexane is thought to be more stable than trans-1,3-dichlorocyclohexane. The n.m.r. spectra of chlorocyclohexane in carbon disulfide has shown that 77% of the chlorine substituents are in the equatorial position at -104° to 25°C. (69). In the intermediate radicals formed from chlorocyclohexane by attack of chlorine atoms, there is no reason to suspect that equatorial conformations are more preferred than in chlorocyclohexane itself. Therefore, axial conformations (i.e. chlorine in the axial position) of the intermediate radical should be taken into account. If planar sp^2 geometry of the radical site is assumed, the predominance of trans-1,2-dichlorocyclohexane over cis-1,2-dichlorocyclohexane can be explained by steric or electronic interactions between a chlorine substituent and a chlorine molecule. If tetrahedral sp^3 geometry of the radial site is assumed, equal ease of approach by a chlorine molecule from either side of an equatorial substituent could be anticipated. The cis to trans ratio of the 1,2-dichlorocyclohexanes seems larger than that of the 1,2-dichlorocyclopentanes. However, the low concentrations of the cis compounds in the photochlorination mixtures and the incomplete resolution of cis-1,2-dichlorocyclohexane peak from cis-1,4-dichlorocyclohexane peak in the chromatogram must be taken into account. The similar magnitude of the cis-trans ratio for 2-attack, as well as 3-attack, in chlorocyclopentane and chlorocyclohexane suggests that the cis-trans ratios observed in the cyclohexane series are not determined mainly by conformational effects.

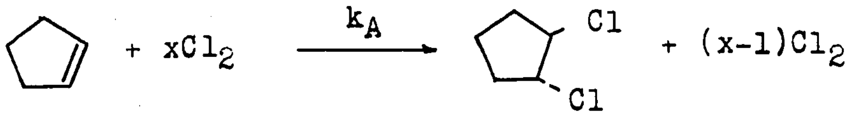
It seems likely that the stereochemistry of the reaction of the 2-chlorocyclohexyl and 2-chlorocyclopentyl radicals with molecular chlorine are closely related to the trans addition of hydrogen bromide to cyclohexene derivatives (63, 64b). A bromine-bridged intermediate radical, a concerted mechanism and a mechanism involving the attack by a bromine atom from only the axial direction followed by a rapid hydrogen abstraction from hydrogen bromide via the least hindered route have been proposed.

If the chlorine substituent of the 3-chlorocyclohexyl radical is in equatorial position, a chlorine molecule may approach easier from the side so that the cis compound would be predominant to about the same extent as the trans compound predominates from the 4-chlorocyclohexyl radical, since it appears that the free energy difference of the products reflects itself in the corresponding transition states (70a). R. J. Gritter and R. J. Albert (70b) recently reported that radicals generated from either cis- or trans-3-tertiary-butylcyclohexanol, where the tertiary-butyl group is assumed to be in equatorial position, reacts with 1-octene to give 1-octyl-3-tertiary-butylcyclohexanol where 64-67% of the hydroxyl groups (cis to trans ratio is 0.49-0.57) are in axial positions. For the reaction of 3-chlorocyclohexyl radical with a chlorine molecule the transition state would resemble the product less than that of the above reaction since the activation energy of the second chain propagation step of photochlorination is supposed to be very low. If the chlorine substituent of the 3-chlorocyclohexyl radical is in axial position, it would appear to be much easier to approach from the side opposite to the substituent. Interaction between the substituent and the incoming chlorine molecule would be larger than in the case of chlorocyclopentanyl radical. The similarity of the _cis_-_trans_ ratios for 3-attack on chlorocyclopentane and chlorocyclohexane suggests the lack of appreciable conformational stability of cyclohexyl radicals and the greater stability of "_trans_" transition states for reaction of the radical with molecular chlorine, both in the cyclopentyl and cyclohexyl systems.

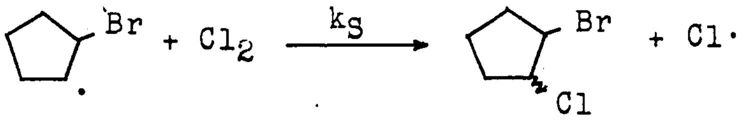
In 4-chlorocyclohexyl radicals there may be little direct influence of the substituent on the products since the _trans_ product is probably favored over the _cis_ product thermodynamically.

R. J. Gritter and R. J. Albert (70b) reported that radicals generated from either _cis_- or _trans_-4-_tertiary_-butylcyclohexanol react with 1-octene to give 1-octyl-4-_tertiary_-butylcyclohexanol where the 59-62% hydroxyl groups (_cis_ to _trans_ ratio 0.61-0.69) are in axial positions. The ratio of _cis_ to _trans_ compounds in the Hunsdiecker reaction of silver salts of _cis_- and _trans_-4-_tertiary_-butylcyclohexanecarboxylic acid with bromine in carbon tetrachloride gave a _cis_- to trans-bromide ratio of 0.54 (70a) while the decomposition of the diacyl peroxides of cis- and trans-4-tertiary-butylcyclohexanecarboxylic acid in tetrabromoethane gave a ratio of cis to trans bromide of 0.82-0.92 (70c). It is peculiar that the decomposition of dimethyl-(4-tertiary-butylcyclohexyl)-carbinyl hypochlorites in carbon tetrachloride gave a ratio of cis- to trans-4-tertiary-butylcyclohexyl chlorides (70d) of 2:1. However, in each case, a common intermediate radical or mixture of radicals appears to be produced from either the cis or trans starting compound.

Photochlorination of 1M solutions of bromocyclopentane in carbon tetrachloride at 40°C. gave poor reproducibility. In addition, a peak of trans-1,2-dichlorocyclopentane, 1.8 to 9 times as large as the peak of 1-bromo-1-chlorocyclopentane, was found in the chromatogram of the chlorination products. Photochlorination at 0°C. gave a smaller peak for trans-1,2-dichlorocyclopentane, the peak now being only 3.4 times as large as the peak of 1-bromo-1-chlorocyclopentane. When more dilute chlorine gas was added over a longer period of time, the amount of trans-1,2-dichlorocyclopentane formed became smaller. Those observations can be explained by the addition of chlorine to cyclopentene as shown below:



$$\text{Rate} = k_A[\text{Cl}_2]^x\,[\text{cyclopentene}]$$



$$\text{Rate} = (k_S/K_E)\,[\text{Cl}_2]\,[\text{cyclopentene}]\,[\text{Br}\cdot]$$

The brown color observed during the course of these photochlorinations and the retardation of the rate were presumably due to bromine formed in the above manner.

P. S. Fredericks and J. M. Tedder (6i) found 1,2-dichlorobutane in the chlorination of 1-bromobutane. They also observed a strong inhibition by bromine on the rate of the reaction. F. F. Rust and W. E. Vaughan (6h) found that above 200°C. the yield of vicinal dichlorides from the chlorination of chloroalkanes decreases rapidly with an increase in temperature, whereas, the yield of other dichlorides changes but slightly. A. B. Ash and H. C. Brown (6b) suggested that this "vicinal effect" is due to the instability of the intermediate radicals $-CH_2Cl-\dot{C}H-$ at high temperatures.

When the photochlorination of bromocyclopentane was performed at -30°C. the ratios of the bromochlorocyclopentanes were reproducible and the size of the chromatogram peak due to trans-1,2-dichlorocyclopentane was only about one half of that of 1-bromo-1-chlorocyclopentane. The result of this photochlorination of bromocyclopentane is listed in Table 5 together with the result of a photochlorination of chlorocyclopentane at -30°C.

The higher reactivity at the 2-position of bromocyclopentane relative to the 2-position of chlorocyclopentane will be discussed later when competitive chlorinations are discussed. The cis to trans ratios of 1-bromo-3-chlorocyclopentane and of 1,3-dichlorocyclopentane are the same within experimental error. The covalent radius of a bromine atom is 14% larger than that of a chlorine atom, which is 38% larger than that of a fluorine atom (71). Therefore, a greater steric effect might have been expected for the bromine substituent. P. S. Fredericks and J. M. Tedder have reported that 18% more of the erythro compound was obtained in the chlorination of 2-chlorobutane than in the chlorination of 2-fluorobutane.

Hydrogen abstraction in the photochlorination of chlorocyclopentane at -30°C. seems a little more selective than in the reaction at 40°C., as C. Walling and M. F. Mayahi (20a) observed for the photochlorination of 1-chlorobutane.

Competitive photochlorinations were performed for mixtures of halocycloalkanes and reference cycloalkanes whose reactivities relative to the parent cycloalkanes were known. These reactivities of the whole molecules and relative reac-

Table 5. Photochlorination of 1*M* bromocyclopentane and 1*M* chlorocyclopentane in carbon tetrachloride solution at -30°C.

Substrate	Product of 1-attack (%)	Products of 2-attack (%)			Products of 3-attack (%)			
		cis	trans	Total	cis	trans	Total	$\frac{\text{cis}}{\text{trans}}$
Bromocyclopentane	3.4	--[a]	43.3	43.3	23.2	30.1	53.3	0.77
Chlorocyclopentane	4.2	--[a]	28.7	28.7	29.5	37.6	67.1	0.79

[a] No peak was observed.

tivities of the various carbon-hydrogen bonds within the halocycloalkanes allows one to calculate the reactivity of a given carbon-hydrogen bond in a halocycloalkane relative to the parent cycloalkane, as described in the introduction. The results are listed in Table 6. The experimental uncertainty of the results of the competitive photochlorinations at 40°C. are about ± 10% while the experimental uncertainty of the reactivity of bromocyclopentane relative to cyclopentane at -30°C. may be ± 20%. However, experimental uncertainty of the reactivity of chlorocyclopentane relative to bromocyclopentane at -30°C. may be less, possibly ± 5%, owing to the similar reactivities and the high boiling points of compounds being chlorinated.

Because of strong polar effects of the halogen substituents the attack by a chlorine atom occurs preferentially at carbon-hydrogen bonds remote from the substituent (6a). Table 6 shows that the 3-positions of the chlorocycloalkanes are deactivated by the chlorine substituent as evidenced by both the competitive chlorinations of chlorocyclopentane with cyclopentane and by the photochlorination of chlorocyclohexane where the hydrogen at the 3-position is 0.81 times as reactive as that of the 4-position. In the above comparison the 3-chlorocyclohexnyl and the 4-chlorocyclohexyl radical have the same number of hyperconjugative resonance structures. The carbon-hydrogen bonds at the 1-positions of chlorocyclo-

Table 6. Relative reactivities of carbon hydrogen bond toward chlorine atoms[a]

Chlorocycloalkane	Reference hydrocarbon	1-Position	2-Position	3-Position	4-Position
Chlorocyclopentane[b] (1M)	Cyclohexane (0.16M)	0.21	0.37	0.75	--
Chlorocyclopentane[c] (1M)	Cyclohexane (0.17M)	0.19	0.31	0.75	--
Chlorocyclohexane[b] (1M)	Cycloheptane (0.52M)	0.26	0.42	0.81	1.0
Bromocyclopentane[d] (1M)	Cyclopentane (0.21M)	0.17	0.54	0.66	--
Chlorocyclopentane[d] (1M)	Bromocyclopentane (1M)	0.18[e]	0.32[e]	0.73[e]	--

[a] Assumed that the relative reactivities of a carbon-hydrogen bond of the parent cycloalkanes are 1.0. However, the reactivity of a carbon-hydrogen bond of cyclopentane relative to that of cyclohexane is 1.04 (10a) which may be unity within experimental error.

[b] In carbon tetrachloride solution at 40°C.

[c] In nitrobenzene solution at 40°C.

[d] In carbon tetrachloride solution at -30°C.

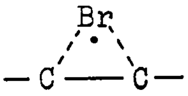
[e] In chlorocyclopentane, 3-position of bromocyclopentane assumed to have a reactivity of 0.66.

alkanes are less reactive than those at the 2-positions which are less reactive than the hydrogen at the 3-position. P. S. Fredericks and J. M. Tedder have reported that in competitive chlorination the 3-position of 1-chlorobutane has the same reactivity as the secondary hydrogen of n-butane within the experimental error (6c). However, in the next paper in the series they report that competitive chlorination of 1-chlorobutane and 2-chlorobutane shows that the primary hydrogen of the latter compound is 0.8 times as reactive as the primary hydrogen of the former compound (6d). P. S. Fredericks and J. M. Tedder also have reported that in the vapor phase chlorinations of 2-halobutanes (fluoride and chloride at 35°C. and 78°C.) the 2-position is the most reactive site (6k). However, if the possible experimental errors they have shown are taken into account, the reactivities of the carbon-hydrogen bond at the 2-position of 2-chlorobutane is the same as that of the 3-position within the experimental error. Apparently polar effects are much less important in the vapor phase since in the chlorination of 1-chlorobutane in the vapor phase at 35°C. the reactivity of the carbon-hydrogen bond at the 1-position relative to that of the 4-position is 0.7 (6i) while in liquid phase at 34°C. the corresponding ratio is 0.3 (21).

About the same reactivities were observed at a given position (1, 2 or 3) in chlorocyclopentane and chlorocyclohexane.

Since the hydrogen at the 1-position of chlorocyclohexane is predominantly in the axial position (69), ease of attack on equatorial and axial hydrogens of the cyclohexane ring would appear to be about the same. Otherwise, different reactivity sequences might have been expected for cyclopentane and cyclohexane derivatives.

The result of the competitive photochlorinations of bromocyclopentane with cyclopentane or chlorocyclopentane shows a higher reactivity for the 2-position of bromocyclopentane than for chlorocyclopentane. For the bromine substituent, the magnitude of polar-inductive effect may be nearly the same as that for the chlorine substituent, since calculated *sigma*' values, which can be thought of as a true measure of polar-inductive effect, are 0.47 for the chlorine substituent and 0.45 for the bromine substituent (72). Therefore, the above observation may not be due to a different magnitude of the polar-inductive effect of the substituent. A possible explanation is stabilization of the intermediate radical by participation of the bromine substituent.



P. S. Skell *et al*. reported that they found 1-bromo-2-chloropropane but did not find 2-bromo-1-chloropropane in the product of the reaction of 2-bromopropane with *tertiary*-butyl hypochloride at -78°C. (73). Similarly I found that in the photochlorination of 2-bromopropane at $-30^{\circ}C.$, 1-bromo-2-chloropropane is formed. No 2-bromo-1-chloropropane and only a trace of 1,2-dichloropropane was found. P. I. Abell and L. H. Piette reported that the e.s.r. spectra of the bromine atom adducts of alkenes and alkynes at $77^{\circ}K.$ are best interpreted by assuming a symmetrical or bridged structure (74). As they pointed out, the bridged structure does not imply a fixed or static structure, but the bridge can be looked upon as resulting from a resonating structure in which the bromine atom oscillates between carbons at a frequency greater or equal to the magnitude of the spectrometer frequency. The above observations together with the fact that only a trace of cis-1-bromo-2-chlorocyclopentane was formed may support the participation of the bromine substituent in the photochlorination of bromocyclopentane. Since in the chlorination with molecular chlorine no drastic change of reactivity by resonance stabilization of intermediate radicals (10) can be expected, the small enhancement of reactivity at the 2-position of bromocyclopentane appears to be of the correct order of magnitude for such an effect. Originally the bromine bridged radical was proposed as an interpretation of the trans addition of hydrogen bromide by a free radical mechanism (63, 64b, 75). Phenyl group participation in the peroxide-catalyzed decarbonylation of 5-phenylpentanal and 5-methyl-5-phenylhexanal was also reported by S. Winstein et al. (77). They found tetralin as a product in the former case and 2-methyl-5-phenylpentane and α,α-dimethyltetralin in the latter case. However, the difficulty is that examples of bromine with an expanded valence shell are known (for example, BrF_3 and Br_3^-), but in these, the bromine is bound only to halogen atoms and not to carbon atoms (76). Recently D. E. Applequist and N. D. Werner (78) reported that the Hunsdiecker reaction of silver salt of (+)-trans-1,2-cyclohexanedicarboxylic acid with bromine gives (-)-trans-1,2-dibromocyclohexane. The mechanism of the reaction proposed by them involves 2-bromocyclohexyl radicals but excludes the presence of a fixed bridged structure of the intermediate radicals.

The reactivities at the 1- and the 3-positions of all the halocycloalkanes investigated is within the experimental error, if both errors in the competitive chlorinations and the chlorinations for determining the isomer distributions are taken into account.

Chlorination of chlorocyclopentane with sulfuryl chloride, trichloromethanesulfonyl chloride and tertiary-butyl hypochlorite

Equations 1-4 represent a general formulation for chain propagation in competitive free radical reactions.

$$R_1H + X\cdot \longrightarrow R_1\cdot + HX \qquad (1)$$

$$R_2H + X\cdot \longrightarrow R_2\cdot + HX \qquad (2)$$

$$R_1\cdot + XY \longrightarrow R_1Y + X\cdot \qquad (3)$$

$$R_2\cdot + XY \longrightarrow R_2Y + X\cdot \qquad (4)$$

In the above general formulation if steps 3 and 4 are faster than steps 1 and 2, the reactivities of R_1H and R_2H control the products. However, if steps 1 and 2 are faster than steps 3 and 4, the reactivities of $R_1\cdot$ and $R_2\cdot$ will have an effect upon the products of the reaction.

The mechanism of chlorination with sulfuryl chloride and light is commonly accepted as follows (7):

$$SO_2Cl \xrightarrow{hv} SO_2Cl\cdot + Cl\cdot$$

$$SO_2Cl\cdot \rightleftharpoons SO_2 + Cl\cdot$$

$$RH + SO_2Cl\cdot \longrightarrow R\cdot + HCl + SO_2$$

$$R\cdot + SO_2Cl_2 \longrightarrow RCl + SO_2Cl\cdot$$

Higher selectivity of sulfuryl chloride than molecular chlorine (7) has been explained by the equilibrium of the chlorosulfonyl radical with sulfur dioxide and the chlorine atom. It was suggested that this equilibrium can be replaced by the equilibrium

$$SO_2Cl\cdot + Ar \longrightarrow SO_2 + Ar\rightarrow Cl\cdot$$

in aromatic solvents (79), where molecular chlorine and sulfuryl chloride show similar selectivities.

It appears likely that the hydrogen abstractions by chlorosulfonyl radicals and by chlorine atoms are the slower steps in chlorinations since the order of the reactivities of carbon-hydrogen bonds of hydrocarbons is primary < secondary < tertiary (2b, 7).

The mechanism of chlorination with tertiary-butyl hypochlorite (25) and light may be as follows:

$$\underline{t}\text{-BuOCl} \xrightarrow{h\nu} \underline{t}\text{-BuO}\cdot + \text{Cl}\cdot$$

$$\underline{t}\text{-BuO}\cdot + \text{RH} \longrightarrow \underline{t}\text{-BuOH} + \text{R}\cdot$$

$$\text{R}\cdot + \underline{t}\text{-BuOCl} \longrightarrow \text{RCl} + \underline{t}\text{-BuO}\cdot$$

If R is benzyl, ΔH for the hydrogen abstraction step and ΔH for the attack on tertiary-butyl hypochlorite by a benzyl radical have been estimated to be -26.5 and -24 kcal./mole respectively (25). An estimated activation energy of the former step is 2 ± 2 kcal./mole and the chain length was calculated to be at least 10^4 (25). The order of the reactivities of carbon-hydrogen bonds of hydrocarbons is also primary < secondary < tertiary. Therefore, chlorination with tertiary-butyl hypochlorite is similar to chlorination with molecular chlorine although selectivities of the former reagent are somewhat greater.

Chlorination with trichloromethanesulfonyl chloride (80) has been reported to be somewhat different from the other chlorinating reagents described above. According to E. S. Huyser and B. Giddings (80a), the mechanism of the chlorination may be as follows:

$$Cl_3CSO_2Cl \xrightarrow{hv} Cl_3C\cdot + SO_2 + Cl\cdot$$

$$Cl_3C\cdot \text{ (or } Cl\cdot) + RH \longrightarrow HCCl_3 \text{ (or HCl)} + R\cdot$$

$$R\cdot + Cl_3CSO_2Cl \longrightarrow RCl + Cl_3CSO_2\cdot$$

$$Cl_3CSO_2\cdot + RH \longrightarrow Cl_3CSO_2H + R\cdot$$

$$Cl_3CSO_2H \longrightarrow HCCl_3 + SO_2$$

Competitive chlorinations of cyclohexane and toluene with trimethanesulfonyl chloride and competitive bromination of these compounds with bromotrichloromethane (80a) eliminated the possibility that the trichloromethyl radical was the hydrogen abstracting species in the reaction involving trichloromethanesulfonyl chloride. They reported that trichloromethanesulfonyl chloride reacts with ethylbenzene to give only α-chloroethylbenzene. Thus, this reagent is more selective than molecular chlorine and sulfuryl chloride. It was also found that cyclohexane is more reactive than toluene toward this reagent. This indicates that the trichloromethanesulfonyl radicals are electron deficient species like chlorine atoms and tertiary-butoxy radicals. However, it was reported that toluene is more reactive than cumene toward this reagent! This fact has been explained as being due to the fact that cumyl radicals have less ability than benzyl radicals to abstract chlorine atoms from trichloromethanesulfonyl chloride. They also reported that the chain length of the chlorination with this reagent is very short (for cyclohexane 6.4, for cumene 0.83).

The results of the photochemical chlorinations of chlorocyclopentane with the above mentioned chlorinating reagents are shown in Table 7. A distinct feature of the reaction of *tertiary*-butyl hypochlorite is that the carbon-hydrogen bond at the 1-position is the most reactive toward this reagent, if the statistical factor is taken into account. Preferential attack at the 3-position over the 2-position by the radicals generated from those reagents shows that these radicals are electron deficient species as has been pointed out previously (25, 79a). The ratios of 2-attack to 3-attack cannot be said to be a true measure of the electron deficiency of those radicals (10c), but must to some extent reflect this electron deficiency. The ratios for molecular chlorine, sulfuryl chloride and trichloromethanesulfonyl chloride are similar. The ratios of 1-attack to 3-attack shows the order of importance of resonance stabilization in the transition states of molecular chlorine ($Cl\cdot$) $<$ sulfuryl chloride ($Cl\cdot$ plus $SO_2Cl\cdot$) $<$ trichloromethanesulfonyl chloride ($CCl_3SO_2\cdot$) provided the sensitivities toward polar effects are about the same. The *tertiary*-butoxy radical seems to be less electron deficient than the other species. This can be explained as the *tertiary*-butyl group is an electron donating group. When the relative reactivities of 1-chlorobutane in the chlorination with molecular chlorine (20a) and with *tertiary*-butyl-hypochlorite (25) are compared, it is observed that the ratios of 3- and

Table 7. Chlorination of 1*M* chlorocyclopentane in carbon tetrachloride solution

Reagent	Product of 1-attack (%)	Products of 2-attack (%)			Products of 3-attack (%)					
		cis	trans	Total	cis	trans	Total	$\frac{cis}{trans}$	$\frac{\text{1-Attack}}{\text{3-Attack}}$	$\frac{\text{2-Attack}}{\text{3-Attack}}$
Molecular chlorine[a]	4.6	0.5	31.2	31.7	25.7	38.1	63.7	0.67	0.072	0.50
Sulfuryl chloride[b] (0.35*M*)	6.4	1.4	31.6	33.0	14.2	46.4	60.6	0.31	0.11	0.54
Trichloromethanesulfonyl chloride[b] (0.35*M*)	14.3	2.1	29.2	31.3	11.4	42.6	54.0	0.27	0.26	0.58
tertiary-Butyl hypochlorite[c] (0.35*M*)	25.0	--[d]	33.6	33.6	9.3	32.2	41.5	0.29	0.60	0.81

[a] Taken from Table 2.

[b] At 79.5° ± 0.5°C.

[c] At 40.0° ± 0.1°C.

[d] No peak was observed.

CH_3-CH_2-CH_2-CH_2Cl 1.0 2.79 1.28 0.36	Chlorination with molecular chlorine at 34°C.
CH_3-CH_2-CH_2-CH_2Cl 1.0 4.19 1.87 1.92	Chlorination with *tertiary*-butyl hypochlorite at 40°C.

2-attack are *ca*. 0.45 in both reactions. It should be noted that E. S. Huyser and B. Giddings (80a) reported that trichloromethanesulfonyl chloride chlorination of ethylbenzene gave no β-chloride at 78°-80°C. (80a) whereas C. Walling and B. B. Jacknow reported that the *tertiary*-butyl-hypochlorite chlorination of ethylbenzene gave 8% of the β-chloride at 40°C. It should also be noted (see p. 66) that toluene is more reactive than cumene toward trichloromethanesulfonyl chloride (80a). Therefore, the lower percentage of the 1,1-dichlorocyclopentane in the trichloromethanesulfonyl chloride chlorination than in the *tertiary*-butyl-hypochlorite chlorination could be attributed to low reactivity of 1-chlorocyclopentyl radicals toward trichloromethanesulfonyl chloride as well as to a difference of electron deficiency of the *tertiary*-butoxy and the trichloromethanesulfonyl radicals. A chain length of 1.3 was calculated for the chlorination of chlorocyclopentane by trichloromethanesulfonyl chloride by assuming that all the termination of chains occurred by coupling of trichloromethyl radicals.

Experimental

Apparatus and procedure

The apparatus used for photochlorination of halocycloalkanes is shown schematically in Fig. 13. The carrier gas (pre-purified nitrogen) was introduced into the system through a drying tube containing glass beads coated with phosphorus pentoxide. By the manipulation of the three-way stopcock B the carrier gas could be directed either directly to the 500 ml. mixing bulb E or through liquid chlorine reservoir D and then to the mixing bulb. From the bulb the gas was introduced into the reaction flask through a gas inlet glass tube with a fine tip which nearly reached the bottom of the flask. The gas leaving the reaction flask passed through a condenser containing ice-water or a Dry Ice-acetone mixture, and a gas trap containing a 10% sodium hydroxide solution. The reaction flask was mounted in a 40°C. constant temperature water bath or acetone bath whose temperature was maintained at -30° ± 1°C. by adding pieces of Dry Ice from time to time. In the former case a 200 watt unfrosted tungsten lightbulb was immersed in the water bath approximately 3 cm. from the flask. In the latter case the flask was illuminated by the lightbulb outside of the bath. The distance from bulb to flask was also approximately 3 cm. As the carrier gas, Matheson grade pre-purified nitrogen was used. Before the reaction was

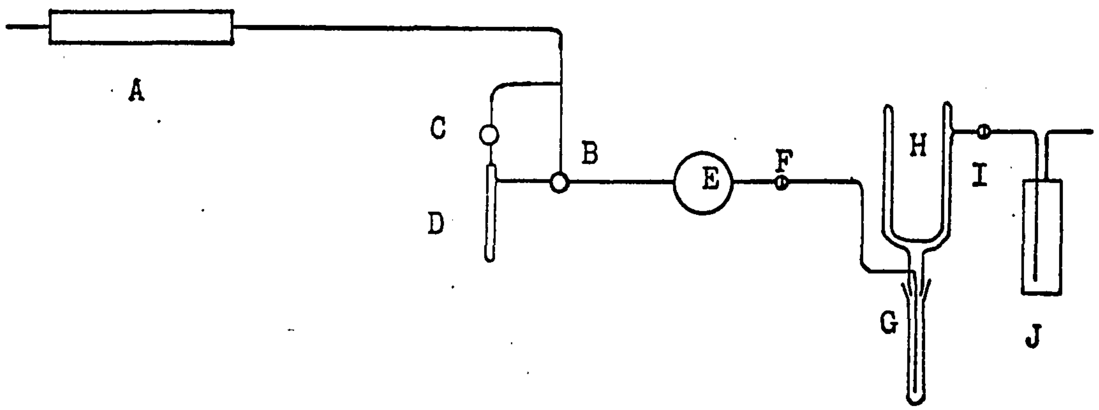


Fig. 13. Photochlorination apparatus

A: drying tube

B: Teflon three-way stopcock

C: glass tube with a tapered joint and a Teflon stopcock

D: liquid chlorine resorvoir

E: 500 ml. mixing bulb

F: spherical joints

G: reaction flask with a tapered joint, approximately 30 ml.

H: condenser

I: spherical joints

J: gas trap

———————— : Pyrex glass tube

———————— : Tygon (polyvinyl chloride plastic) tubing started, chlorine gas was condensed in the liquid chlorine reservoir by using a Dry Ice-acetone bath. Material to be chlorinated was placed in the flask and degassed by the nitrogen by-passing the reservoir. Then the stopcocks B and C were adjusted in order to allow the nitrogen to pass over the liquid chlorine storage tube. The Dry Ice-acetone bath was taken away from the liquid chlorine reservoir and the desired amount of chlorine was allowed to vaporize. The amount of liquid chlorine vaporized was measured by calibration of the reservoir. After evaporation of the desired amount of liquid chlorine the stopcocks were adjusted so the nitrogen by-passed the reservoir. The nitrogen flow rate was sufficiently low so that the temperature of the reaction mixture did not deviate from that of the surrounding bath. After the addition was completed, the reaction mixture was degassed by the passage of nitrogen to remove the hydrogen chloride formed. In the case of competitive photochlorinations where a volatile cycloalkane, e.g. cyclopentane and cyclohexane, were used, the top of C was directly connected to F with a glass tubing and chlorine was vaporized very slowly with low flow rate of nitrogen so that the amount of nitrogen gas passed through the reaction mixture was a minimum. Degassing after the reaction was not performed in such cases. When tertiary-butyl hypochlorite was used as the chlorinating reagent, the same apparatus was used and the nitrogen flow passed through the reaction mixture in order to stir the mixture during the two hour reaction period and to sweep out the hydrogen chloride formed. In the case of sulfuryl chloride chlorination the reaction mixture was placed in a Pyrex glass flask similar to one used in photochlorination fitted with a water cooled reflux condenser. The reaction mixture was illuminated by a 200 watt unfrosted tungsten lightbulb mounted approximately 5 cm. from the flask, and was heated by a gas flame so that gentle boiling of the reaction mixture occurred during the three hour reaction period. The temperature of the reaction mixture was measured with an Anschutz thermometer hanging by a platinum wire from the top of the condenser. In the case of trichloromethanesulfonyl chloride chlorination a quartz reaction flask was used. The reaction mixture was illuminated with a General Electric UA-2 lamp during the five hour reaction period. Otherwise the reaction apparatus was the same as used for the sulfuryl chloride chlorination.

Analytical procedure

Isomeric dihalo-hydrocarbons formed in the chlorination reactions were analyzed by gas liquid chromatography in an instrument using a hot wire thermal conductivity gauge. Analysis of chlorination mixtures of chlorocyclopentane and bromocyclopentane were made using a 2 m. Perkin-Elmer B column (reportedly di-2-ethylhexylsebacate) at 140°C. The only exceptions were the analyses of trichloromethanesulfonyl chloride chlorination mixtures and sulfuryl chloride chlorination mixtures of chlorocyclopentane. In those cases a 300 foot Perkin-Elmer R Golay column (reportedly polypropylene glycol) was used at 75°C. Analyses of chlorination mixtures of chlorocyclohexane were made by a combination of a 2.2 m. polyphenyl ether column (20% on 80/100 mesh Chromosorb W) and a 1.5 m. diisodecyl phthalate column (10% on 80/100 mesh Chromosorb W) at 150°C. for dichlorides other than 1,1-dichlorocyclohexane and cis-1,2-dichlorocyclohexane. For analysis of 1,1-dichlorocyclohexane the 2 m. Perkin-Elmer B column was used at 150°C. and for analysis of cis-1,2-dichlorocyclohexane two 1.8 m. polyphenyl ether columns (10% on 80/100 mesh Chromosorb W) were used at 150°C. Determination of the relative reactivity of chlorocyclopentane vs. cyclohexane in carbon tetrachloride by competitive photochlorination was made by measuring the disappearance of the two reactants (hereafter relative reactivities of halocycloalkanes were determined by measuring disappearance of reactants unless otherwise mentioned). A 1 m. β,β'-oxydipropionitrile column (20% on 80/100 mesh firebrick) was used at 90°C. and bromobenzene was added as the internal standard in this case. Determination of the relative reactivity of chlorocyclopentane vs. cyclohexane in nitrobenzene was made by using the 2 m. Perkin-Elmer B column at 140°C. utilizing the solvent as an internal standard. In this case both disappearance of chlorocyclopentane and cyclohexane, and appearance of chlorocyclohexane were measured. The values of the relative reactivity from both measurements agreed with 12% difference. In the former case chlorocyclopentane was decomposed in the injector of g.l.c. and formed cyclopentene probably due to hydrogen chloride remaining in the reaction mixture. The necessary correction was made. Determination of the relative reactivity of chlorocyclohexane vs. cycloheptane was made by using the 2 m. Perkin-Elmer B column at 140°C. with chlorobenzene as the internal standard. Both determinations of the relative reactivities of bromocyclopentane vs. cyclopentane and chlorocyclopentane was made by using a 1 m. polypropylene glycol column (20% on 80/100 mesh Chromosorb W) at 87°C. with bromobenzene as the internal standard. Qualitative analysis of photochlorination products of isopropyl bromide and _n_-propyl bromide were performed by using the 300 foot Perkin-Elmer R Golay column at 50°C.

Reagents

Sulfuryl chloride (Eastman Kodak Co. practical grade) was distilled through a Vigreux column prior to chlorination. Trichloromethanesulfonyl chloride (Eastman Kodak Co. practical grade) was used without further purification. _tertiary_-Butyl hypochlorite is described later in the synthesis of 3-chlorohexene. Chlorocyclopentane (Matheson, Coleman and Bell) was used without further purification. Its purity was indicated to be 99.5% by g.l.c. Chlorocyclopentane (Eastman Kodak Co.) was used without further purification. Its purity was shown to be 99.8% by g.l.c. Bromocyclopentane (Chemical Intermediates and Research Laboratories, Inc.) was rectified in a Todd column packed with glass helices at 50 mm. Hg and had a purity of 99.5% when analyzed by g.l.c. Phillips 99 mole per cent minimum purity cyclopentane was washed with fuming sulfuric acid and water, dried and rectified in 30 cm. Daufton column. Its purity was indicated to be 99.9% by g.l.c.. Spectrograde Eastman Kodak cyclohexane was used. The cycloheptane wash was purified by Professor Russell who rectified material from Madison Laboratories in a twenty plate helices-packed column and showed its purity to be 99.9%. Isopropyl bromide and *n*-propyl bromide (both from Matheson, Coleman and Bell) were used without further purification. Carbon tetrachloride from Fisher Scientific Co. or Mallinckrodt was passed through silica gel and stored over Molecular Sieves (Linde Co.). Nitrobenzene from Matheson, Coleman and Bell was distilled through a Vigreux column and the center fraction passed through silica gel and stored over Molecular Sieves. Acetonitrile (Matheson, Coleman and Bell), carbon disulfide (Mallinckrodt) and benzene (Mallinckrodt, thiophene free) were passed through silica gel before use. Chlorobenzene

(Matheson, Coleman and Bell) and bromobenzene (Eastman Kodak) were used without further purification as internal standards for g.l.c. measurements.

Synthesis of dihalocycloalkanes

1,1-Dichlorocyclopentane The method described by E. A. Braude and W. F. Forbes (81) was followed to synthesize this compound. From 170 g. of cyclopentanone and 400 g. of phosphorous pentachloride, 54 g. of 1-chlorocyclopentane, b.p. 102°-106°C./740 mm., and 66 g. of 1,1-dichlorocyclopentane, b.p. 132°-140°C./740 mm., were obtained after a rapid distillation through a 30 cm. Daufton column. The total yield was 50% based on cyclopentanone used. After a distillation through a Todd column packed with glass helices, pure 1,1-dichlorocyclopentane, b.p. 141°-141.2°C./746 mm., n_D^{21} = 1.4709 was obtained.

cis-1,2-Dichlorocyclopentane This compound has not been reported in the literature. It was prepared in a similar manner to the reported preparation (55) of cis-1,2-dichlorocyclohexane. trans-2-Chlorocyclopentanol, b.p. 83°-84.5°C./18 mm., was prepared by the method of H. B. Donahoe and C. A. Vanderwerf (82). The chlorohydrin (15 g.) was mixed with 29 g. of freshly distilled pyridine in a dropping funnel. This mixture was dropped slowly onto 42 g. of thionyl chloride contained in a 500 ml. three-necked flask fitted with a stirrer, thermometer and condenser, and maintained at 70°-80°C. Stirring and heating was continued for two hours after addition was complete. Excess thionyl chloride was destroyed by dropwise addition of 65 ml. of ice water and the organic layer separated and washed with 6 ml. of 10% sodium carbonate solution. The product was then steam distilled, dried over calcium chloride and fractionated at a pressure of 20 mm. The yield of a fraction boiling at 71°-74°C. was 1.4 g. or 8%. This fraction consists of ca. 75% of cis-1,2-dichlorocyclopentane and ca. 25% of trans-1,2-dichlorocyclopentane based on g.l.c. analysis. Purification by g.l.c. gave 97% pure cis-1,2-dichlorocyclopentane, $n_D^{25} = 1.4822$.

trans-1,2-Dichlorocyclopentane This compound was prepared according to the method of H. L. Goering and F. H. McCarron (83). The fraction boiling at 50.0°-50.5°C. at a pressure of 20 mm. had the same refractive index as given in the above reference, $n_D^{25} = 1.4781$.

cis-1,3-Dichlorocyclopentane A. This compound has not been mentioned in the literature. Attempted synthesis of this compound along with its geometric isomer, trans-1,3-dichlorocyclopentane, by reactions of cis-1,3-cyclopentanediol with concentrated hydrochloric acid and with thionyl chloride in the presence of pyridine gave poor results. In the former case 10 g. of the diol and 40 ml. of concentrated hydrochloric acid were heated in a sealed Carius tube at 100°C. for 12 hours. Black amorphous material was the only product. In the latter case a mixture of 10 g. of the diol and 46 g. of freshly distilled pyridine were added dropwise to 67 g. of thionyl chloride placed in a three-necked 250 ml. flask. The reaction conditions were similar to those employed in the synthesis of cis-1,2-dichlorocyclopentane. The reaction mixture turned black and contained a lot of black resinous material. The mixture was directly steam distilled and 1 g. of oil was obtained. It was established that the oil consisted of 9% trans-1,2-dichlorocyclopentane, 52% trans-1,3-dichlorocyclopentane and 39% cis-1,3-dichlorocyclopentane by g.l.c. analysis.

B. A solution of cis-1,3-cyclopentanediol ditoluene-p-sulphonate (5 g.) and lithium chloride (21 g.) in absolute ethanol (90 ml.) was refluxed for 6 hours, then neutralized with alcoholic potassium hydroxide solution, concentrated under vacuum, diluted with water, extracted with ether, and dried over anhydrous sodium sulfate. After evaporation of the ether a heavy liquid and crystalline solid remained. The liquid portion was separated, dissolved in ether, and analyzed by g.l.c. The predominant peak in the chromatogram, presumably due to cis-1,3-dichlorocyclopentane, had the same retention time as the fourth peak of the dichlorocyclopentanes prepared by photochlorination of chlorocyclopentane. No attempt to isolate pure cis-1,3-dichlorocyclopentane was made because of the low concentration of the substance in the reaction product.

C. 1.2 g. of 4-chlorocyclopentene and 4 ml. of Skelly A were placed in a Carius tube. The tube was cooled with liquid nitrogen and connected to a vacuum line from which 1.8 g. of anhydrous hydrogen chloride was condensed into the tube. After the tube was sealed it was kept in ice for 3 weeks. Then the tube was opened, the contents were taken up with ether, washed with 10% sodium carbonate solution and water, and dried over calcium chloride. In the g.l.c. spectrum of this solution there were two peaks, presumably due to <u>cis</u>- and <u>trans</u>-1,3-dichlorocyclopentane, other than the peaks due to the solvent and the starting material. No attempt was made to isolate the pure 1,3-dichlorocyclopentanes.

D. A solution of chlorocyclopentane (150 g.) in a 50:50 mixture of carbon tetrachloride and benzene (500 ml.) was placed in a 1 l. three-necked flask fitted with a fritted glass inlet, calcium chloride drying tube and thermometer. The flask was immersed in a -40°C. Dry Ice-acetone bath. A 200 watt incandescent lamp was hung above the flask so that its content could be irradiated. Chlorine gas diluted with nitrogen was passed through the solution and the reaction was stopped when 40 g. of chlorine was added. The thermometer registered -10°C. during the reaction. After the solution was degassed by passing nitrogen and most of the solvent was distilled out by a simple distillation head, the isomeric dichlorocyclopentanes were separated by a Todd column packed with glass helices at a pressure of 70 mm. N.m.r. spectrum of fraction b.p. 102.6°C./70 mm. was determined and proved to be cis-1,3-dichlorocyclopentane. Purity of this fraction was determined by g.l.c.: cis-1,3-dichlorocyclopentane 96.4%, trans-1,3-dichlorocyclopentane 0.5%, cis-1,2-dichlorocyclopentane 3.1%. $n_D^{20} = 1.4864$, $n_D^{25} = 1.4839$.

trans-1,3-Dichlorocyclopentane This compound has not been reported in the literature. It was synthesized along with cis-1,3-dichlorocyclopentane as described in B. and C. above. This compound was isolated in nearly 100% purity from the photochlorination product of chlorocyclopentane as described in D. above. N.m.r. spectrum confirmed its structure. B.p. 89.2°C./70 mm., $n_D^{20} = 1.4822$, $n_D^{25} = 1.4800$.

cis-1,3-Cyclopentanediol A mixture of cis-3,4- and cis-3,5-cyclopentenediol (84) was kindly supplied by Professor DePuy. cis-3,4-Cyclopentanediol, the lower boiling component, was removed by fractional distillation at 68.5°-71.5°C./1 mm. with a spinning band column. The residue was distilled through a 30 cm. Daufton column at 97.5°-100.5°C./1 mm. The unsaturated diol (10 ml.) in 95% ethanol (100 ml.) was hydrogenated catalytically (85) in the presence of platinum oxide catalyst. Hydrogenation was repeated ten times. After distillation through the 30 cm. Daufton column ca. 70 ml. of a substance b.p. 123°-127°C./10 mm. was obtained. It is solid at room temperature. It was derivatized to give a <u>bis</u>-<u>p</u>-nitrobenzoate m.p. 182.5°-183.0°C. and a <u>bis</u>-<u>p</u>-toluenesulfonate m.p. 90.0°-92.5°C. The melting points of the derivatives agree with those in references (56, 57b, 84, 85) for derivatives of <u>cis</u>-1,3-cyclopentanediol.

<u>4-Chlorocyclopentene</u> This compound has not been reported in the literature. A solution of 3-cyclopentene-1-ol (29.4 g.) and Skelly A (85 ml.) was added dropwise to a mixture of phosphorous pentachloride (39 g.) and Skelly A (85 ml.) placed in a 1 l. three-necked flask fitted with a stirrer and thermometer. The temperature was kept at -10°-0°C. during the addition. Stirring was continued for ten hours after addition was complete. The temperature was gradually raised to room temperature during the additional stirring. The mixture was poured over ice, and the organic layer separated, washed with 10% sodium carbonate solution and water, and dried over calcium chloride. After most of the solvent was distilled under atmospheric pressure the residue was fractionated at reduced pressure using a small Vigreux column. The yield of chloride boiling at 39°C./60 mm. was 2.6 g. or 7.2%. The n.m.r. spectrum of the material confirmed the structure. Reactions of 4-cyclopentenol with concentrated hydrochloric acid under reflux and with thionyl chloride in the presence of pyridine at 40°-50°C.

did not give the corresponding chloride.

3-Cyclopenten-1-ol The method of synthesis described by E. L. Albred, J. Sonnenberg and S. Winstein (59) was modified in the light of the article by H. C. Brown and B. C. Subba Rao (86) mainly because of hazardous nature of diborane. Cyclopentadiene was prepared by the method of R. B. Moffett (87). A solution of cyclopentadiene (190 g.) and sodium borohydride (23 g.) in 700 ml. of diglyme was placed in a 2 l. three-necked flask fitted with a dropping funnel in which a solution of boron triflouride etherate (126 g.) in diglyme (150 ml.) was placed. The flask was cooled in an ice bath and the solution of boron trifluoride etherate was added dropwise. Stirring and cooling was continued for one hour after addition was complete. During this period a slow stream of nitrogen was passed through the flask. The contents of the flask were allowed to stand for a second hour. A reflux condenser was then substituted for the nitrogen outlet. Water (120 ml.), and then 3M sodium hydroxide (240 ml.) were added to the flask for hydrolysis. Hydrogen perioxide (240 ml. of 30%) was added so that slow reflux occurred. After the temperature of the solution dropped to room temperature, the upper organic layer was separated. Practically no dicyclopentadiene remained in the lower water-diglyme layer after three extractions with 50 ml. portions of ether. Then the water-diglyme layer was extracted continuously with ether

(800 ml.) until no volume decrease of the water-diglyme layer occurred. The ether extract was dried over anhydrous sodium sulfate, distilled with 30 cm. Daufton column, and the fraction boiling at 70°-78.5°C./37 mm. was collected and refractionated in a Todd column packed with Monel helices. The fraction boiling at 67°-67.2°C./36 mm. (24.3 g.) showed n_D^{21} = 1.4678; the fraction boiling at 67.2°-69.0°C./36 mm. (5.1 g.), n_D^{21} = 1.4652. The total yield based on the sodium borohydride used was 20%.

1-Bromo-1-chlorocyclopentane Synthesis of 1-bromo-1-chlorocyclohexane was reported by E. Havinga *et al*. (51) and H. L. Goering and L. L. Sims (63). For the present synthesis a method similar to Goering and Sims' methods A and C was adopted.

A. 1-Chlorocyclopentene (10 g.) was dissolved in 200 ml. of anhydrous ether in a 500 ml. flask equipped with a condenser and a fritted glass gas inlet. The flask was cooled in an ice bath and anhydrous hydrogen bromide was passed through the solution for about two hours. The reaction mixture was washed with water and dried over anhydrous sodium sulfate. Rapid distillation with a simple distillation head at a pressure of 20 mm. gave *ca*. 2 ml. oil. It was shown to be *ca*. a 50:50 mixture of 1-chlorocyclopentene and 1-bromo-1-chlorocyclopentane by g.l.c. The second distillation gave a fraction b.p. 52°-57°C./20 mm. which contained *ca*. 60% desired compound.

B. Two Carius tubes, each containing 8.1 g. of 1-chlorocyclopentene were frozen in liquid nitrogen, and connected to a vacuum line. Hydrogen bromide (78 g.) was added to each tube. The tubes were sealed and allowed to stand at room temperature for three days. The tubes were opened and their contents combined. The reaction mixture was washed with water and dried over calcium chloride. Rapid distillation with a simple distillation head at a pressure of 41 mm. gave a fraction boiling at 75°-79°C., 17.4 g. It was shown to be 83% 1-bromo-1-chlorocyclopentane and 13% 1-chlorocyclopentene by g.l.c. A further distillation of this fraction using a 30 cm. Daufton column failed to give a fraction containing more than 80% 1-bromo-1-chlorocyclopentane.

trans-1-Bromo-2-chlorocyclopentane The method of reference (63) for trans-1-bromo-2-chlorocyclohexane was followed. A solution of 60 g. of cyclopentene in 400 ml. of chloroform was prepared in a 1 l. three-necked flask fitted with fritted glass gas inlet and calcium chloride drying tube. A slurry of 165 g. of N-bromosuccinimide (recrystallized from water) in 200 ml. chloroform was added in portions as anhydrous hydrogen chloride was passed through the solution. The N-bromosuccinimide stayed in the bottom of the flask and its product succinimide floated on the surface of the solution. Therefore, progress of the reaction could be easily ascertained. During the reaction the flask was cooled with an ice-water bath. After the reaction the solution was filtered, washed with 10% sodium carbonate and water, and dried over calcium carbonate. A rapid distillation with a simple column at a pressure of 13 mm. gave 93 g. of material, b.p. 62°-96° C./13 mm. The second distillation using the 30 cm. Daufton column gave a total of 79 g. of distillate, b.p. 55.4°-67° C./12 mm. The yield was 46% based on N-bromosuccinimide used. Further distillation using a Todd column packed with glass helices at a pressure of 38 mm. gave a fraction boiling at 78.0°C., $n_D^{20} = 1.5123$, $n_D^{25} = 1.5100$.

cis-1-Bromo-2-chlorocyclopentane The method of preparation for cis-1-bromo-2-chlorocyclohexane given in reference (63) was followed. For this reaction a flat bottom flask with three female standard taper joints was used. To the center joint a quartz tube mercury vapor lamp surrounded with cooling water jacket was fitted. A frittered glass gas inlet long enough to reach the bottom of the flask and a calcium chloride drying tube were fitted to the other joints. A solution of 1-chlorocyclopentene (49.1 g.) in pentane (1500 ml.) was placed in the flask cooled in an ice bath. The solution was stirred with a magnetic stirrer during the one hour reaction. The reaction mixture was washed with water three times, once with 10% sodium carbonate solution and once again with water, and dried over calcium chloride. A rapid distillation with a simple distillation column at a pressure of 4 mm. gave *ca*. 45 ml. of distillate, b.p. 50°-66°C. Further distillation using the 30 cm. Daufton column gave four fractions (overall b.p. range 63.2°-65.0°C., 66.3 g. or 75% yield). The second fraction (17.4 g.) had a b.p. 63.9°C./4 mm. n_D^{20} = 1.5227 while the third fraction (34.3 g.) had a b.p. 63.9°-64.5°C./4 mm. n_D^{20} = 1.5227.

cis- and *trans*-1-Bromo-3-chlorocyclopentane A. 3-Chlorocyclopentene was prepared by the method of Moffet (87). Hydrogen bromide (9.8 g.) was condensed from a vacuum line on a solution of 3-chlorocyclopentene (8.2 g.), *n*-hexane (50 ml.) and cyclohexene hydroperoxide (0.2 g.), which was kindly given by Dr. D. G. Hendry, in a Carius tube frozen with liquid nitrogen. Another tube was prepared which contained benzoyl peroxide (0.6 g.) instead of cyclohexene hydroperoxide. The tubes were allowed to stand at room temperature for ten days. The solution turned black and considerable solid was observed at the end of this period. The reaction products were mixed with dimethylaniline in order to remove unreacted 3-chlorocyclopentene, washed with 6*N* sulfuric acid and three times, with saturated sodium acid carbonate once and with water three times, then dried over calcium chloride. No g.l.c. peak was found which corresponded to the peaks observed in the gas-liquid chromatogram of the chlorination product of bromocyclopentane. Similar reactions of 3-chlorocyclopentene with hydrogen bromide without solvent in the presence of anhydrous ferric chloride catalyst or in the absence of the catalyst at -70°C. failed to give any bromochlorocyclopentane.

B. A solution of 4-chlorocyclopentene (1.1 g.) and Skelly A (6 ml.) was similarly treated with hydrogen bromide as mentioned under the preparation of cis-1,3-dichlorocyclopentane C. Upon analysis of the reaction product by g.l.c. two peaks, presumably due to cis- and trans-1-bromo-3-chlorocyclopentane, were observed in addition to the solvent peak.

C. A solution (500 ml.) of bromocyclopentane (157 g.) in carbon tetrachloride was photochlorinated with chlorine (43 g.) as described in the preparation of cis-1-dichloro-3-cyclopentane D. The reaction product was distilled using a Todd column at a pressure of 18.5 mm. Practically pure trans-1-bromo-3-chlorocyclopentane, n_D^{20} = 1.5147, and 91.7% pure cis-1-bromo-3-chlorocyclopentane, contaminated by 1.9% trans-1-bromo-3-chlorocyclopentane and a total of 6.4% of cis-1-bromo-2-chlorocyclopentane and an unknown compound. The boiling points were obscured because of slow reflux. The n.m.r. spectra of the above fraction support the assignments of structure.

1-Chlorocyclopentene This compound was obtained along with 1,1-dichlorocyclopentane as mentioned above. In case only 1-chlorocyclopentene is needed 1,1-dichlorocyclopentane can be converted to 1-chlorocyclopentene by treating with quinoline (88). A mixture of 1,1-dichlorocyclopentane (32 g.) and quinoline (46 g.) was distilled through a short Vigreux column. After being washed with 1:1 sulfuric acid and water, and dried over calcium chloride 15 g. of 1-chlorocyclopentene was obtained, 63% yield, b.p. 102°-106°C./740 mm.

1,1-Dichlorocyclohexane The method in reference (55) was followed to synthesize this compound. A fraction 66.8°-67.8°C./20 mm. was found by g.l.c. to be 93.2% pure 1,1-dichlorocyclohexane, n_D^{20} = 1.4812.

trans-1,2-Dichlorocyclohexane The method in reference (55) was followed to synthesize this compound. A fraction, b.p. 80.0°-81.0°C./20 mm., was 97.1% pure *trans*-1,2-dichlorocyclohexane, n_D^{20} = 1.4908.

cis-1,2-Dichlorocyclohexane Again the method in reference (55) was followed to synthesize this compound. *trans*-2-Chlorocyclohexanol was prepared by the method of Newman and Vanderwerf (89), and a fraction of the chlorohydrin, b.p. 80.0°-86.5°C./15 mm., n_D^{25} = 1.4849, was obtained. This fraction was used as the starting material for preparing *cis*-1,2-dichlorocyclopentane and material, b.p. 115.0°-116.3°C./50 mm., n_D^{25} = 1.4930, n_D^{20} = 1.4951, was obtained. By g.l.c. this fraction was found to be 87% pure.

cis- and *trans*-1,3-Dichlorocyclohexane Both compounds were unreported in the literature.

A. An attempted synthesis of these compounds was performed by adding 1,3-cyclohexanediol (K and K Laboratories, Inc., cis and trans mixture, 8.3 g.) and freshly distilled pyridine (33 g.) into thionyl chloride (50 g.) placed in a 200 ml. three-necked flask fitted with a thermometer, stirrer, condenser and dropping funnel, and maintained at 45°C. Stirring and heating was continued for six hours after the addition was complete. The reaction mixture was added to ice water, then steam distilled. Only a few drops of oil were obtained.

B. A solution of 1,3-cyclohexanediol (6 g.) in a 50:50 mixture (120 ml.) of Skelly A and chloroform was added to a mixture of phosphorous pentachloride (28 g.) and Skelly A (30 ml.) placed in a 200 ml. three-necked flask fitted with a dropping funnel, stirrer and thermometer, and maintained at -10°--5°C. Stirring and cooling was continued for twelve hours after addition was complete. The reaction mixture was poured into ice and the organic layer was separated, washed with 10% sodium carbonate and water, and dried over calcium chloride. It was shown that the solution contained mainly trans-1,2-dichlorocyclohexane and a little of cis- and trans-1,3-dichlorocyclohexane.

C. To 3-chlorocyclohexene (6.9 g.) placed in a Carius tube and frozen with liquid nitrogen was added anhydrous ferric chloride (0.15 g.). The tube was connected to a vacuum line and hydrogen chloride (3.4 g.) was introduced into the tube. The tube was sealed and kept at ca. -10°C. for ten days. The reaction mixture was taken up with hexane, washed with water and dried over calcium chloride. It was shown by g.l.c. that the dichlorocyclohexanes were present to the extent of 6% trans-1,2-dichlorocyclohexane, 32% trans-1,3-dichlorocyclohexane, 11% trans-1,4-dichlorocyclohexane, 46% cis-1,3-dichlorocyclohexane and 5% cis-1,4-dichlorocyclohexane. The same experiment was performed for another mixture except anhydrous gallium (III) chloride (90) was used instead of ferric chloride. The yield and ratio of dichlorides in the latter case were not significantly different from those in the former case judged by chromatograms. The solutions from both tubes were combined and distilled using the 30 cm. Daufton column at a pressure of 37 mm. A mixture of dichlorocyclohexanes, b.p. 95°-105°C., was obtained in 2% yield. Most of the trans-1,4-dichlorocyclohexane was removed by freezing the mixture with Dry Ice-acetone mixture. The two isomers of 1,3-dichlorocyclohexane were then isolated by using g.l.c. with 1.5 m. diisodecyl phalate (10%) column and 2 m. polyphenyl ether (20%) column.

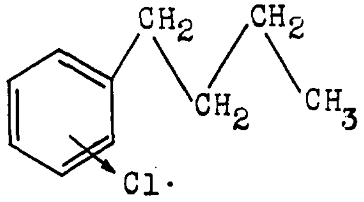
cis- and trans-1,4-Dichlorocyclohexane Although some references (91, 92, 93) describe a process for the synthesis of cis-1,4-dichlorocyclohexane via trans-4-chlorocyclohexanol, a simpler method is available to obtain both isomers (51, 84). 1,4-Cyclohexanediol (K and K Laboratories, Inc., *cis* and *trans* mixture, 20 g.) and concentrated hydrochloric acid (86 ml.) in a sealed Carius tube was heated at 100°C. for seven hours. An upper layer of oil gradually appeared during the reaction. This layer was separated, added to ether, washed, and dried over anhydrous sodium sulfate. After the ether was evaporated the oil was cooled gradually to -20°C. by using an ice-hydrochloric acid freezing mixture. Crystals grown during this period were separated by filtration. Thus crude *trans*-1,4-dichlorocyclohexane (3.0 g.) was obtained. Upon recrystallization from ethanol pure material (1.3 g.), m.p. 102.0°-102.8°C., was obtained. The filtrate was distilled using the Todd column packed with glass helices at a pressure of 17 mm. A fraction, b.p. 90.5°-91.5°C./17 mm., $n_D^{20} = 1.4947$, was shown to be 93% pure *cis*-4-dichlorocyclohexane by g.l.c.

3-Chlorocyclohexene A synthesis of this compound was described in reference (95). *tertiary*-Butyl hypochlorite was prepared by the method of H. M. Teeter and E. W. Bell (96). To a mixture of cyclohexene (466 ml.) and benzoyl peroxide (2 g.) *tertiary*-butyl hypochlorite (76.4 g.) was added dropwise so that gentle refluxing occurred. After addition was complete the mixture was refluxed an additional fifteen minutes. Excess cyclohexene was distilled and the residue was fractionated using a 30 cm. Daufton column at a pressure of 84 mm. 3-Chlorocyclohexene (27.3 g.), b.p. 79°-81°C./84 mm., $n_D^{20} = 1.4882$, in 38% yield was obtained.

PART II. CHLORINATION OF ARALKYL HYDROCARBONS

Introduction

Greater selectivities of chlorine atoms complexed with aromatic rings compared with those of free chlorine atoms have been reported (2b, 10a, 20a, 34). Photochlorination of butylbenzene was performed in order to ascertain if there is any preferred intramolecular attack at the β-, γ- or ω-position.



The reactivities of the α carbon-hydrogen bonds of a series of phenyl substituted toluenes, i.e. toluene, diphenylmethane and triphenylmethane, together with those of phenylcyclopentane and phenylcyclohexane relative to the carbon-hydrogen bond of cyclohexane were measured at several concentrations of the aromatic rings and the curves were extrapolated to infinite dilution to obtain the relative reactivities toward free chlorine atoms. The per cent chlorination was not allowed to exceed 10% for these competitive photochlorinations. The relative reactivities of the α carbon-hydrogen bonds and a carbon-hydrogen bond of cyclohexane, k_α / k_{CY}, were calculated from the expression

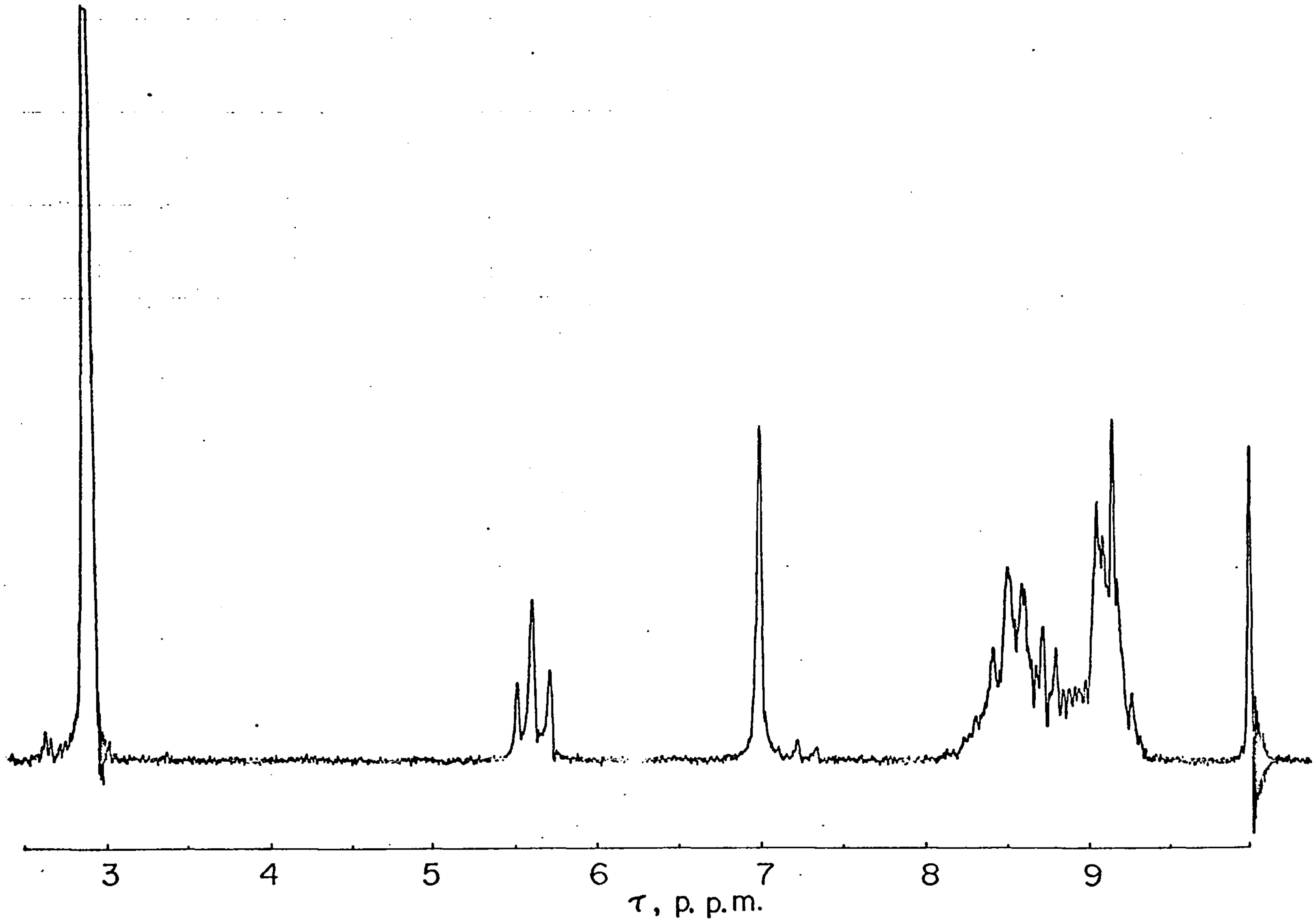
$$\frac{k_\alpha}{k_{CY}} = \frac{12\,[\alpha\text{-Chloroaralkyl hydrocarbon}]\,[\text{Cyclohexane}]}{\underline{n}\,[\text{Chlorocyclohexane}]\,[\text{Aralkyl hydrocarbon}]}$$

where n represents the number of α hydrogen atoms of the aralkyl hydrocarbon. In cases where the ratio of the hydrocarbons changed significantly during chlorination relative reactivities were calculated from the integrated expression given on page 18.

Identification of Chlorobutylbenzenes

The details of the syntheses of α, β, γ and ω-chlorobutylbenzene are described in the experimental part. The n.m.r. spectra of chlorobutylbenzenes and hydroxybutylbenzenes, except for ω-chlorobutylbenzene and the corresponding alcohol, are shown in Fig. 14-19. The spectrum of a chloride and that of the corresponding alcohol resemble each other. It can be concluded that the chlorides are unarranged products of the alcohols. The n.m.r. spectrum of α-propylbenzyl alcohol (Fig. 14) and that of α-chlorobutylbenzene (Fig. 15) show the characteristic triplets due to benzylic protons at τ = 5.6 and 5.3 respectively. The protons at the β, γ and ω-positions compose $A_3B_2C_2$ systems and the absorptions due to those protons show complicated patterns. The n.m.r. spectrum of 1-phenyl-2-butanol and that of β-chlorobutylbenzene are shown in Fig. 16 and Fig. 17 respectively. Absorptions at τ = 6-7 are due to the β-protons of those compounds and are approximately a triplet of triplets. Absorption at τ = 7-7.5 is due to the benzylic

Fig. 14. Proton magnetic resonance spectrum of α-propylbenzyl alcohol at 60 Mc./sec. in carbon tetrachloride



3
4
5
6
7
8
9
τ, p. p.m.

Fig. 15. Proton magnetic resonance spectrum of α-chlorobutylbenzene at 60 Mc./sec. in carbon tetrachloride

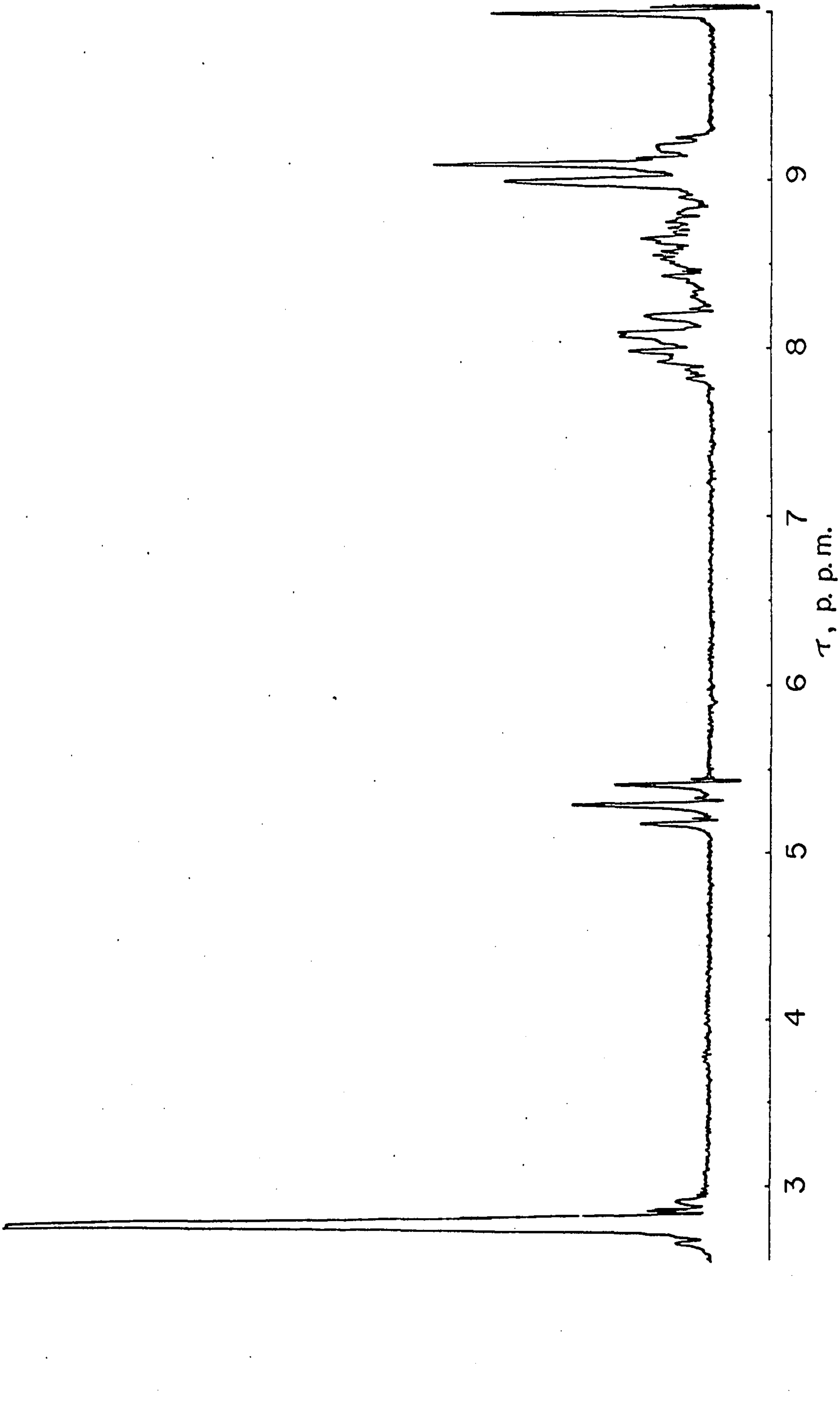
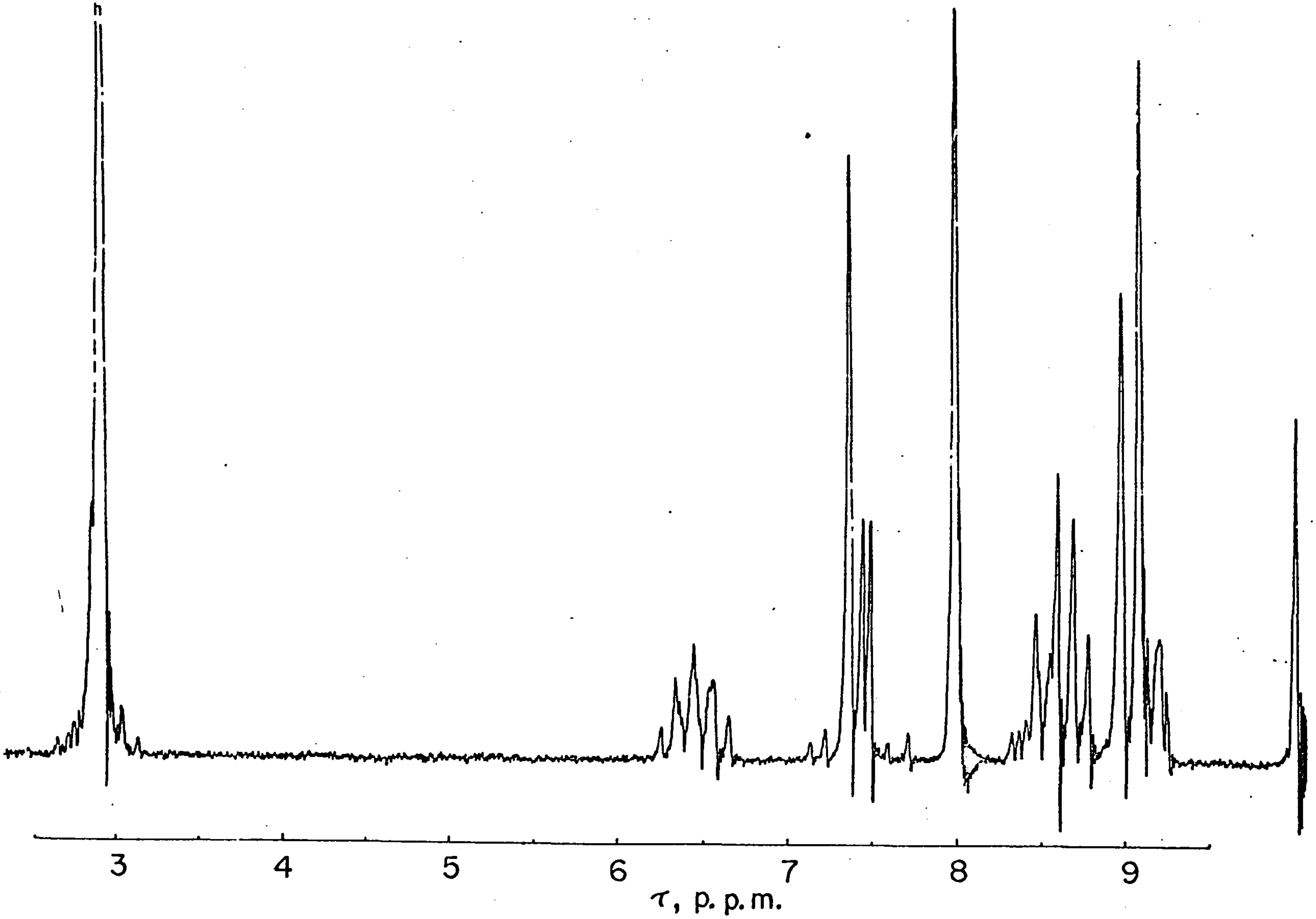

3
4
5
6
7
8
9
τ, p.p.m.

Fig. 16. Proton magnetic resonance spectrum of 1-phenyl-2-butanol at 60 Mc./sec. in carbon tetrachloride



98b

Fig. 17. Proton magnetic resonance spectrum of β-chlorocyclopentane at 60 Mc./sec. in carbon tetrachloride

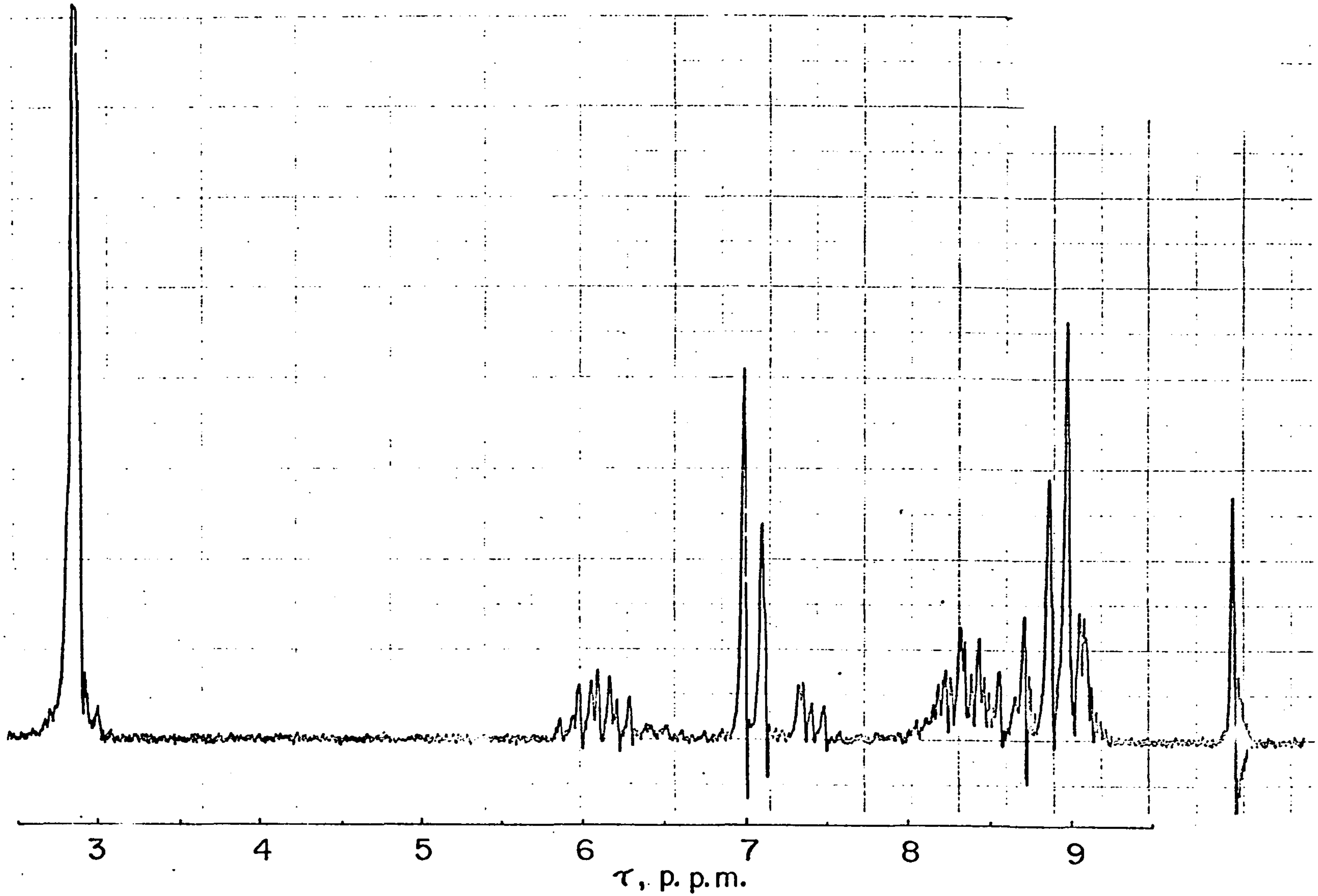

3
4
5
6
7
8
9
τ, p.p.m.

Fig. 18. Proton magnetic resonance spectrum of 4-phenyl-2-butanol at 60 Mc./sec. in carbon tetrachloride

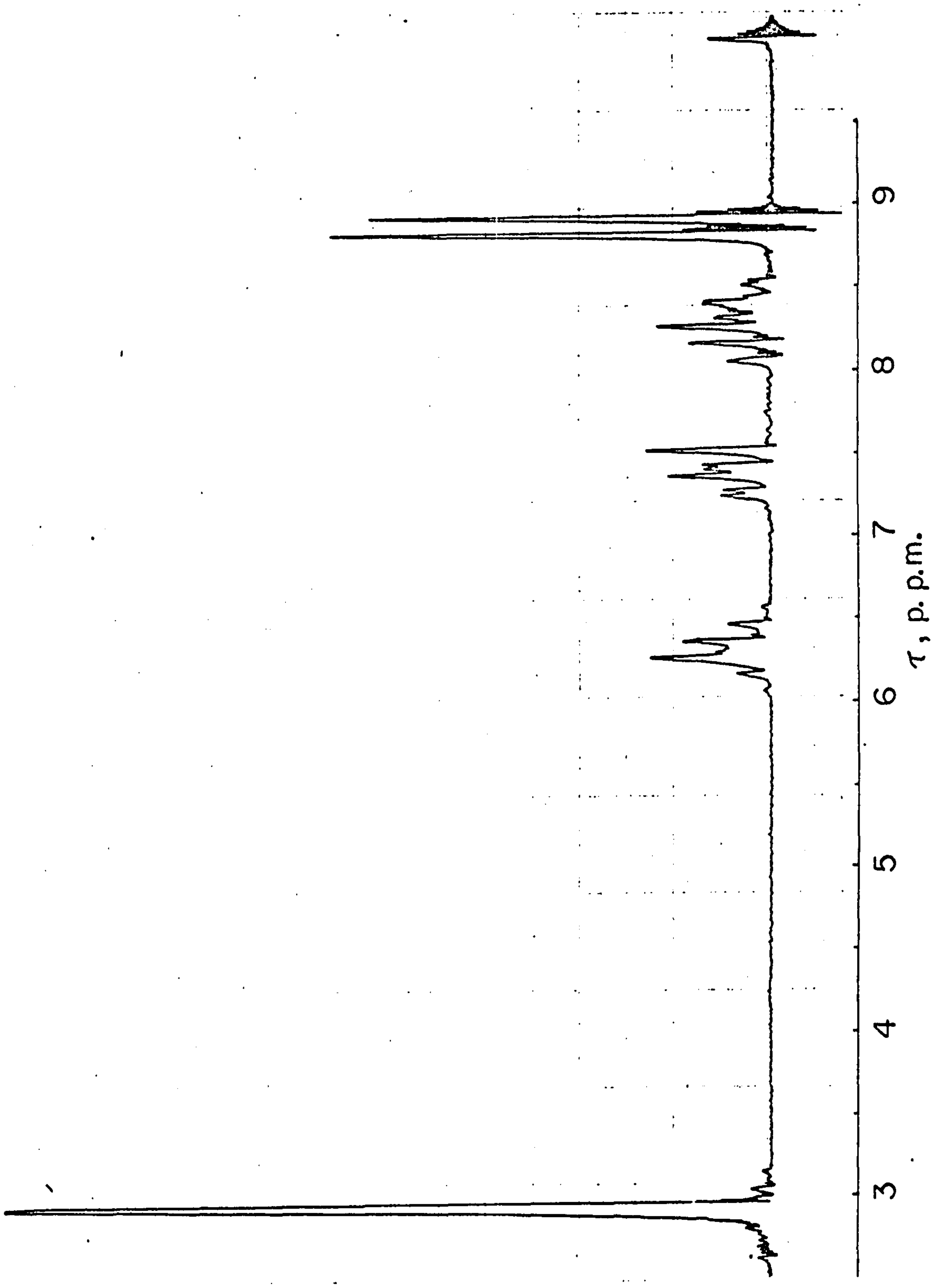
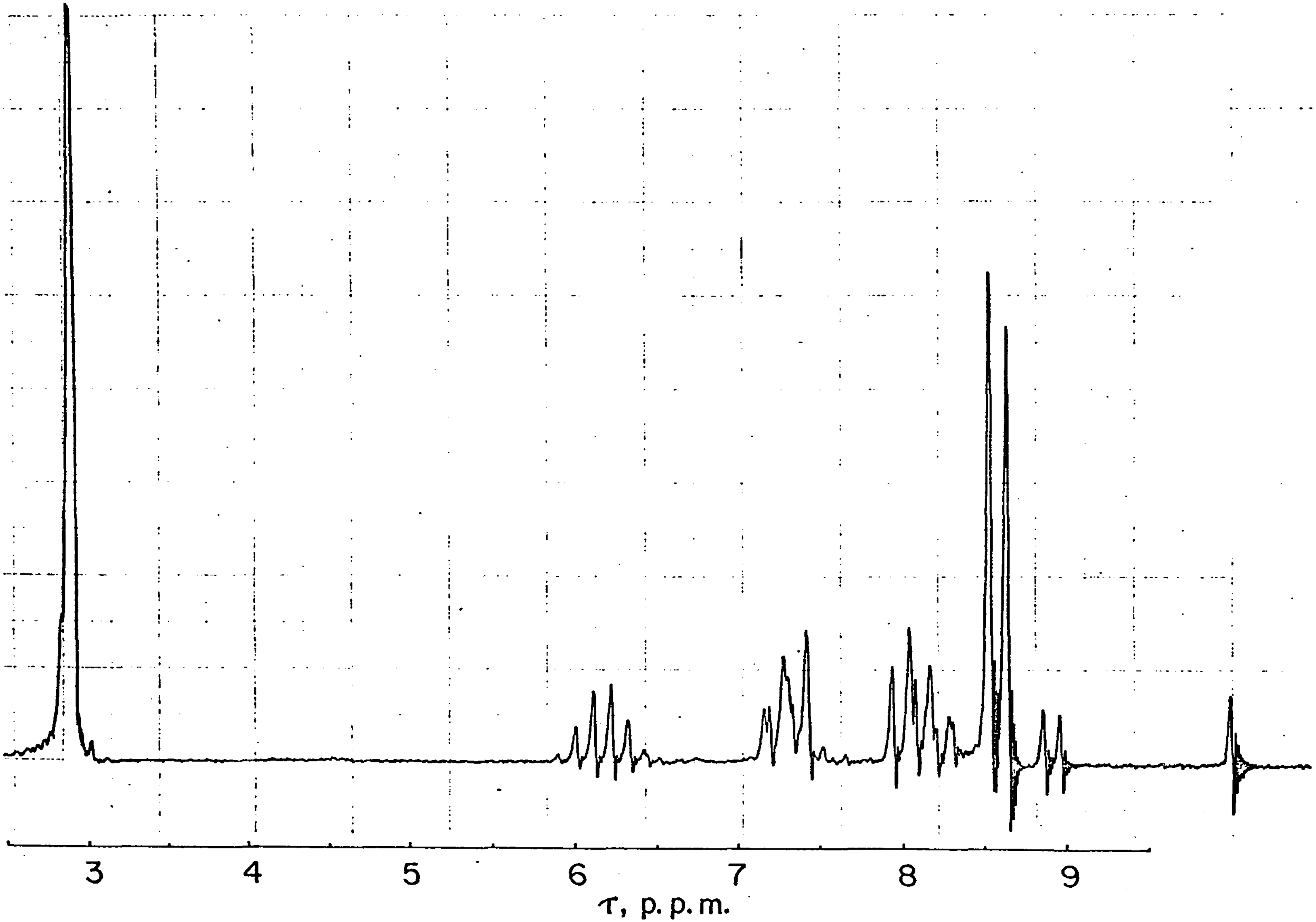

3
4
5
6
7
8
9
τ, p.p.m.

Fig. 19. Proton magnetic resonance spectrum of γ-chlorobutylbenzene at 60 Mc./sec. in carbon tetrachloride


3
4
5
6
7
8
9
τ, p.p.m.

protons. Small peaks at τ = 7.2-7.5 in Fig. 17 seem to be due to the presence of the alcohol as an impurity in the chloride. Complicated absorptions at τ = 8-9.5 are due to the ethyl groups. The hydroxyl proton absorption appeared at τ = 8 in Fig. 16. It appears that the magnetic field experienced by the α, β and γ-protons in these molecules are affected by the presence of an asymmetric center. In Fig. 18 and Fig. 19 the n.m.r. spectrum of 4-phenyl-2-butanol and that of γ-chlorobutylbenzene are shown. Absorption at τ = 6-6.5 is due to the -protons and seems to be triplet of qualtets. In Fig. 17 the hydroxylic proton absorption overlapped with them. Absorptions at τ = 7-8.5 are due to the α and β-protons. The doublets at τ = 8.9 in Fig. 18 and τ = 8.6 in Fig. 19 are the absorptions of methyl protons. The small doublet at τ = 8.9 in Fig. 19 is due to the unreacted alcohol in the chloride.

Results and Discussion

Photochlorination of butylbenzene

The relative reactivities of the carbon-hydrogen bond at each position of the butyl group of butylbenzene are presented in Table 8 as a function of benzene ring concentration. The same data found in Table 8 are presented in Fig. 20 and Fig. 21. In these figures aromatic concentration is obtained by adding the concentrations of butylbenzene and of benzene.

Table 8. Photochlorination of butylbenzene at 40°C.

MMole	Conc.[a]	Solvent	MMole chloro-derivatives				$\frac{k_\alpha}{k_\omega}$	$\frac{k_\beta}{k_\omega}$	$\frac{k_\gamma}{k_\omega}$	$\frac{k_\alpha}{k_\beta}$	$\frac{k_\gamma}{k_\beta}$
			alpha	beta	gamma	omega					
94.2	6.28	none	2.56	1.35	1.69	0.277	13.9	7.31	9.15	1.90	1.25
44.9	2.99	CCl_4[b]	2.25	1.26	1.60	0.401	8.45	4.72	5.99	1.81	1.27
19.9	0.99	CCl_4	1.94	1.11	1.48	0.441	6.61	3.78	5.04	1.75	1.33
19.8	0.99	benzene[c]	2.84	1.42	1.76	0.210	20.3	10.1	12.6	2.05	1.24
0	0	CCl_4	extraporated				5.6	2.8	3.8	1.7	1.4

[a] Mole/l at 40°C.

[b] CCl_4 = carbon tetrachloride.

[c] 9.23 Mole/l .

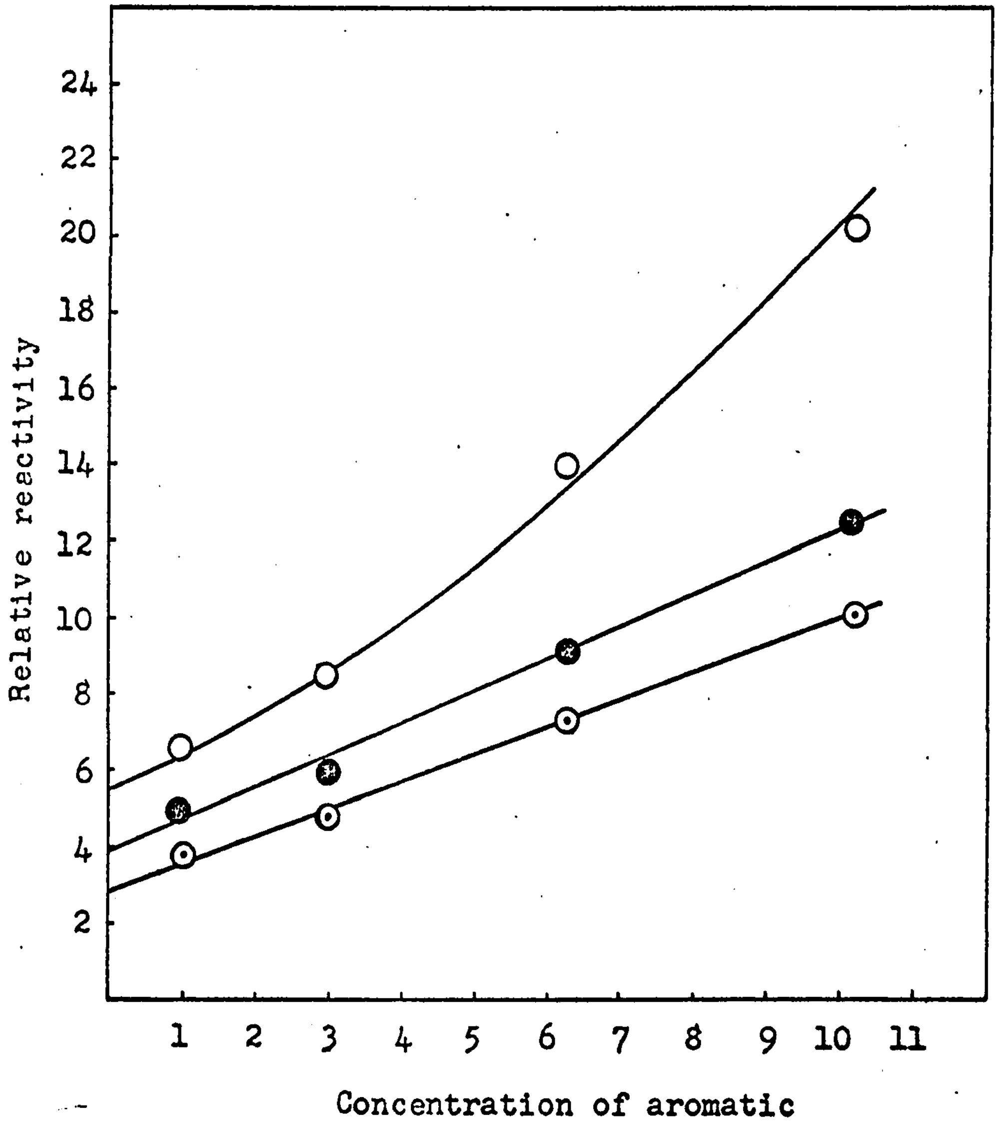


Fig. 20. Effect of concentration of aromatic rings on the relative reactivity of carbon-hydrogen bonds of butylbenzene relative to the ω-position at $40^{\circ}C$.

○ : k_{α}/k_{ω}

⊙ : k_{β}/k_{ω}

● : k_{γ}/k_{ω}

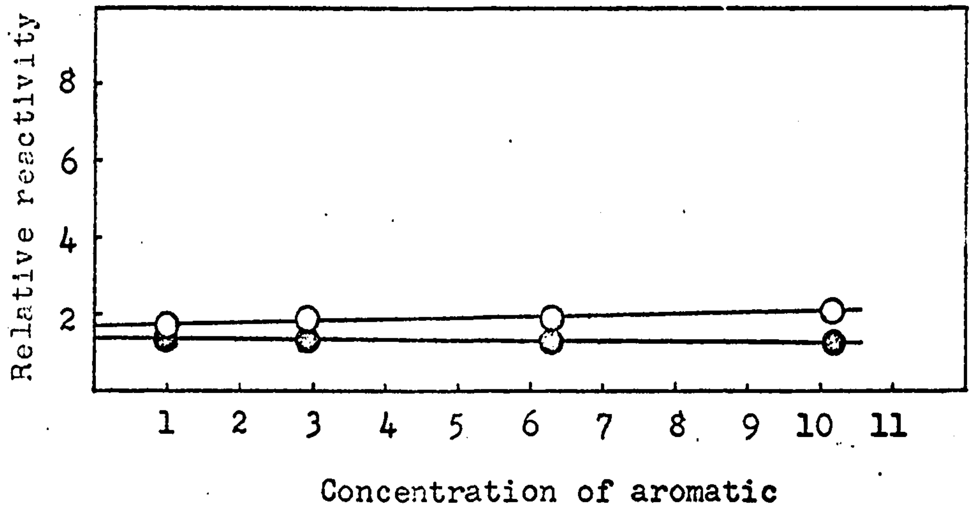


Fig. 21. Effect of concentration of aromatic rings on the relative reactivity of carbon-hydrogen bonds of butylbenzene relative to the β-position at 40°C.

○ : k_α/k_β

● : k_γ/k_β

This is an approximation since butylbenzene would be expected to be more basic than benzene.

Relative reactivities of carbon-hydrogen bonds toward intermolecular attack are functions of the concentration of the aromatic hydrocarbon. For example at 40°C. the relative reactivity of a tertiary and a primary hydrogen atom of 2,3-dimethyl-butane toward the chlorine atom is 3.9 if the alkane is used as its own solvent. When the solvent is 4.0M benzene, the relative reactivity is 17.0. When the solution contains 8.0M benzene, the relative reactivity increases to 40 (2b). The relative reactivities of carbon-hydrogen bonds toward intramolecular attack would be expected not to be affected by a change in the concentration of aromatic rings. If a preferred intramolecular attack occurs at some position on the alkyl chain, the relative reactivity of this hydrogen atom should be higher than normally expected at low aromatic ring concentration and the curve as a function of aromatic concentration should have some peculiarities since as the concentration of aromatic hydrocarbon is increased the chlorination should pass from a process involving a free chlorine atom and/or intramolecular attack to one involving mainly intermolecular attack. The curves in Fig. 16 seem reasonable if no intramolecular attack is assumed.

Solvent effects due to complexing solvent (intermolecular) are observed and the steeper curve of k_α / k_ω is without doubt due to the greater stability of the α-propylbenzyl radical. The relative reactivity of the *omega* hydrogen atoms can be taken as a standard since no effect of the phenyl group should be present at this position unless a preferred intramolecular attack had occurred. The value of k_γ / k_ω at infinite dilution is 3.8. The relative reactivities of the secondary hydrogen atoms and the primary hydrogen atoms of *n*-pentane toward the free chlorine atom have been reported to be 3.7 at 25°C. (10a). Extrapolated values at infinite dilution (Fig. 20) are accompanied with relatively large uncertainties compared with values determined directly by experiments. The uncertainties of the extrapolated values in Fig. 20 may be as high as ± 1.0. Thus, the value of 3.8 is reasonable, if little or no inductive effect of the phenyl group at the *gamma*- and *omega*-positions is assumed.

The value of k_α / k_ω at infinite dilution is 5.6. This value is higher than the reactivity of the *alpha* hydrogen atom of ethylbenzene relative to the primary hydrogen atom of 2,3-dimethylbutane,* 3.5, and is reminiscent of the reactivities of the *alpha* hydrogen atoms of indan and tetralin relative to the primary hydrogen atom of 2,3-dimethylbutane

---

*H. D. McBride. Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Relative reactivity of ethylbenzene toward chlorine atoms. Private communication to Dr. Glen A. Russell, Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. 1960.

(23), 6.1 and 5.8 respectively. The relative reactivity of the alpha hydrogen atom of butylbenzene will be discussed later in connection with the value of k_α/k_β at infinite dilution. Turning to Fig. 21, the value of k_γ/k_β is 1.4 and rather independent of solvent. This value can be ascribed to the inductive effect of the phenyl group on the hydrogen atoms at the beta-position or to the fact that the gamma-radical can be stabilized by 5 hyperconjugative structures but the beta-radical by only 4. When the curve of k_α/k_β (Fig. 21) is compared with the corresponding curves for indan and tetralin (23), solvent effects are apparent only for the cyclic aralkyl compounds. A possible explanation is that the resonance stabilization of the incipient alkyl radical is more important in higher aromatic concentrations (i.e., when the attacking chlorine atom is complexed). Therefore, the formation of the α-propylbenzyl radical, in which there is steric inhibition of resonance from the interaction between the ortho hydrogen atoms and the hydrogen atoms and the ethyl group on the beta carbon atom, is not particularly favored by complexing solvents whereas for alpha-radicals from indan and tetralin there is no such interaction and the formation of these radicals is favored by complexing solvents (16). However, it appears that such interaction is not important when the attacking species is the free chlorine atom (23). This also best explains negative solvent effects in the photochlorinations of phenylcyclohexane and phenylcyclopentane. The value of k_α/k_β at infinite dilution is 1.7. This is not significantly higher than the estimated value of the corresponding values for indan and tetralin, 1.2 and 1.15 respectively (23), if the uncertainties accompanied with extrapolation are taken into account. However, a difference between butylbenzene and indan or tetralin is that in the case of the latter compounds the α hydrogen atom is activated by the <u>ortho</u> methylene substituent. It has been reported that in the series of <u>n</u>-pentane, <u>n</u>-hexane and <u>n</u>-heptane the relative reactivities observed for the whole molecule increases as the chain lengthens to a greater extent than would be expected from the values calculated from the relative reactivities of the primary and the secondary hydrogen atoms of <u>n</u>-pentane (97). Moreover, the secondary hydrogen atom of butane is more reactive than that of propane (2d).

In conclusion, it appears that no evidence for a preferred intramolecular attack at any position of the alkyl chain of butylbenzene was found.

Competitive chlorination of aralkyl hydrocarbons with cyclohexane

Cyclohexane was chosen as the reference hydrocarbon because of its physical properties and because its reactivity is known relative to many other aliphatic hydrocarbons. The data for competitive chlorinations with cyclohexane as a function of the aromatic concentration are in Table 9. These data are shown graphically in Fig. 22 and Fig. 23.

The results of the competitive chlorination of toluene and cyclohexane in nitrobenzene solution agrees well with the previous data in reference (10a). The low reactivity of toluene at higher aromatic concentrations suggests compensating effects. Complexing a chlorine atom with an aromatic molecule should decrease the importance of $R^{+}H\cdot Cl^{-}$ as a contributing structure to the transition state and increase the importance of structures such as R·H-Cl. Table 10 lists the relative reactivities of toluene, diphenylmethane and triphenylmethane toward various radicals together with the relative reactivities of ethylbenzene and cumene. The chlorine atom is the most reactive species. The tertiary-butoxy radical and the phenyl radical show similar selectivities toward hydrogen atoms of aliphatic hydrocarbons. For example, the relative reactivities of the secondary hydrogen atom and the primary hydrogenation of n-butane are 1:7.9 and the relative reactivities of the tertiary hydrogen atom and the primary hydrogen atom of 2,3-dimethylbutane are 1:44 toward the tertiary-butoxy radical (25). Corresponding ratios toward the phenyl radical are 1:9.5:47 (98). However, electron affinity of the tertiary-butoxy radical is greater than for the phenyl radical. Thus, the hydrogen atom of triphenylmethane is more reactive toward the phenyl radical than toward

Table 9. Competitive photochlorination of cyclohexane and aralkyl hydrocarbons at 40°C.

Aralkyl hydro-carbon (mole)	Cyclo-hexane (mole)	Conc. aralkyl hydro-carbon[a]	Added solvent[b]	Chlorination products, mmole		k_α / k_{CY}[c]
				Chloro-cyclo-hexane	Alpha-chloro aralkyl	
			Toluene			
0	--	0	NB or CY	extrapolated		0.5[d]
0.0150	0.00734	1.00	NB	0.872	0.213	0.45
0.0150	0.00188	1.00	NB	0.381	0.407	0.49
0.0297	0.01467	2.00	NB	1.077	0.211	0.35
0.0299	0.00360	1.99	NB	0.525	0.447	0.38
0.0449	0.00549	3.00	NB	0.782	0.613	0.35
			Diphenylmethane			
0	--	0	NB or CY	extrapolated		1.5[d]
0.0076	0.0075	0.50	NB	0.652	0.270	1.57
0.0151	0.0149	1.01	NB	1.40	0.283	1.15
0.0149	0.0149	0.99	NB	1.59	0.332	1.20
0.0149	0.112	0.99	none	2.57	0.082	1.44
0.0151	0.0146	1.01	NB	1.98	0.654	1.84
0.0225	0.0226	1.50	NB	1.09	0.301	1.64
0.0325	0.0323	2.17	NB	1.12	0.275	1.42
0.0323	0.0858	2.15	none	3.42	0.326	1.50
0.0547	0.0514	3.64	none	2.08	0.802	2.15
			Triphenylmethane			
0	--	0	NB	extrapolated		3.7[d]
0.0075	0.00750	0.50	NB	0.631	0.246	4.54
0.0150	0.0376	1.00	NB	2.619	0.390	4.48
0.0225	0.0224	1.50	NB	0.927	0.415	5.28

---

[a] Mole/l. at 40°C.

[b] NB = nitrobenzene, CY = cyclohexane.

[c] Per hydrogen atom.

[d] From Fig. 22.

Table 9. (Continued)

Aralkyl hydrocarbon (mole)	Cyclohexane (mole)	Conc. aralkyl hydrocarbon	Added solvent	Chlorination products, mmole		k_{α}/k_{CY}
				Chloro-cyclohexane	Alpha-chloro aralkyl	
			Phenylcyclohexane			
0	--	0	NB	extrapolated		3.6[e]
0.0177	0.0185	1.18	NB	0.837	0.214	3.17
0.0178	0.0185	1.18	NB	0.596	0.159	3.31
0.0353	0.0361	2.35	NB	1.409	0.348	2.99
0.0353	0.0361	2.35	NB	1.135	0.263	2.84
0.0522	0.0536	3.48	none	1.029	0.211	2.50
			Phenylcyclopentane			
0	--	0	NB	extrapolated		4.7[e]
0.0150	0.0152	1.00	NB	0.600	0.210	4.21
0.0189	0.0189	1.26	NB	0.498	0.160	3.81
0.0379	0.0375	2.52	NB	0.635	0.164	3.08
0.0379	0.0375	2.52	NB	0.888	0.227	3.03

[e] From Fig. 23.

the <u>tertiary</u>-butoxy radical although the difference in the reactivities of the tertiary hydrogen atom of cumene toward both radicals is small. In the case of the chlorine atom, the reactivities of the secondary hydrogen atoms of ethylbenzene and diphenylmethane are probably identical within experimental uncertainty whereas the reactivity of the tertiary hydrogen atom of triphenylmethane is higher than that of cumene by 30% which is larger than the experimental uncertainty. One might have expected that the tertiary

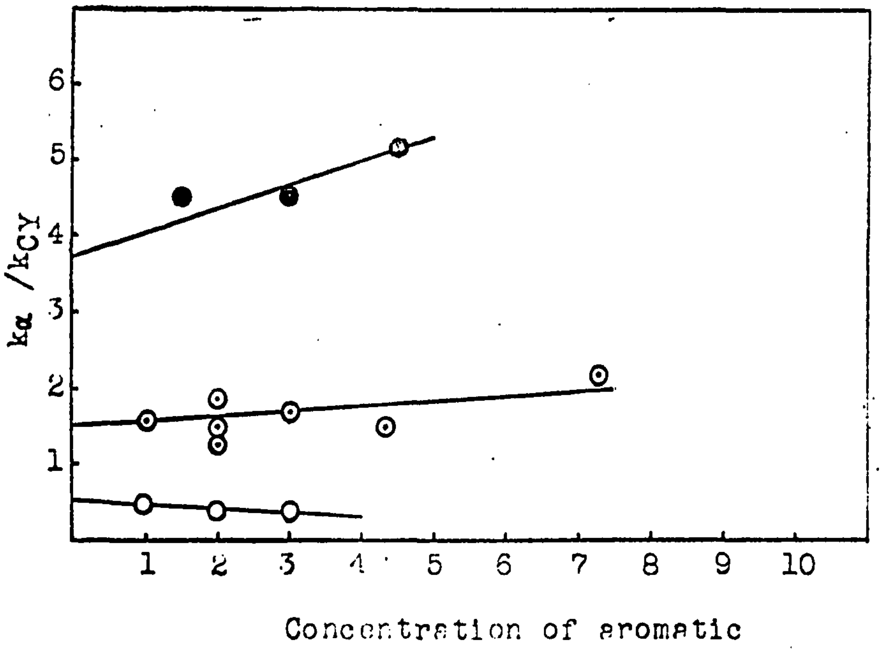


Fig. 22. Effect of concentration of aromatic rings on the reactivities of alpha-hydrogen atoms of toluene, diphenylmethane and triphenylmethane relative to a hydrogen atom of cyclohexane at 40°C.

○ : toluene

⊙ : diphenylmethane

● : triphenylmethane

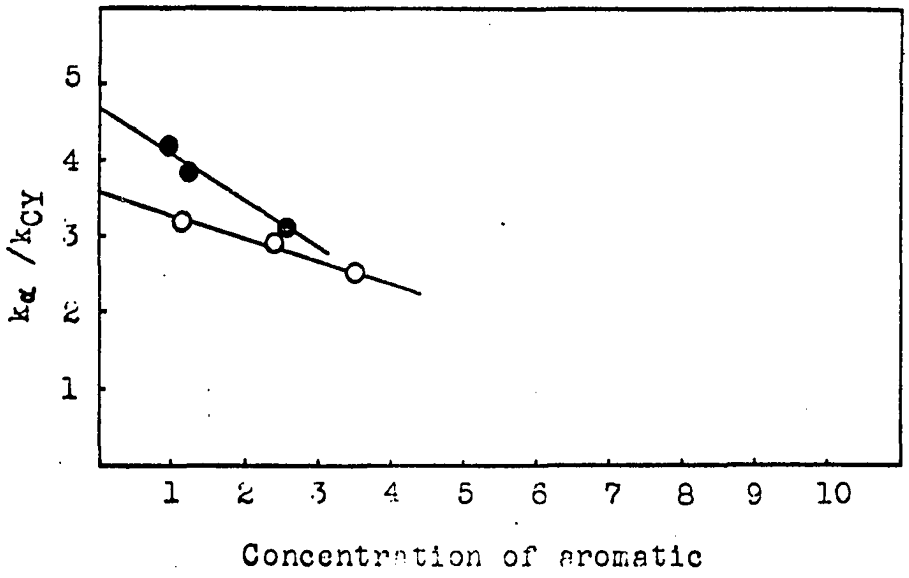


Fig. 23. Effect of concentraton of aromatic rings on the reactivities of _alpha_-hydrogen atoms of phenylcyclopentane and phenylcyclohexane relative to a hydrogen atom of cyclohexane at 40°C.

○ : phenylcyclohexane

● : phenylcyclopentane

Table 10. Relative reactivities of some aralkyl hydrocarbons toward various radicals

Hydrocarbon	Cl· 40°C.	CCl_3·[a] 40°C.	Br·[a] 40°C.	Φ·(98) 60°C.	t-BuO·(25) 40°C.
Toluene	1.0[b]	1.0[b]	1.0[b]	1.0[b]	1.0[b]
Ethylbenzene	2.5[c]	50	16	4.42	3.18
Cumene	5.5[d]	260	36	9.78	6.84
Diphenylmethane	2.0	50	10	7.55	4.70
Triphenylmethane	7.2	200	18	38.7	9.60

[a] Results of Mr. C. DeBoer.

[b] Assumed.

[c] Results of Mr. H. D. McBride.

[d] Reference 23.

hydrogen atom of cumene would be more reactive than that of triphenylmethane since the chlorine atom is a highly electron deficient species. However, it seems likely that the relative effects of substitution of methyl and phenyl groups is also a function of the reactivity of the radical. For example, the relative reactivities of the secondary hydrogen atom of ethylbenzene and the tertiary hydrogen atom of cumene toward the trichloromethyl radical are 1:5.2. The corresponding ratio toward the bromine atom is 1:2.2. The relative reactivities of the secondary hydrogen atom of ethylbenzene and diphenylmethane are 1:1 whereas the corresponding ratio toward the bromine atom is 1.6:1. If these ratios were controlled only by the electron affinities of the attacking species, one might think that the difference of reactivity ratios of the secondary hydrogen atom of diphenylmethane and the tertiary hydrogen atom of triphenylmethane toward the trichloromethyl radical and toward the bromine atom would be more pronounced. The observed ratios are 1:4.0 and 1:1.8 respectively. (Compare with 1:5.2 and 1:2.2 shown above.) Therefore, it seems likely that the effect due to high reactivity can cancel the effect due to high electron affinity. This would suggest a weakness in assigning statistical factors based on the number of hydrogen atoms in computing relative reactivities. Although there is some variation of the effect of substitution of the methyl and the phenyl group as discussed above, toward the chlorine atom the effects of the activation of the hydrogen atom by the methyl group and by the phenyl group are nearly equivalent. This is ascribed to the high reactivity and the high electron affinity of the chlorine atom. The change of the slope of lines in Fig. 22 from toluene to triphenylmethane is an indication of the change of the bond dissociation energy of the alpha-hydrogen atoms of these compounds. In Fig. 23 the lines for phenylcyclohexane and phenylcyclopentane have negative slopes. The corresponding line for cumene (23) has a nearly zero slope which could not be expected from the lower bond dissociation energy of cumene compared with cyclohexane. A possible explanation is that steric inhibition of resonance from the interaction of the ortho hydrogen atoms and the beta hydrogen atoms of the incipient alpha radicals derived from those compounds (16) at high aromatic concentration. In the case of phenylcyclohexane and phenylcyclopentane, there is no free rotation of the carbon-carbon bond of the cycloalkane ring. Therefore, the stronger interaction can be expected for phenylcyclohexane and phenylcyclopentane than for cumene. However, it appears that such interaction is not important when the attacking species is the free chlorine atom (23).

The higher reactivities of the tertiary hydrogen atom of phenylcyclohexane (3.6 if the reactivity of a hydrogen atom of cyclohexane is assumed 1.0) and phenylcyclopentane (4.7) than that of cumene (2.9), could be explained by larger electron donating ability of the cyclohexane ring and the cyclopentane ring than two methyl groups to the alpha carbon-hydrogen bond as discussed during the comparison of the relative reactivity of the alpha hydrogen atoms of ethylbenzene and butylbenzene. However, the secondary hydrogen atoms of n-pentane are more reactive than those of cyclohexane and cyclopentane toward free chlorine atom (10a) (I strain).

The photochlorination of 1.50M fluorene and 1.49M cyclohexane in nitrobenzene solution was also performed. No peak due to chlorocyclohexane was found in the chromatogram of the chlorination products. This might imply that a very fast ionic substitution into the aromatic ring had occurred. This result indicates that the reactivity of the alpha hydrogen atom of fluorene relative to a hydrogen atom of cyclohexane must be greater than 16. The solubility of fluorene in cyclohexane is only 0.67 mole/l. at 40°C. The result of a photochlorination of 0.25M fluorene in cyclohexane solution indicated a relative reactivity of 3.0. The latter value is more reasonable. However, at lower concentration of aralkyl hydrocarbon analysis of the alpha chloride is accompanied with larger experimental uncertainty. Further investigation of the photochlorination of fluorene was abandoned.

Experimental

Apparatus and procedure

The same photochlorination apparatus and procedure described in Part I was used.

Analytical procedure

For the analyses of chlorobutylbenzenes (except for α-chlorobutylbenzene), a Perkin-Elmer Model 154D Vapor Fractometer with a 300 foot 1/8" internal diameter Golay column packed with polypropylene glycol was used at 128°C. Nitrobenzene was used as the internal standard. The isomeric β, γ and ω-chlorobutylbenzenes were synthesized and the peaks due to the separate isomers identified. The thermoconductivities of these isomers have been assumed to be identical. The retention times increased with increasing separation of the phenyl and the chlorine substituents. In the injector of the chromatograph, a glass covered heating element was installed in order to prevent decomposition of the chlorides. However, α-chlorobutylbenzene still decomposed to give an extra peak, presumably due to β-ethylstyrene, and the extent of decomposition was not reproducible. For the analysis of α-chlorobutylbenzene selective hydrolysis of aliquots of the chlorination product in 80% ethanol solution with stirring (heterogeneous) at 60°C. was employed. The hydrolysis was followed by directly titrating with 0.1N sodium hydroxide the hydrogen chloride liberated. The hydrolysis was complete in 24 hours as evidenced by the constancy of the sodium hydroxide titer. Under the same conditions the other isomeric chlorobutylbenzenes are not hydrolyzed. The hydrolyzed product was titrated potentiometrically with 0.05N silver nitrate after the sodium hydroxide titer became constant. Blank corrections were applied.

The alpha-chlorides formed in the competitive photochlorinations of diphenylmethane, triphenylmethane, fluorene, phenylcyclopentane and phenylcyclohexane with cyclohexane were determined by selectively hydrolyzing aliquots of the reaction mixture in 80% ethanol at room temperature. The titration procedure was the same as described for α-chlorobutylbenzene. The chlorocyclohexane was determined by g.l.c. as described in Part I with the 2 m. Perkin-Elmer B column (reportedly di-2-ethylhexylsebacate) at 110°C. Toluene was used as the internal standard. Excellent agreement was found when the Rauscher method (99) for the determination of total chlorine was employed and the difference between total chlorine and easily hydrolyzed chlorine was assumed to be chlorocyclohexane.

Reagents

Aldrich butylbenzene (puriss grade), Phillips toluene (99.9 mole % minimum purity) and Eastman Kodak diphenylmethane, triphenylmethane, and phenylcyclohexane were employed. Eastman-Kodak fluorene was recrystallized from absolute ethanol, m.p. 113.5°-114.4°C. Phenylcyclopentane was prepared from bromocyclopentane (100 g.) and benzene (595 ml.) in the presence of anhydrous aluminum bromide (11 g.). The general method for the Friedel-Crafts reaction described in references (100) and (101) was followed. Phenylcyclopentane, b.p. 216.0°-216.5°C., $n_D^{20} = 1.5288$, was obtained in 50% yield. Both Eastman-Kodak cyclohexane (spectrograde) and Phillips cyclohexane (99 mole % minimum purity) were used. The nitrobenzene, carbon tetrachloride and benzene used were described previously in Part I.

Synthesis of chlorobutylbenzenes

α-Chlorobutylbenzene The synthesis of this compound from the reaction of α-propylbenzyl alcohol with thionyl chloride is reported (102). α-Propylbenzyl alcohol (45 g.) was placed in a 100 ml. three-necked flask fitted with a frittered glass gas inlet tube and a calcium chloride drying tube. As anhydrous hydrogen chloride was passed into the alcohol, heat was evolved and a water layer separated in the bottom of the flask. Cooling by an ice-water bath was applied when necessary. The addition of anhydrous hydrogen chloride was continued until the amount of the water layer became constant. After the water layer was removed the organic layer was dried with anhydrous magnesium sulfate overnight. Hydrogen chloride was removed by evacuation of the flask containing the chloride. After distillation through a simple Claisen head at a pressure of 1 mm., 41 g. (81% yield) of the product was obtained, b.p. 60°-61°C./1 mm., $n_D^{20} = 1.5164$. An analysis of this product by hydrolysis, as described earlier in this section, indicated that the chloride was 97% pure.

β-Chlorobutylbenzene This compound has not been reported in the literature. A mixture of 1-phenyl-2-butanol (22 g.) and pyridine (23.8 ml.) was added dropwise to thionyl chloride (22.4 ml.) placed in a 250 ml. three-necked flask fitted with a dropping funnel, stirrer and thermometer. During the addition the temperature was kept at 0°-5°C.

Stirring was continued for 24 hours after addition was complete. The mixture was poured over ice, transferred to a separatory funnel, ether (20 ml.) added, and the organic layer separated, washed with water six times and dried over anhydrous magnesium sulfate. This material was distilled at a pressure of 1 mm. by using a 30 cm. Daufton column and a fraction 63.2°-64°C. (4.5 g., 18% yield) was collected. By g.l.c. analysis this product was shown to be composed of 91% of the desired chloride and 9% of unreacted 1-phenyl-2-butanol. A higher yield might be expected for this reaction and the similar reaction for the preparation of the γ-chlorobutylbenzene if the temperature were increased since some unreacted alcohol was recovered. However, too high a temperature will result in the formation of olefins.

γ-Chlorobutylbenzene J. von Braun and L. Neuman (103) synthesized this compound by decomposition of the benzamide of γ-aminobutylbenzene. Later W. Schlenk and E. Bergman (104) attempted to synthesize this compound by the reaction of 4-phenyl-2-butanol with thionyl chloride. They reported that the chloride was decomposed during the distillation at a pressure of 16 mm.

4-Phenyl-2-butanol (40 g.) was reacted with thionyl chloride (40.4 ml.) in the presence of pyridine (43 g.) in a similar manner to the procedure described for β-chlorobutylbenzene. The fraction, b.p. 61°-64°C./1 mm., $n_D^{20} = 1.5131$, was found to be composed of 96% of the chloride and 4% of 4-phenyl-2-butanol by g.l.c. analysis. The yield was 10.1 g. (23%).

ω-Chlorobutylbenzene This compound was synthesized by the method described by J. von Braun (105). N-Benzoyl-4-phenyl-1-butylamine was prepared from 4-phenyl-1-butylamine (50 g. Aldrich Chem. Co.) and benzoyl chloride (54 g.) by the Schotten Bauman reaction. After the recrystallization from 95% ethanol, the amide, m.p. 83°-83.5°C., was obtained in 70% yield. The benzamide (60 g.) and phosphorous pentachloride (50 g.) were placed in a 250 ml. distilling flask and heated to 150°C. to distill out phosphoryl chloride. Then the temperature was raised from 180°C. to 250°C. to distill the mixture of benzonitrile and ω-chlorobutylbenzene. For the separation of the benzonitrile vacuum distillation through a 30 cm. Daufton column was employed, instead of the hydrolysis in concentrated hydrochloric acid at 160°C. used by J. von Braun. A fraction (12 g.), b.p. 118.5°C./14 mm., n_{25}^{D} = 1.5167, was obtained. It was found to be 100% pure by g.l.c. analysis.

α-Propylbenzyl alcohol This compound was prepared from n-propyl bromide (242 g.) and benzaldehyde (189 g.) by the Grignard reaction. The crude product was obtained in 80% yield. After the distillation through a Todd column packed with Monel helices, a fraction, b.p. 110°-113°C./10 mm.,

n_D^{20} = 1.5137, was obtained.

<u>1-Phenyl-2-butanol</u> This compound has not been reported in the literature. An attempted synthesis was made by following the method described for 1-phenyl-2-propanol in reference (106). The reaction gave a very poor yield probably due to the self condensation of phenylacetaldehyde and purification by recrystallization of the half-ester of phthalic acid (107) was required. Thus, the alcohol was prepared from 1-phenyl-2-butanone (100 g., K and K Laboratories) by reduction with lithium aluminum hydride (7.7 g.) by following the general method described in reference (108). After distillation through a Todd column packed with Monel helices, a fraction, b.p. 74°-75°C./1 mm., n_D^{20} = 1.5161, was obtained in 74% yield.

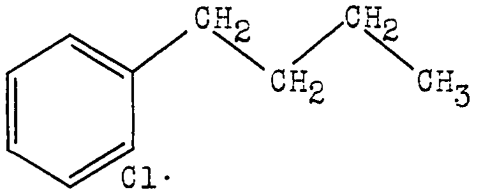
<u>4-Phenyl-2-butanol</u> This compound was prepared from benzalacetone (250 g., Matheson, Coleman and Bell) by hydrogenation in the presence of copper-chromium oxide catalyst under 2000 p.s.i. at 150°-175°C. (109). The crude product gave a positive test with 2,4-dinitrophenylhydrazine. By the distillation through a Todd column packed with Monel helices, a fraction (100 g.) which was negative to 2,4-dinitrophenylhydrazine, b.p. 124°C./14 mm., n_D^{20} = 1.5172, was obtained.

SUMMARY

A study of the chlorination, principally by chlorine and light, of chloro and bromocyclopentane and chlorocyclohexane was performed. Dihalocycloalkanes in the chlorination products were analyzed by gas liquid chromatography. Authentic samples of all the dihalocycloalkanes were synthesized. The tendency for the attack of the chlorine atom to occur preferentially at carbon-hydrogen bonds remote from the halogen substituent has been observed. It appears that the inductive effect of the chlorine substituent is negligible for a hydrogen atom in the 4-position. The higher reactivity of the hydrogen atoms at the 2-position of bromocyclopentane, ca. twice as high as those of chlorocyclopentane, is reminiscent of participation of the bromine substituent which was first suggested by H. L. Goering et al. (63, 64b, 75) for stereospecific addition of hydrogen bromide to olefins through free radical mechanism.

Significant stereochemistry has been observed in the reaction of halocycloalkyl radicals with molecular chlorine. Similar stereochemistry for the reaction of chlorocyclopentyl and chlorocyclohexyl radicals with molecular chlorine could be interpreted as being due to the lack of appreciable conformational stability of cyclohexyl radicals and the greater stability of "trans" transition states for the reaction both in the cyclopentyl and cyclohexyl systems.

A study of directive effects in the chlorination of aralkyl hydrocarbons was also undertaken. A possible preferred attack at the β, γ, or ω-position of butylbenzene by intramolecular reactions of the complexed chlorine has been investigated. No evidence was found for such an intramolecular process.



The chlorination of toluene, diphenylmethane and triphenylmethane has shown that the substitution of a methyl or a phenyl group for a hydrogen atom produces essentially the same change in the reactivity of remaining <u>alpha</u> hydrogen atoms toward a chlorine atom.

REFERENCES CITED

1. E. W. R. Steacie, "Atomic and Free Radical Reactions", 2nd ed. Vol. 2. Reinhold Publishing Corporation, New York, N. Y., 1954.

2. (a) H. C. Brown and G. A. Russell, J. Am. Chem. Soc., 74, 3995 (1952).

   (b) G. A. Russell, J. Am. Chem. Soc., 80, 4987 (1958).

   (c) K. B. Wiberg and L. H. Slaugh, J. Am. Chem. Soc., 80, 3033 (1958).

   (d) C. Walling and B. Miller, J. Am. Chem. Soc., 79, 4181 (1957).

3. P. G. Ashmore and J. Chanmugain, Trans. Faraday Soc., 49, 254 (1953).

4. (a) H. O. Prichard, J. B. Pyke and A. F. Trotman-Dikenson, J. Am. Chem. Soc., 77, 2629 (1955).

   (b) J. H. Knox, Chem. and Ind., 1631 (1955).

   (c) J. H. Knox and R. L. Nelson, Trans. Faraday Soc., 55, 937 (1959).

   (d) J. H. Knox and A. F. Trotman-Dickenson, Special Publication 9, 35 (1957). The Chemical Soc., London.

5. H. B. Hass, E. T. McBee and P. Weber, Ind. Eng. Chem., 27, 1190 (1935), 28, 333 (1936).

6. (a) H. C. Brown and A. B. Ash, J. Am. Chem. Soc., 77, 4019 (1955).

   (b) A. B. Ash and H. C. Brown, Record of Chem. Progress, 9, 81 (1948).

   (c) M. S. Kharasch and H. C. Brown, J. Am. Chem. Soc., 61, 2142 (1939).

   (d) D. V. Tishchenko and A. Churbakov, Zhur. Obshchei Khim., 7, 658 (1937).

   (e) D. V. Tishchenko and A. Churbakov, Zhur. Obshchei Khim., 7, 663 (1937).

(f) D. V. Tishchenko, Zhur. Obshchei Khim., 7, 897 (1937).

(g) D. V. Tishchenko and N. Zhokhovets, Zhur. Obshchei Khim., 18, 43 (1948).

(h) F. F. Rust and W. E. Vaughan, J. Org. Chem., 6, 479 (1941).

(i) P. S. Fredericks and J. M. Tedder, J. Chem. Soc., 144 (1960).

(j) P. S. Fredericks and J. M. Tedder, J. Chem. Soc., 3520 (1961).

(k) P. S. Fredericks and J. M. Tedder, Chem. and Ind., 490 (1959).

7. G. A. Russell and H. C. Brown, J. Am. Chem. Soc., 77, 4031 (1955).

8. C. Walling, "Free Radicals in Solution". John Wiley and Sons, Inc., New York, N. Y., 1957.

9. A. N. Nesmeyanov, R. Kh. Freidlina, V. N. Kost and M. Ya. Khorlina, Tetrahedron, 16, 94 (1961).

10. (a) G. A. Russell, J. Am. Chem. Soc., 80, 4997 (1958).

(b) G. A. Russell, J. Org. Chem., 23, 1407 (1958).

(c) G. A. Russell, Tetrahedron, 8, 101 (1959).

(d) G. A. Russell, Tetrahedron, 8, 101 (1959).

(e) G. A. Russell and H. C. Brown, J. Am. Chem. Soc., 77, 4578 (1955).

(f) G. A. Russell, J. Am. Chem. Soc., 78, 1047 (1956).

(g) F. R. Mayo and C. Walling, Chem. Revs., 46, 191 (1950).

(h) C. Walling and E. A. McElhill, J. Am. Chem. Soc., 73, 2927 (1951).

11. G. S. Hammond, J. Am. Chem. Soc., 77, 334 (1955).

12. G. A. Russell and H. C. Brown, J. Am. Chem. Soc., 77, 4031 (1955).

13. S. D. Ross, M. Markarian and M. Nazzeurski, J. Am. Chem. Soc., 71, 396 (1949).

14. S. D. Ross, M. Markarian and M. Nazzeurski, J. Am. Chem. Soc., 69, 2468 (1947).

15. E. L. Eliel, Substitution at Saturated Carbon Atoms, in M. S. Newman, ed., "Steric Effects in Organic Chemistry". John Wiley and Sons, Inc., New York, N. Y., 1956.

16. J. A. Meyer, V. Stannett and M. Szwarc, J. Am. Chem. Soc., 83, 25 (1961).

17-18. H. C. Brown, R. S. Fletcher and R. B. Johansen, J. Am. Chem. Soc., 73, 212 (1951).

19. C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker and J. Herbert, J. Am. Chem. Soc., 75, 2078 (1953).

20. (a) C. Walling and M. F. Mayahi, J. Am. Chem. Soc., 81, 1485 (1959).

(b) C. Walling and P. S. Fredericks, J. Am. Chem. Soc., 84, 3326 (1962).

21. C. G. Overberger, W. F. Hale, M. B. Berenbaum and A. B. Finestone, J. Am. Chem. Soc., 76, 6185 (1954).

22. A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys., 19, 329 (1951).

23. D. G. Hendry, Influence of solvent on free radical reactions. Unpublished Ph. D. thesis. Library, Iowa State University of Science and Technology, Ames, Iowa. 1962.

24. J. E. Leffler, "The Reactive Intermediate of Organic Chemistry". Interscience Publishers Inc., New York, N. Y., 1956.

25. C. Walling and B. B. Jacknow, J. Am. Chem. Soc., 82, 6108 (1960).

26. R. A. Gregg and F. R. Mayo, Disc. Faraday Soc., 2, 328 (1947).

27. (a) C. Walling and F. R. Mayo, J. Polymer Sci., 3, 895 (1948).

(b) C. C. Price and J. G. Walsh, J. Polymer Sci., 6, 239 (1951).

28. (a) F. M. Lewis and M. S. Matheson, J. Am. Chem. Soc., 71, 747 (1949).

(b) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, J. Am. Chem. Soc., 71, 1661 (1949).

(c) L. M. Arnett, J. Am. Chem. Soc., 74, 2027 (1952).

29. (a) J. E. Leffler and R. A. Hubbard, J. Org. Chem., 19, 1089 (1954).

(b) M. G. Alder and J. E. Leffler, J. Am. Chem. Soc., 76, 4169 (1954).

(c) M. D. Cohen, J. E. Leffler and L. M. Barbato, J. Am. Chem. Soc., 76, 4169 (1954).

30. R. C. Petersen, J. H. Markgraf and S. D. Ross, J. Am. Chem. Soc., 83, 3819 (1961).

31. K. J. Laidler and H. Eyring, Ann. N. Y. Acad. Sci., 39, 303 (1940).

32. J. G. Kirkwood and F. H. Westheimer, J. Chem. Phys., 6, 506, 513 (1938).

33. R. Gane and C. K. Ingold, J. Chem. Soc., 2153 (1931).

34. G. A. Russell, J. Am. Chem. Soc., 79, 2977 (1957).

35. H. C. Brown and J. D. Brady, J. Am. Chem. Soc., 74, 3570 (1952).

36. C. Walling and B. B. Jacknow, J. Am. Chem. Soc., 82, 6113 (1960).

37. G. A. Russell, J. Org. Chem., 24, 300 (1959).

38. A. P. Stefani and M. Szwarc, J. Am. Chem. Soc., 84, 3661 (1962).

39. C. Walling and A. Padwa, J. Am. Chem. Soc., 84, 2845 (1962).

40. P. S. Skell, R. G. Allen and N. D. Gilmour, J. Am. Chem. Soc., 83, 504 (1961).

41. L. Palfray and B. Rothstein, *Compt. rend.*, *190*, 189 (1930).

42. R. Cornubert, A. Rio and P. Senechal, *Bull. soc. chim. France*, 46 (*1955*).

43. M. S. Kharasch, J. S. Sallo and W. Nudenberg, *J. Org. Chem.*, *21*, 129 (1956).

44. W. G. Dauben and K. S. Pitzer, Conformational Analysis, in M. S. Newman, ed., "Steric Effects in Organic Chemistry," 1. John Wiley and Sons, Inc., New York, N. Y., 1956.

45. K. Kozima and T. Yoshino, *J. Am. Chem. Soc.*, *75*, 166 (1953).

46. L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry". Pergamon Press, New York, N. Y., 1959.

47. R. U. Lemieux, R. K. Kulling, H. J. Bernstein and W. G. Schneider, *J. Am. Chem. Soc.*, *80*, 6098 (1958).

48. A. Atkinson and O. Hassel, *Acta Chem. Scand.*, *13*, 1737 (1959).

49. E. Halmoy and O. Hassel, *Z. physik. Chem.*, *B18*, 234 (1932).

50. K. Kozima, K. Sakashita and S. Maeda, *J. Am. Chem. Soc.*, *76*, 1965 (1954).

51. W. Kwestroo, F. A. Meijer and E. Havinga, *Rec. trav. chim.*, *73*, 717 (1954,.

52. F. A. L. Anet, *Can. J. Chem.*, *39*, 2262 (1961).

53. (a) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, *84*, 793 (1962).

    (b) F. A. L. Anet, *J. Am. Chem. Soc.*, *84*, 747 (1962).

54. H. J. Lucas and C. W. Gould, Jr., *J. Am. Chem. Soc.*, *63*, 2541 (1941).

55. B. Carroll, D. G. Kubler, H. W. Davis and A. M. Whaly, *J. Am. Chem. Soc.*, *73*, 5382 (1951).

56. K. A. Seagebarth, *J*. *Org*. *Chem*., *25*, 2212 (1960).

57. (a) W. G. Young, H. K. Hall and S. Winstein, *J*. *Am*. *Chem*. *Soc*., *78*, (1956).

(b) L. N. Owen and P. N. Smith, *J*. *Chem*. *Soc*., 4035 (*1952*).

58. (a) K. von Auwers, *Ann*., *420*, 84 (1920).

(b) A. Skita, *Ber*., *53*, 1792 (1920).

(c) A. Skita and W. Faust, *Ber*., *64*, 2878 (1931).

59. E. V. Albred, J. Sonnenberg and S. Winstein, *J*. *Org*. *Chem*., *25*, 26 (1960).

60. G. A. Olah and W. S. Tolgyesi, *J*. *Am*. *Chem*. *Soc*., *83*, 5031 (1961).

61. (a) N. C. Deno, H. G. Richey, J. D. Hodge and M. J. Wisotsky, *J*. *Am*. *Chem*. *Soc*., *84*, 1498 (1962).

(b) N. C. Deno, H. G. Richey, J. S. Liu, J. D. Hodge, J. J. Houser and M. J. Wisotsky, *J*. *Am*. *Chem*. *Soc*., *84*, 2016 (1962).

62. W. S. Rapson and R. Robinson, *J*. *Chem*. *Soc*., 1533 (*1935*).

63. H. L. Goering and L. L. Sims, *J*. *Am*. *Chem*. *Soc*., *77*, 3465 (1955).

64. (a) C. Walling, M. S. Kharasch and F. R. Mayo, *J*. *Am*. *Chem*. *Soc*., *61*, 1711 (1939).

(b) H. L. Goering, P. I. Abell and B. F. Aycock, *J*. *Am*. *Chem*. *Soc*., *74*, 3588 (1952).

(c) H. L. Goering and D. W. Larsen, *J*. *Am*. *Chem*. *Soc*., *79*, 2653 (1957).

65. R. E. Buckel and J. W. Long, *J*. *Am*. *Chem*. *Soc*., *73*, 998 (1951).

66. C. O. Guss and R. Rosenthal, *J*. *Am*. *Chem*. *Soc*., *77*, 2549 (1955).

67. A. A. Maryott and E. R. Smith, *National* *Bureau* *of* *Standards* *Circular*, *514*, 1 (1951).

68. T. L. Cottrel, "The Strengths of Chemical Bonds". Academic Press, Inc., New York, N. Y., 1954.

69. L. W. Reeves and K. O. Strømme, Can. J. Chem., 38, 1241 (1960).

70. (a) E. L. Eliel and R. V. Acharya, J. Org. Chem., 24, 151 (1959).

(b) R. J. Gritter and R. J. Albert, J. Org. Chem., 27, 4708 (1962).

(c) H. H. Lau and H. Hart, J. Am. Chem. Soc., 81, 4897 (1959).

(d) F. D. Greene, Chin-Chiium Chu and J. Walia, J. Am. Chem. Soc., 84, 2463 (1962).

71. T. Moeller, "Inorganic Chemistry". John Wiley and Sons, Inc., New York, N. Y., 1952.

72. R. W. Taft, Jr., Separation of Polar, Steric, and Resonance Effects in Reactivity, in M. S. Newman, ed., "Steric Effects in Organic Chemistry", 556. John Wiley and Sons, Inc., New York, N. Y., 1956.

73. P. S. Skell, R. G. Allen and N. D. Gilmour, J. Am. Chem. Soc., 83, 504 (1961).

74. P. I. Abell and L. H. Piette, J. Am. Chem. Soc., 84, 916 (1962).

75. H. L. Goering and P. W. Larsen, J. Am. Chem. Soc., 81, 5937 (1959).

76. E. S. Gould, "Mechanism and Structure in Organic Chemistry". Henry Holt and Company, Inc., New York, N. Y., 1959.

77. S. Winstein, R. Heck, S. Lapporte and R. Baird, Experimentia, 12, 138 (1956).

78. D. G. Applequist and N. D. Werner, J. Org. Chem., 28, 48 (1963).

79. G. A. Russell, J. Am. Chem. Soc., 80, 5002 (1958).

80. (a) E. S. Huyser and B. Giddings, J. Org. Chem., 27, 3391 (1962).

(b) E. S. Huyser, J. Am. Chem. Soc., 82, 5446 (1960).

81. E. A. Braude and W. F. Forbes, J. Chem. Soc., 1755 (1951).

82. H. B. Donahoe and C. A. Vanderwerf, Organic Synthesis, 30, 24 (1950).

83. H. L. Goering and F. H. McCarron, J. Am. Chem. Soc., 78, 2270 (1956).

84. M. Korack, D. R. Nielsen and W. H. Rideout, J. Am. Chem. Soc., 82, 4328 (1950).

85. A. T. Blomquist and W. G. Mayes, J. Org. Chem., 10, 134 (1945).

86. H. C. Brown and B. C. Subba Rao, J. Am. Chem. Soc., 81, 6428 (1959).

87. R. B. Moffett, Organic Synthesis, 32, 41 (1952).

88. (a) N. A. Domnin and L. I. Ukhova, J. Gen. Chem. U.S.S.R. (Eng. Transl.), 21, 577 (1951).

(b) N. A. Domnin and A. S. Beletskaya, J. Gen. Chem. U.S.S.R. (Eng. Transl.), 24, 1015 (1954).

89. M. S. Newman and C. A. Vanderwerf, J. Am. Chem. Soc., 67, 233 (1945).

90. W. C. Johnson and C. A. Haskew, Inorganic Synthesis, 1, 26 (1939).

91. (a) W. Nudenberg and L. W. Butz, J. Am. Chem. Soc., 66, 307 (1944).

(b) R. C. Olberg, H. Pines and V. N. Ipatief, J. Am. Chem. Soc., 66, 1096 (1944).

92. (a) L. N. Owen and P. A. Robins, J. Chem. Soc., 320 (1949).

(b) E. A. Fehnel, S. Goodyear and J. Berkowitz, J. Am. Chem. Soc., 73, 4978 (1951).

93. T. W. Lunney, A. M. Whaley and H. W. Davis, J. Am. Chem. Soc., 74, 3428 (1952).

94. B. Rothstein, *Ann. chim.*, Series 10, *14*, 461 (1930).

95. C. A. Grob and A. Gagneux, *Helv. Chim. Acta*, *40*, 130 (1957).

96. H. M. Teeter and E. W. Bell, *Organic Synthesis*, *32*, 20 (1952).

97. G. C. Chambers and A. R. Ubbelohde, *J. Chem. Soc.*, 285 (*1955*).

98. R. F. Bridger, Directive Effects in Abstraction Reaction of Phenyl Radicals. Unpublished Ph.D. thesis. Library, Iowa State University of Science and Technology, Ames, Iowa, 1963.

99. W. H. Rauscher, *Ind. Eng. Chem.*, *Anal. Ed.*, *9*, 296 (1937).

100. C. C. Price, The Alkylation of Aromatic Compounds by the Friedel Crafts Method, in R. Adams, ed., "Organic Reactions", Vol. 3, 1. John Wiley and Sons, Inc., New York, N. Y., 1946.

101. L. F. Fieser, "Experiments in Organic Chemistry", 3rd ed. D. C. Heath and Company, Boston, Mass., 1955.

102. (a) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, *97*, 379 (1932).

(b) V. Protiva, J. Pliml, M. Borovicka and V. Rericha, *Chem. Listy*, *46*, 346 (1952).

103. J. von Braun and L. Neuman, *Ber.*, *50*, 50 (1917).

104. W. Schlenk and E. Bergman, *Ann.*, *479*, 58 (1930).

105. J. von Braun, *Ber.*, *43*, 2837 (1910).

106. (a) M. M. G. Austerwell and G. Corin, *Compt. rend.*, *150*, 1693 (1910).

(b) K. v. Auwers and O. Jordan, *Biochem. Z.*, *144*, 31 (1924).

107. J. B. Conant and W. R. Korner, *J. Am. Chem. Soc.*, *46*, 232 (1924).

108. R. F. Nystron and W. G. Brown, *J. Am. Chem. Soc.*, *69*, 1197 (1947).

109. H. Adkins and R. Connor, *J. Am. Chem. Soc.*, *53*, 1091 (1931).

ACKNOWLEDGMENTS

The author wishes to express sincere appreciation to Professor Glen A. Russell for suggestions of the problem, for the guidance, and the patience during the course of the work.

The author also wishes to express gratitude to Dr. R. W. King for determining n.m.r. spectra and for useful advice, and to Dr. D. G. Hendry and the other members of the Russell group for helpful suggestions.

The financial support of Petroleum Research Fund, Procter and Gamble, and Union Carbide Corporation has been helpful and is much appreciated.