NUCLEAR MAGNETIC RESONANCE STUDIES

OF SOME

1,1-DIFLUORO-3-PHENYLCYCLOBUTANE DERIVATIVES

Thesis by

Masaaki Takahashi

In Partial Fulfillment of the Requirement

For the Degree of

Master of Science

in Chemistry

California Institute of Technology

Pasadena, California

1962

ABSTRACT

1, 1-Difluoro-2, 2-dichloro-3-methyl-3-phenylcyclobutane has been prepared by the cycloaddition of α-methylstyrene to 1,1-difluoro-2, 2-dichloroethylene. A 2 cps long-range H-F spin-spin coupling has been observed over five consecutive saturated bonds in 1,1-difluoro-2, 2-dichloro-3-methyl-3-phenylcyclobutane, involving one of the fluorines at the 1-position and the protons of the 3-methyl group. Analysis of the spectrum and that of the stereospecifically labeled 4-deutero derivatives suggest that the fluorine involved is the one cis to the methyl group.

The n. m. r. studies of 1,1-difluoro-3-bromo-3-phenylcyclobutane which was obtained by bromination of 1,1-difluoro-3-phenylcyclobutane with N-bromosuccinimide indicate that this molecule has on the average a more nearly planar cyclobutane ring than that of 1,1-difluoro-2, 2-dichloro-3-methyl-3-phenylcyclobutane. The four protons of the 2- and 4-positions are nearly magnetically equivalent, so that the spectrum of this compound is almost that of an ABX_4 system rather than an ABX_2Y_2 system. The theoretical calculations suggest that the chemical shift difference between X and Y is on the order of 1-2 cps. The chemical shift difference between the fluorines decreases in 1,1-difluoro-2, 2-dichloro-3-methyl-3-phenylcyclobutane and 1,1-difluoro-3-bromo-3-phenylcyclobutane with increasing temperature, suggesting that rapid ring-inversion is taking place.

ACKNOWLEDGMENT

TABLE OF CONTENTS

INTRODUCTION

Cycloaddition reactions of alkene to alkene and alkene to alkyne are important synthetic pathways to four-membered carbon ring systems (1, 2, 3).

Particularly, the cycloaddition of fluoroalkenes to alkenes give fluorinated cyclobutane derivatives that would be very difficult to synthesize by conventional methods (3, 4). 1,1-Difluoro-2,2-dichloro-3-phenylcyclobutane has been prepared by cycloaddition of styrene to 1,1-difluoro-2,2-dichloroethylene (4).

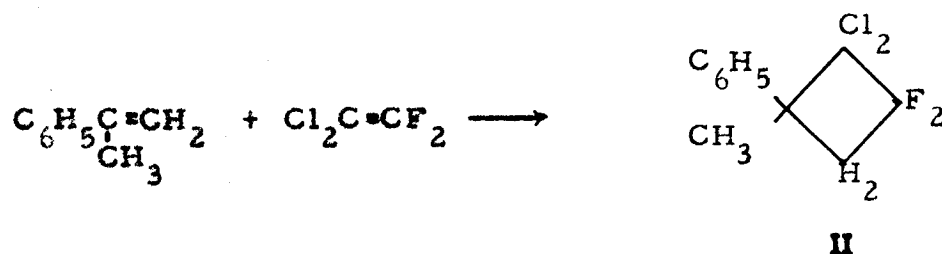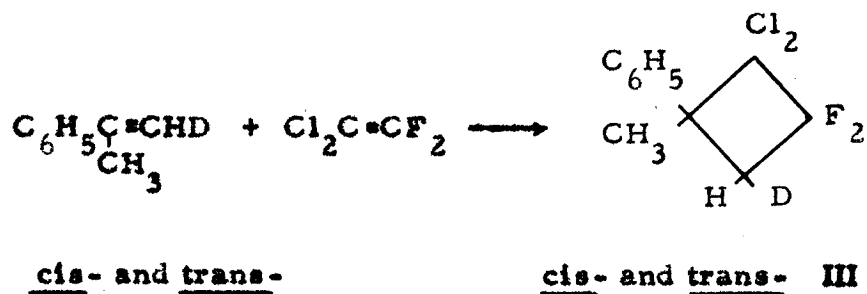$$C_6H_5CH{=}CH_2 + Cl_2C{=}CF_2 \longrightarrow$$

I
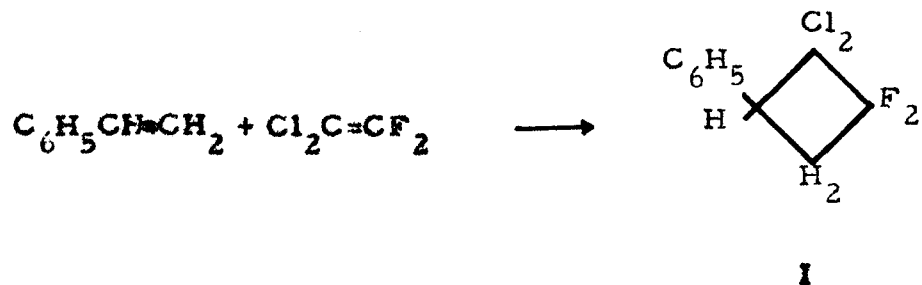
The structure of I for the adduct has been well established (3, 4). The orientation produced in this reaction has been explained on the basis of a diradical mechanism by Roberts and Sharts (3).

$$C_6H_5CH=CH_2 + Cl_2C=CF_2 \longrightarrow$$

Ia   or   Ib

I
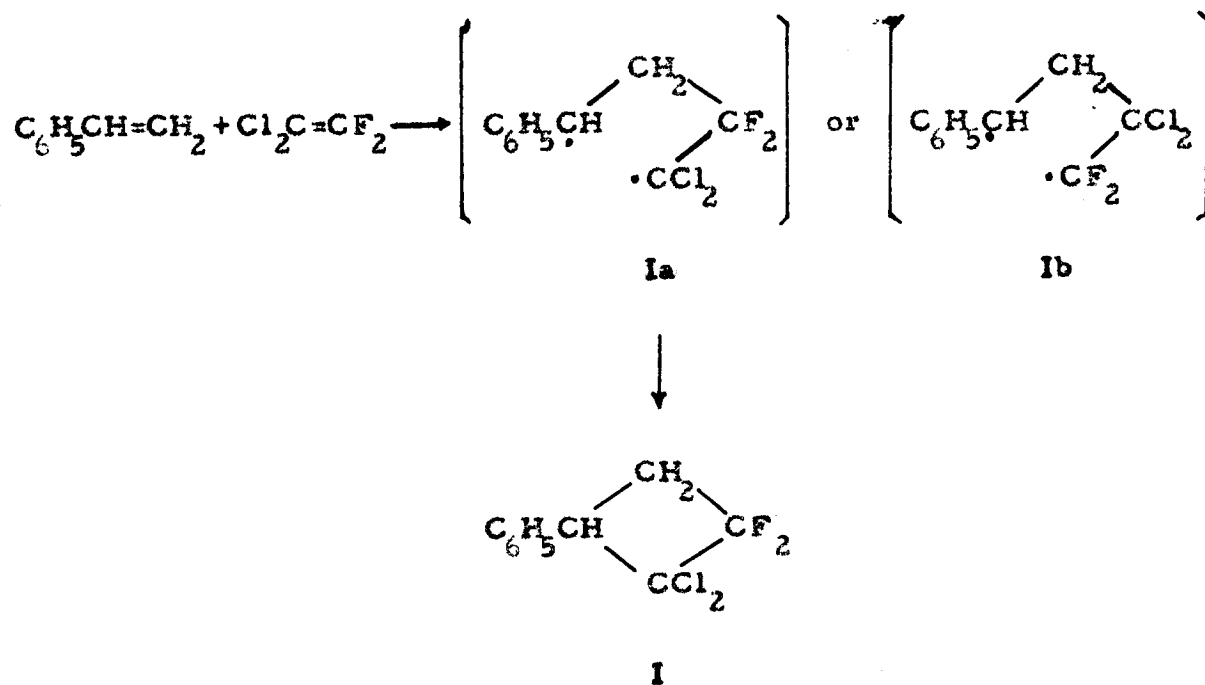
The intermediate diradical Ia is considered to be more favorable than Ib, since a difluoromethyl radical should be less stable than a dichloromethyl radical. (5).

Substituted styrenes also undergo cycloaddition reactions. In the present work, 1,1-difluoro-2,2-dichloro-3-methyl-3-phenylcyclobutane and cis- and trans-4-deutero derivatives have been prepared by addition of α-methylstyrene and cis- and trans-β-deutero-α-methylstyrene to 1,1-difluoro-2,2-dichloroethylene.

$$C_6H_5\overset{|}{\underset{CH_3}{C}}=CH_2 + Cl_2C=CF_2 \longrightarrow$$

II

$$C_6H_5\overset{\underset{\displaystyle CH_3}{|}}{C}=CHD \ + \ Cl_2C=CF_2 \ \longrightarrow$$


cis- and trans-   cis- and trans-   III

Structures II and III for the adducts have been assigned on the basis of n.m.r. spectra and analogy with the formation of 1,1-difluoro-2,2-dichloro-3-phenylcyclobutane.

The theoretical calculations of n.m.r. spectra have proved extremely useful for analysis of complex spectra. A program suitable for use with an IBM 7090 computer has been developed by Wiberg and Nist (6), which produces theoretical energies and intensities for all of the possible transitions corresponding to a given set of chemical shifts and coupling constants for up to seven nuclei with spin of 1/2. A satisfactory match between calculated and experimental spectra was achieved for 1,1-difluoro-2,2-dichloro-3-methyl-3-phenylcyclobutane and 1,1-difluoro-3-bromo-3-phenylcyclobutane.

1,1-Difluoro-2,2-dichloro-3-methyl-3-phenylcyclobutane

1,1-Difluoro-2,2-dichloro-3-methyl-3-phenylcyclobutane (II)

was prepared by heating a mixture of α-methylstyrene and 1,1-difluoro-

2,2-dichloroethylene in a sealed tube at 130° for 24 hours. Structure II

for the adduct rather than 1,1-difluoro-2,2-dichloro-4-methyl-4-

phenylcyclobutane is in good agreement with the magnitudes of the

coupling constants between the methylene protons and the gem-fluorines.

It is also supported by analogy to formation of 1,1-difluoro-2,2-dichloro-

3-phenylcyclobutane (3).

$$Cl_2$$
$$C_6H_5$$
$$CH_3$$
$$F_2$$
$$H_2$$
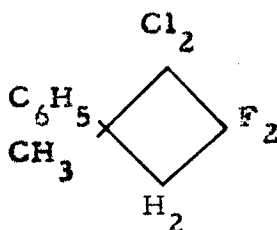
II

The fluorine n. m. r. spectrum of II shows the resonances of two non-

equivalent fluorines $(F_1$ and $F_2)$ with a chemical shift difference of

435 cps, each split by the F_1-F_2 coupling $(J_{12} = 187$ cps) and couplings

with the two nonequivalent methylene protons attached to the 4-carbon

$(J_{HF_1} = 1.9$ and 9.5 cps, $J_{HF_2} = 13.2$ and 20.3 cps) (Fig. 1A).

In addition, the higher field fluorine resonance shows further splitting

into 1:3:3:1 quartets with $J = 2.0$ cps (Fig. 1C). This strongly implies

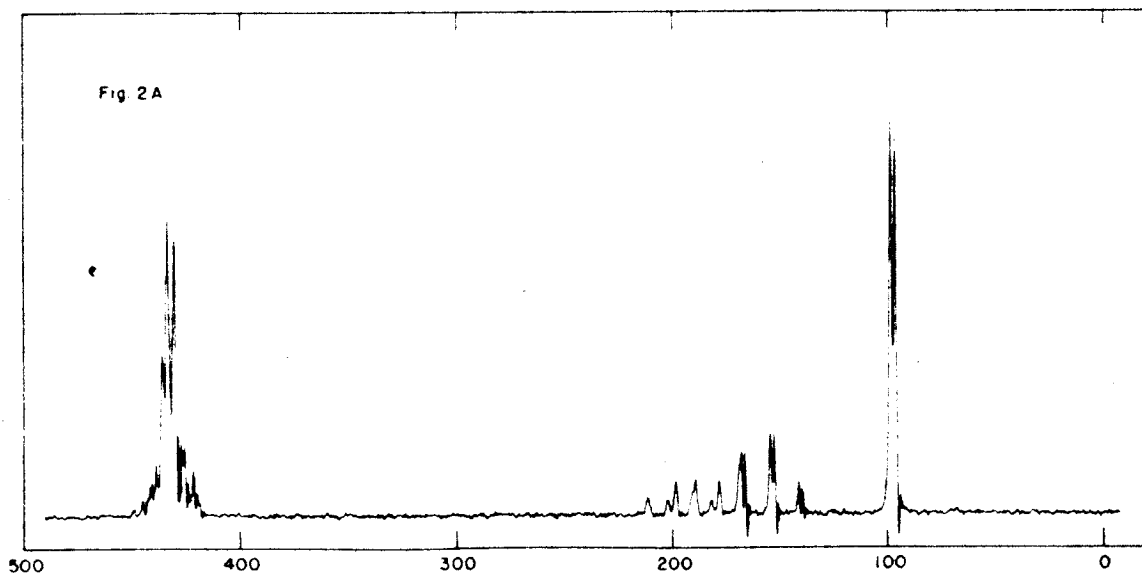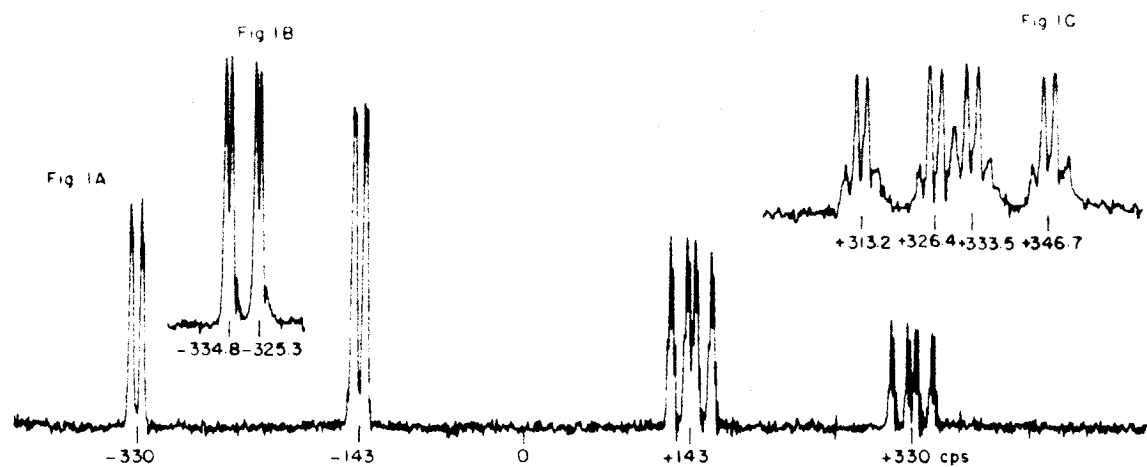a coupling with three equivalent protons, presumably with the protons

Fig. 1. Fluorine n.m.r. spectra (56.4 Mc.)

    1A. 1,1-Difluoro-2,2-dichloro-3-phenyl-3-methylcyclobutane (II)
    1B. The low-field fluorine resonance of II.
    1C. The high-field fluorine resonance of II.

Fig. 2A. Proton n.m.r. spectrum of II (60 Mc.)
        The calibration is cps downfield from tetramethylsilane

of the methyl group at the 3-position and, indeed, the proton n.m.r.
spectrum of II shows a doublet methyl resonance with J = 2.1 cps
(Fig. 2A). Several long-range H-F spin-spin couplings have been re-
ported (7,8) but couplings over five consecutive saturated single bonds
appear to be previously unknown.

This five-bond, H-F coupling is indicated to be a cis-interaction
by the following rather involved argument. First, the methylene
resonances consist of sixteen peaks as shown in Figure 2B. The sum
of relative areas of the eight low-field peaks is equal to that of the eight
high-field peaks and, therefore, each group has been considered to
represent separate methylene protons designated as H_3 (low-field) and
H_4 (high-field), respectively.

Three different coupling constants are found for each proton; i.e.,
13.1, 9.4, and 20.5 cps for H_3 and 13.1, 1.8, and 13.7 cps for H_4. A
series of theoretical calculations demonstrated that the spectrum is well
fitted by taking J_{13} = 9.4 cps, J_{14} = 1.8 cps, J_{23} = 20.5 cps, J_{24} = 13.7
cps, and J_{34} = 13.1 cps (Fig. 2C). The theoretical calculations were
set up for the two protons and two fluorines as an ABXY system having
different combinations of observed chemical shifts and coupling constants
using the program described by Wiberg and Nist (6) on an IBM 7090
computer.

It is possible to draw two conformers of II (II_A and II_B) if it is
assumed that the cyclobutane ring is nonplanar. These would be expected

Fig 2B

220 210 200 190 180 170 160 150 140

Fig 2C

216 23 206 56 203 3 196 36 193 44 186 79 183 29 173 68 173 15 170 63 160 02 159 75 157 50 157 16 146 67 144 06
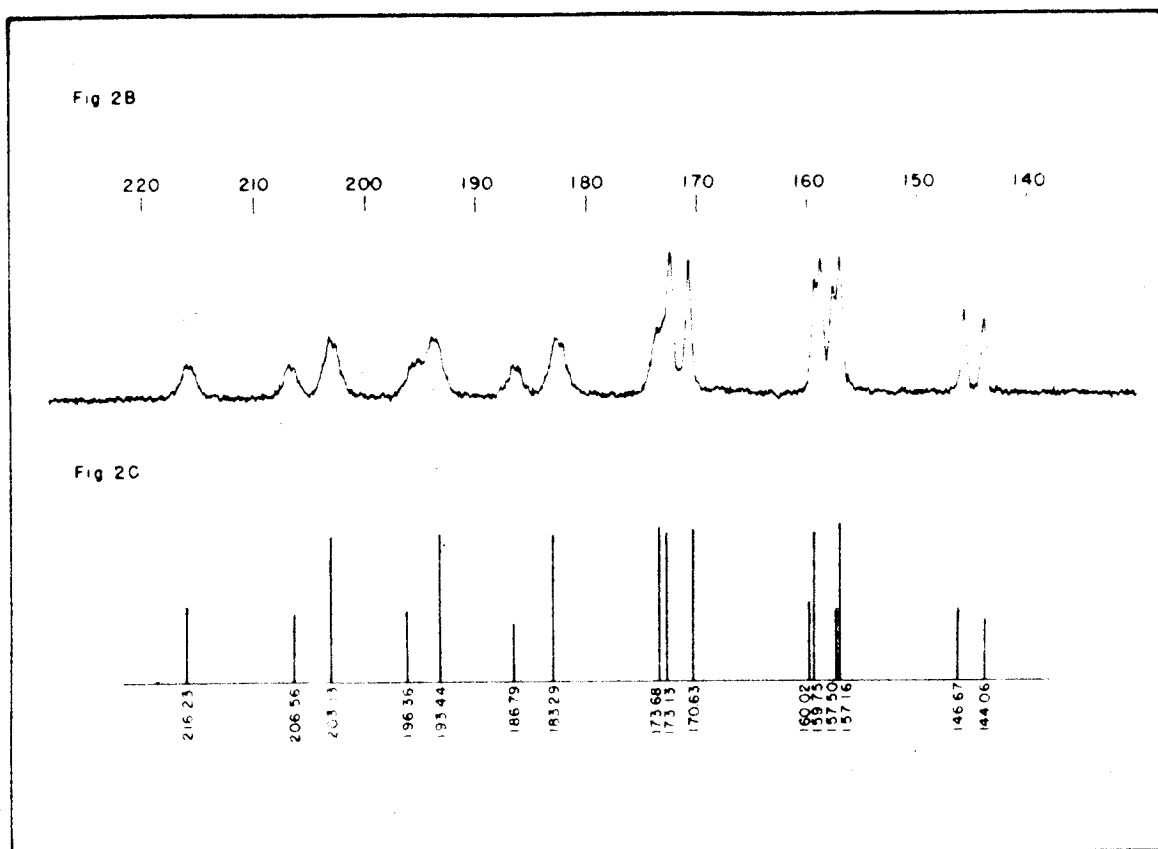
Fig. 2B. The methylene resonances of II (60 Mc.)
The calibration is cps downfield from tetramethylsilane
and the total chart width equal to 100 cps.

Fig. 2C. Calculated methylene resonances of II.

to have "axial" and "equatorial" groups like those of cyclohexane, and of the two, II_A with the phenyl group "equatorial" and the methyl group "axial" is likely to be favored. The degree of puckering of the ring is probably considerable since the chemical shift difference between the fluorines (435 cps) is about half of the 874 cps difference between the fluorines of 1,1-difluorocyclohexane when this substance undergoes slow ring-inversion at -80° (16).
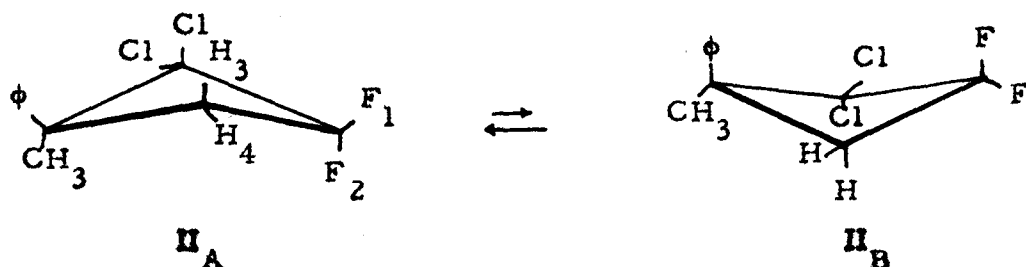
It has been observed that <u>trans</u> (axial-axial) couplings between protons on neighboring carbon atoms in saturated ring systems are larger than <u>gauche</u> (axial-equatorial or equatorial-equatorial) couplings (9). Similar arguments appear to apply to H-F couplings (3). On this basis, one can take F_2 to be <u>trans</u> to H_3. The whole argument hinges on this point, if further analysis should show that <u>trans</u> H-F couplings tend to be smaller than the corresponding <u>gauche</u> couplings, then the assignment here has to be reversed.

The stereochemical relationships of H_3 and H_4 with respect to the phenyl group have been established by substitution of deuterium at the 4-position. Mixtures of II and <u>trans</u>-4-deutero-1,1-difluoro-2,2-
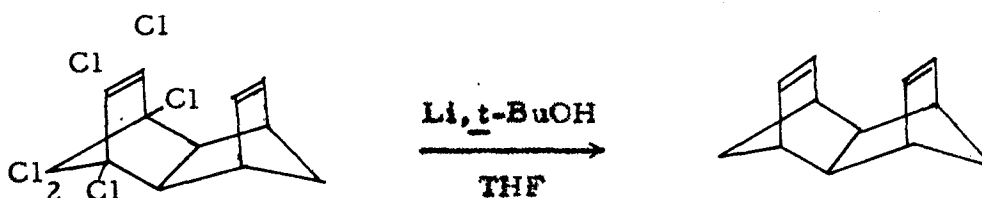
dichloro-3-methyl-3-phenylcyclobutane (trans-III) and cis-4-deutero-1,1-difluoro-2,2-dichloro-3-methyl-3-phenylcyclobutane (cis-III) have been synthesized by addition of trans- and cis-,,-deutero-α-methylstyrene (10) to 1,1-difluoro-2,2-dichloroethylene.

trans-III   cis-III
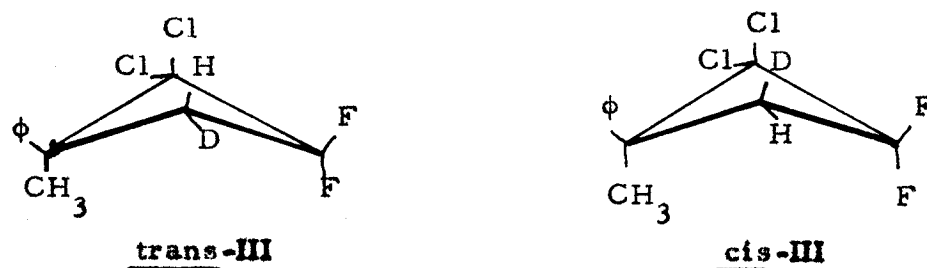
The total area of the low-field methylene peaks was larger than that of the high-field methylene peaks for the mixture in which trans-III predominated. The high-field methylene proton H_4 is therefore trans, and low-field methylene proton H_3 cis to the phenyl group. The complete assignment of chemical shifts is then as in II_A and the long-range coupled fluorine (F_2) is cis to the methyl group. The five-bond H-F coupling may well be exerted through space (8,11) instead of through the bonds, particularly because groups involved are expected to be rather close together in space.

Reaction of 1,1-Difluoro-2,2-dichloro-3-methyl-3-phenylcyclobutane
with Lithium and t-Butyl Alcohol

Winstein (12) has achieved smooth removal of chlorine in some
cyclic systems by treating with lithium metal and t-butyl alcohol in
tetrahydrofuran.

The method has been applied to 1,1-difluoro-2,2-dichloro-3-methyl-
3-phenylcyclobutane (II) in hope of preparing 1,1-difluoro-3-methyl-
3-phenylcyclobutane (IV). Rather vigorous reaction occurred at 45°,
and a colorless oil of b.p. 40-40.5° was obtained. This product gave
a positive unsaturation test, and its infrared spectrum also suggested
the presence of a double bond. The proton n.m.r. spectrum showed
phenyl-, vinyl-, methylene-, and methyl resonances in the approximate
ratio of 5:1:2:3 (Fig. 3A). The fluorine n.m.r. spectrum showed only
one fluorine resonance which was split into a broad 1:3:3:1 quartet (Fig.
3B). On this basis, the product is considered to be 1-fluoro-3-methyl-
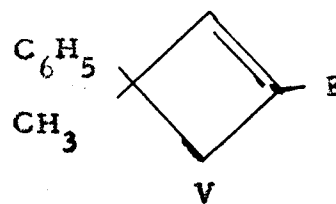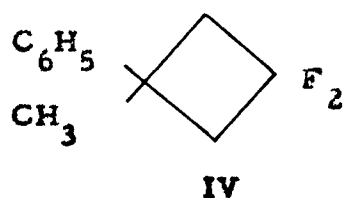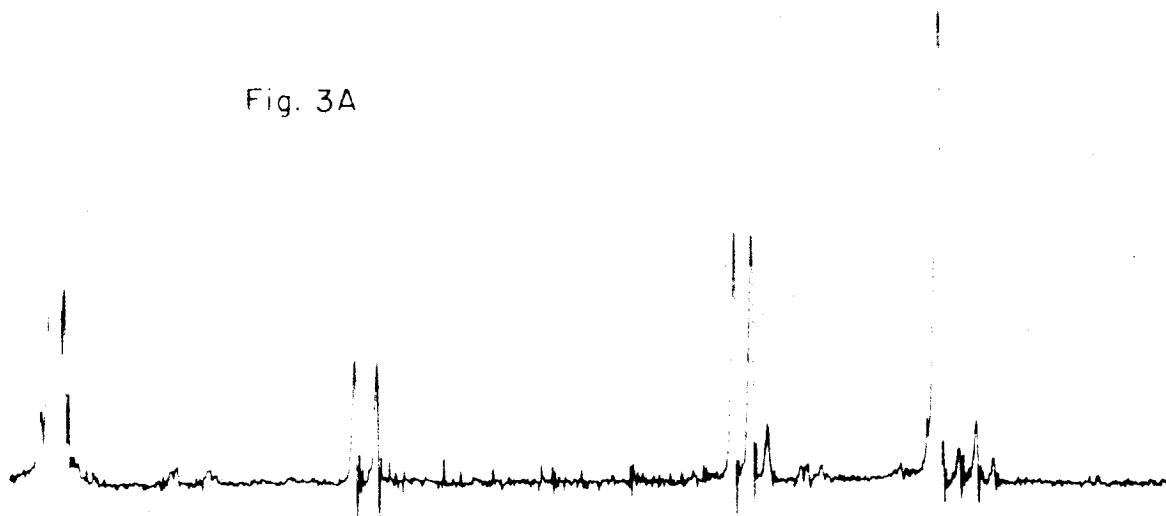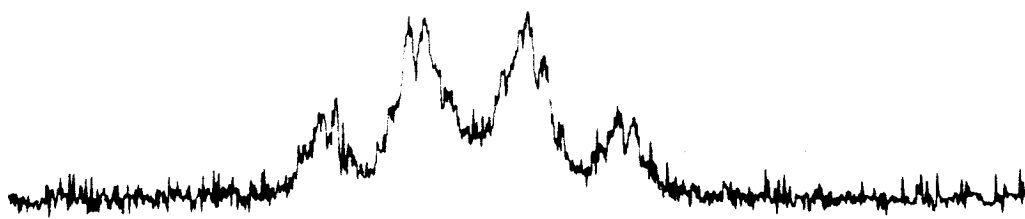3-phenylcyclobutene-1 (V).

Fig. 3A

Fig. 3B

Fig. 3A. The proton n. m. r. spectrum of **V** (60 Mc.)

Fig. 3B. The fluorine n. m. r. spectrum of **V** (56. 4 Mc.)

1,1-Difluoro-3-bromo-3-phenylcyclobutane

Knutson (13) and Vogel (14) attempted the synthesis of 1,1-difluoro-3-bromo-3-phenylcyclobutane (VI) by bromination of 1,1-difluoro-3-phenylcyclobutane (VII) with N-bromosuccinimide in carbon tetrachloride, but they were unable to isolate VI in pure form. A successful preparation was later achieved by Manatt (15).
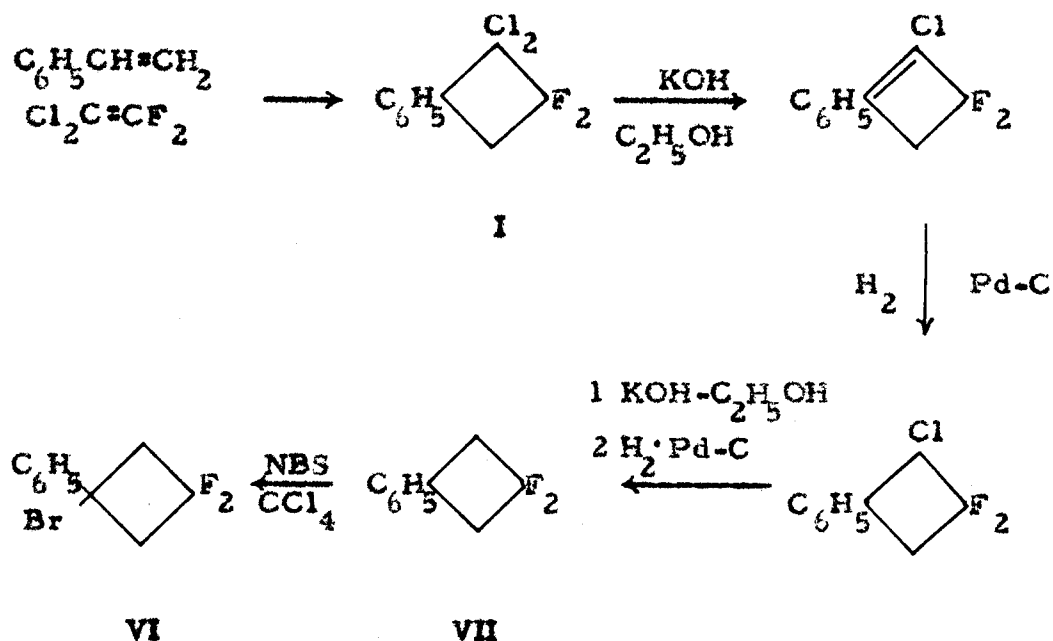
The n.m.r. spectrum of VI has not been carefully analyzed heretofore. Manatt (15) only reported that the proton spectrum showed broad triplet methylene peaks. The fluorine n.m.r. spectrum was not taken.

In the present research, both proton and fluorine n.m.r. spectra of VI have been taken of pure samples under high resolution. The proton spectrum shows 1:1:1:1 quartet methylene resonances with the two

different coupling constants of 10.1 cps and 12.4 cps (Fig. 4A). The

fluorine spectrum shows two pairs of quintets corresponding to two

non-equivalent fluorines (F_1 and F_2) with a chemical shift difference

of 225 cps. Each resonance is split by the F_1-F_2 coupling ($\underline{J}$ = 192 cps)

and coupling with the four nearly equivalent methylene protons of the

2- and 4- positions ($\underline{J}_{HF_1}$ = 10.2 cps and $\underline{J}_{HF_2}$ = 12.2 cps) (Fig. 4B).

The n.m.r. spectrum of VI was expected to be that of an

ABX_2Y_2 system, such that A,B represent the two nonequivalent fluorines

F_1 and F_2, and X_2Y_2 represent two pairs of nonequivalent protons.

However, the actual spectrum suggests that the chemical shift differ-

ence between X and Y is so small that the spectrum is very nearly

that of an ABX_4 system.

A series of theoretical calculations has been made on the basis

of an ABX_2Y_2 system varying the coupling constants and chemical

shifts. Comparison of calculated and experimental spectra suggests

that the degree of nonequivalence of X, Y is small and, since the H-F

coupling constants are close to one another, the methylene resonances

appear as quartets consisting of many closely spaced bands which cannot

be resolved in the actual spectrum. The quintet splitting of the fluorine

spectrum can be explained on the same basis. The chemical shift

difference between X and Y is considered to be the order of 1-2 cps;

e.g. the spectrum is well fitted by taking $\underline{J}_{AX}$ = 9.9 cps, $\underline{J}_{AY}$ = 10.3
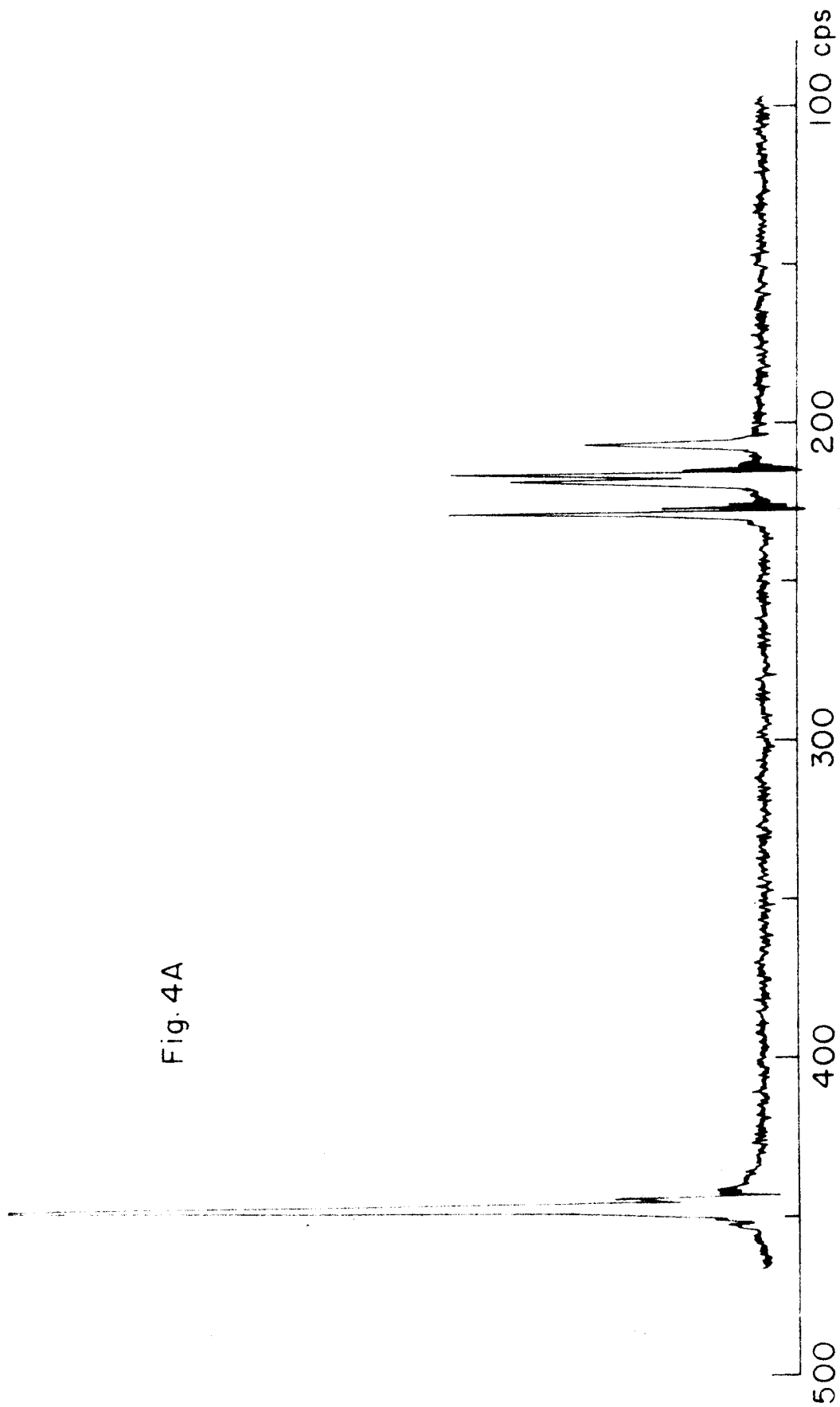
Fig. 4A. The proton n.m.r. spectrum of VI (60 Mc.)
The calibration is cps downfield from tetramethylsilane.

Fig. 4B

−32. −52.5 −70.' +28.1 +52.5 +70.9
−42.3 −60.7 +4..3 +64.7

−244.5 −52.5 0 +52.5 +244.5

Fig. 4C

−399 +399

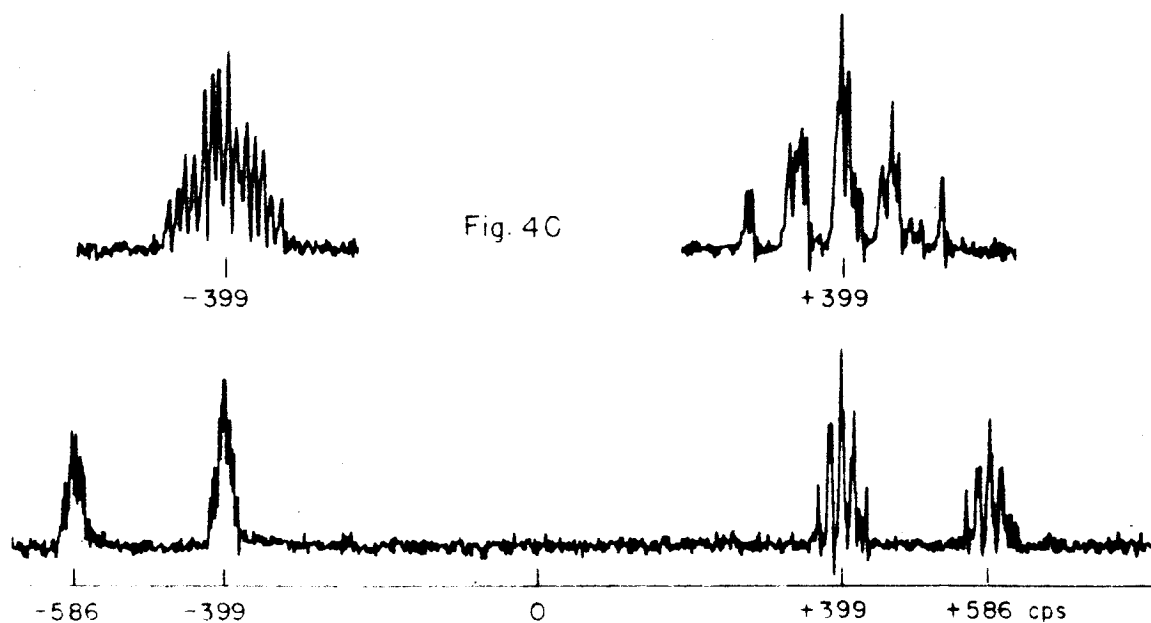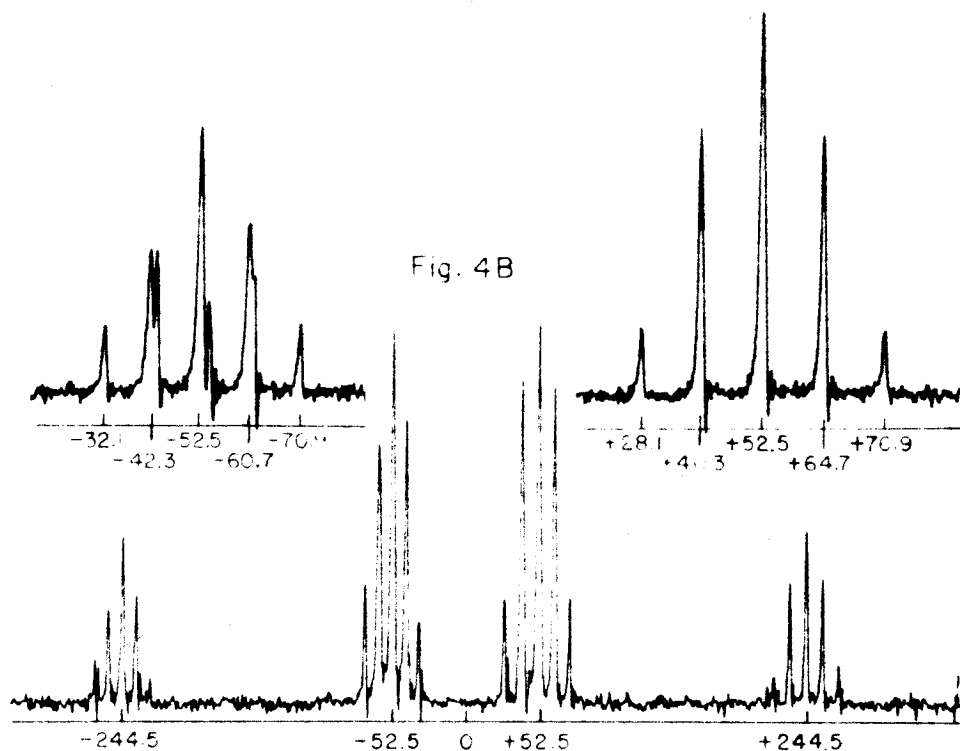−586 −399 0 +399 +586 cps

Fig. 4B. The fluorine n. m. r. spectrum of **VI** (56. 4 Mc.)

Fig. 4C. The fluorine n. m. r. spectrum of
1, 1-difluoro-3-phenylcyclobutane (56. 4 Mc.)

cps, $J_{BX} = 12.3$ cps, $J_{BY} = 12.5$ cps, $J_{XY} = 13.0$ cps, and

$\Delta \nu_{XY} = 1.0$ cps.

From these observations, it may be deduced that the cyclobutane ring of VI is likely to be on the average nearly planar. This seems to be reasonable since the chemical shift difference between the fluorines (225 cps) is small compared with the 966 cps difference between the fluorines of 1,1-difluoro-3-phenylcyclobutane (Fig. 4C). If we assume that the chemical shift difference between the fluorines is independent of whether a 3-bromine or 3-hydrogen is present in 1,1-difluoro-3-phenylcyclobutane except insofar as they might affect the conformational equilibria, then if the compound with the 3-hydrogen exists almost exclusively with the phenyl equatorial, the 3-bromo compound has the phenyl equatorial an average of 60% of the time.

Temperature Dependence of the Fluorine Chemical Shift in
1,1-Difluoro-3-phenylcyclobutane Derivatives

The variation of the n.m.r. spectra with temperature can often distinguish between the slow and rapid ring-inversion of cyclic conformers. Thus if the apparent chemical shifts are temperature dependent, rapid ring-inversion is indicated. (17)

The temperature dependence of the fluorine chemical shift in 1,1-difluoro-2,2-dichloro-3-methyl-3-phenylcyclobutane (II) and 1,1-difluoro-3-bromo-3-phenylcyclobutane (VI) has been investigated. In the both compounds, the chemical shift difference between the fluorines decreases considerably with increasing temperature. However, the fluorine-fluorine coupling constants are almost unchanged with temperature. Table 1 shows the chemical shift differences between the fluorines of several gem-difluoro compounds at various temperatures.

Unsymmetrically substituted cyclobutane systems, for example, 1,1-difluoro-3-phenylcyclobutane derivatives, are likely to be nonplanar; there exists a ring-inversion between the two conformers, A and B. However, if the ring-inversion frequency is sufficiently high to average the environment of the fluorine atoms, one can only observe an average structure C in the fluorine n.m.r. spectrum.

Table 1

Compound	Temperature, °C	Fluorine Chemical Shift Difference (cps)[*]
1,1-Difluorocyclohexane	-80	874
1,1-Difluoro-3-phenyl- cyclobutane (VII)	25	966
1,1-Difluoro-2,2-dichloro- 3-methyl-3-phenyl- cyclobutane (II)	31	435
	194	383
1,1-Difluoro-3-bromo-3- phenylcyclobutane (VI)	31	225
	99	168
1,1-Difluoro-2,2-dichloro-3- phenylcyclobutane (I)	25	550**

[*] at 56.4 Mc

** calculated from the fluorine spectrum of I taken at 40 Mc

A   B

X = H, CH_3, Br

C
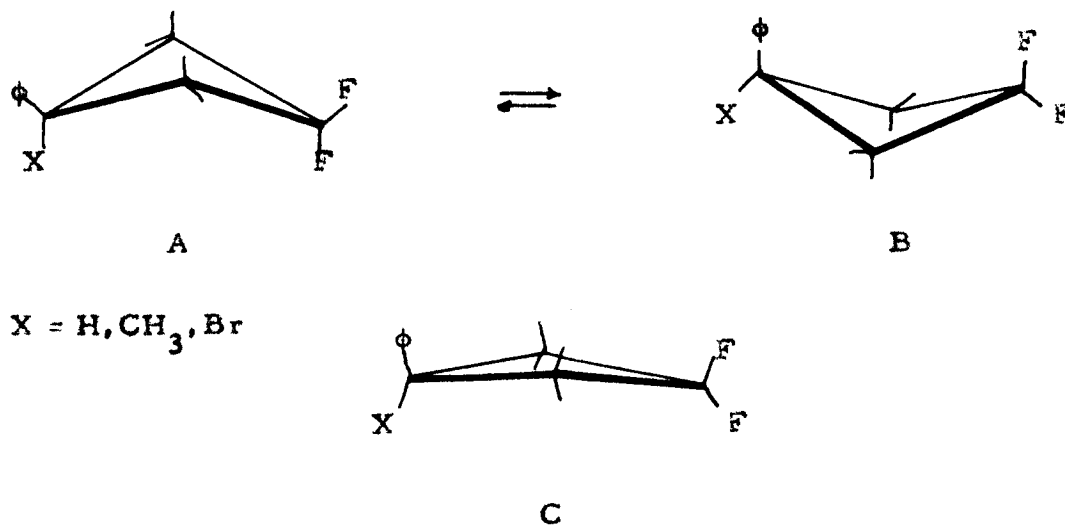
Then the chemical shift will be averaged over the two conformers,

$$\delta = c_1 \delta_1 + c_2 \delta_2$$

where c_1, c_2 are the fractional populations. If the two conformers have different energies, E_1 and E_2,

$$\frac{c_1}{c_2} = \frac{ae^{-E_1/kT}}{be^{-E_2/kT}}$$

where a, b are temperature independent coefficients. If it is assumed that $E_1 \ll E_2$ so that $c_1 \simeq 1.0$ and $c_2 \simeq 0$ in 1,1-difluoro-3-phenyl-cyclobutane, one can calculate approximate fractional populations of II and VI taking $v_1 = 966$ cps, $v_2 = -966$ cps for VI and $v_1 = 550$ cps, $v_2 = -550$ cps for II.

On this basis, there exist 90% of conformer A and 10% of conformer B in II, and 60% of conformer A and 40% of conformer B in VI at the room temperature. Thus the degree of nonplanarity of the average structure IIC is likely to be considerable, and, on the other hand, the average structure VIC appears as nearly planar.

This is all wrong.
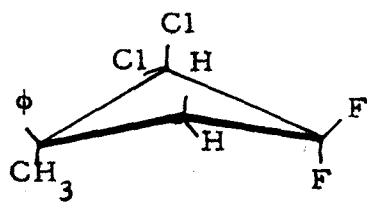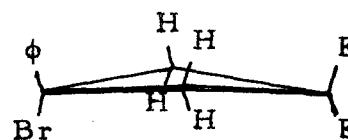
IIC   VIC

EXPERIMENTAL

<u>1, 1-Difluoro-2, 2-dichloro-3-methyl-3-phenylcyclobutane (II).</u>—
A mixture of 59 g. (0.50 mole) of α-methylstyrene and 74 g. (0.55
mole) of 1,1-difluoro-2, 2-dichloroethylene (Genetron 1112, General
Chemical Division) was heated in a sealed glass tube at 130° for 24 hr.
The tube was cooled with Dry Ice, opened, and the light-yellow oil dis-
tilled through a 10-cm. Vigreux column. The yield of crude adduct
was 66 g. (61%) of b. p. 91-98° (2.5-3.0 mm) was collected. Redistil-
lation through a 20-cm. Vigreux column gave 56 g. (52%) of product
of b.p. 84-86° (1.5 mm).

<u>Anal.</u> Calcd. for $C_{11}H_{10}F_2Cl_2$: C, 52.50; H, 3.98; Cl, 28.30.
Found: C, 52.58; H, 4.01; Cl, 28.20.

<u>trans-β-Deutero-α-methylstyrene</u> (10).— In a 200-ml. round-
bottomed three-necked flask equipped with a magnetic stirrer, helium
inlet and dropping funnel, was placed 75 ml. of anhydrous ether. A
flow of helium was passed through the flask and 1.7 g. (0.25 mole) of
lithium wire was added, followed by 21 g. (0.12 mole) of <u>trans-β-bromo-</u>
α-methylstyrene (prepared from α-methylstyrene dibromide) (10). After
a few minutes, the solution became cloudy red brown. The flask was
then cooled and maintained between -30°- -40° for 40 min. A solution
of 7.3 g. (0.12 mole) of deuteroacetic acid in 25 ml. anhydrous ether was

then added until the color disappeared. About 50% of the calculated

amount of acid was required. The reaction mixture was poured into

a beaker and combined with 100 ml. of pentane. The excess lithium

was decomposed by water. The solution was separated from the solution

of lithium salts and dried overnight over anhydrous sodium sulfate.

After the removal of solvent by evaporation, the residue was diluted

with 2 g. of pentane and chromatographed on 150 g. of acid-washed

alumina using pentane as eluent. The first 50 ml. of eluent was col-

lected. After removal of the pentane, the product was distilled through

a 10-cm. Vigreux column. There was collected 5.0 g. (42%) of color-

less oil, b.p. 82-85°, 61-62 mm.), which consisted of 18% of α-methyl-

styrene, 55% of trans-β-deutero-α-methylstyrene, and 27% of cis-β-

deutero-α-methylstyrene, as judged by electronic integration of the

appropriate peaks in its n.m.r. spectrum.

cis-β-Deutero-α-methylstyrene was prepared from cis-β-

bromo-α-methylstyrene (obtained by photo-isomerization of trans-β-

bromo-α-methylstyrene) (10). The procedure was the same as for the

trans-isomer. Analysis by n.m.r. of the product gave 36% of α-

methylstyrene, 21% of trans-β-deutero-α-methylstyrene, and 43% of

cis-β-deutero-α-methylstyrene.

trans-4-Deutero-1,1-difluoro-2,2-dichloro-3-methyl-3-phenyl-

cyclobutane (trans-III).— A mixture (5.0 g., 0.04 mole) consisting

of 18% α-methylstyrene, 55% of trans-β-deutero-α-methylstyrene and

27% of cis-β-deutero-α-methylstyrene was heated with 6.2 g. (0.05 mole) of 1,1-difluoro-2,2-dichloroethylene at 130° for 20 hr. Distillation gave 4.8 g. (45%) of adduct of b.p. 83-85° (1.5 mm). Integration of the n.m.r. peaks indicated that 45% of **II**, 36% of trans-**III**, and 18% of cis-**III** were formed.

cis-4-Deutero-1,1-difluoro-2,2-dichloro-3-methyl-3-phenylcyclobutane (cis-**III**).— A mixture of 0.4 g. (0.03 mole) of 36% of α-methylstyrene, 21% of trans-β-deutero-α-methylstyrene and 43% of the cis isomer was heated with 1,1-difluoro-2,2-dichloroethylene and gave 0.5 g. (59%) of adduct with b.p. 83-85° (1.5 mm) which by electronic integration of its n.m.r. spectrum was indicated to be 56% **II**, 12% trans-**III**, and 32% cis-**III**.

1-Fluoro-3-methyl-3-phenylcyclobutene-1 (**V**).— In a clean, dry 500-ml. three-necked flask fitted with a condenser, stirrer and helium inlet were placed 150 ml. of dry tetrahydrofuran, 25.0 g. (0.10 mole) of **II**, and 14.8 g. (0.20 mole) of anhydrous t-butyl alcohol. A flow of helium was started and 2.8 g. (0.40 g. atom) of lithium wire was added to the flask. No reaction occurred at the room temperature for 5 min. so the flask was warmed to 45° and then to 60°. The mixture began to reflux and became slightly cloudy. After 2 hr., the product was treated with a mixture of ice and water in order to decompose excess lithium. The solution was acidified with conc. hydrochloric acid and extracted four times with pentane. The pentane layer was washed with water and

dried over anhydrous magnesium sulfate overnight. After the removal of pentane and tetrahydrofuran, the residue was fractionated under reduced pressure and gave:

Frac.	b.p., °C (1 mm.)	Wt., g.
1	36-40	0.5
2	40-40.5	1.9
3	42-65	1.5
4	65-83	7.1

Fractions 3 and 4 were identified as unreacted II. Fraction 2 amounted to a 12% yield of dehalogenation product, which gave a positive permanganate test and also showed $C=C$ in its infrared spectrum. The proton n.m.r. spectrum (Fig. 3A) showed four signals assigned as phenyl, vinyl, $-C\underline{H}_2-$, and $C\underline{H}_3-$ protons. Integration of the peaks gave ratios of 5.4:1.0:1.92:2.92, respectively. The fluorine n.m.r. spectrum showed only one fluorine resonance split into broad quartet of 1:3:3:1.

<u>1,1-Difluoro-3-bromo-3-phenylcyclobutane (VI)</u>.— 1,1-Difluoro-3-phenylcyclobutane (VII) was prepared from I by elimination of hydrogen chloride followed by catalytic hydrogenation essentially as described by Manatt (15). VI was prepared from VII as follows.

In a dry 100-ml. round-bottomed flask fitted with a reflux condenser were placed 10 g. (0.06 mole) of VII, 10.6 g. (0.06 mole) of N-bromosuccinimide, 50 ml. of reagent grade carbon tetrachloride, and 0.5 g. of benzoyl peroxide. When the mixture was heated a vigorous

exothermic reaction started, following which the reaction mixture was

refluxed for 1.5 hr. The succinimide was removed by filtration, and

the carbon tetrachloride distilled under reduced pressure. The residue

was distilled through a 10-cm. Vigreux column using a magnetic stirrer

to prevent pumping. The yield of VI was 10.5 g. (71%); b. p. 87-88°

(1.5 mm).

REFERENCES

1. D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, *J. Am. Chem. Soc.*, 71, 490-496 (1946).

2. C. M. Sharts, Ph. D. Thesis, California Institute of Technology, 1959.

3. J. D. Roberts and C. M. Sharts, in A. C. Cope, Ed., "Organic Reactions," Vol. XII (in press).

4. E. F. Silversmith, Y. Kitahara, M. C. Caserio and J. D. Roberts, *J. Am. Chem. Soc.*, 80, 5840 (1958).

5. C. Walling, "Free Radicals in Solution," John Wiley, New York, 1957, p. 253.

6. K. B. Wiberg and B. J. Nist, "Theoretical NMR Spectra," W. A. Benjamin, Inc., New York, in press.

7. J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, 1959, Chap. 3.

8. D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, 83, 246 (1961).

9. J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., 1959, Chap. 8.

10. D. R. Davis and J. D. Roberts, *J. Am. Chem. Soc.*, 84 (1962), in press.

11. L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, 35, 1243 (1961).

12. S. Winstein, et al., *Chem. & Ind.*, (in press).

13. Unpublished research of D. Knutson.

14. Unpublished research of M. Vogel.

15. S. Manatt, Ph. D. Thesis, California Institute of Technology, 1959.

16. Unpublished experiments by K. Nagarajan, J. D. Roberts, Journal of Vsesouznoe Chemical Society, (in press).

17. Reference 9, Chap. 13.

18. The author is indebted to Mr. L. Sloan of the Jet Propulsion Laboratory for his assistance with the theoretical NMR spectra calculations on an IBM 7090 computer.