

Nuclear Magnetic Resonance Studies of 1,3-Butadienes. IV. H,H and H,F Couplings in Some Cyclic Model Compounds¹

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Abstract: The high-resolution proton magnetic resonance spectra of 6-methyl-6-acetoxycyclohexadien-2,4-one (I), 4-fluoro-6-methyl-6-acetoxycyclohexadien-2,4-one (II), and eucarvone (III) have been recorded and analyzed in terms of chemical shifts and coupling constants. The magnitudes of $^3J_{HH}$, $^3J_{HF}$, $^4J_{HH}$, and $^4J_{HF}$ in these and other cyclic systems are discussed and their usefulness in conformational studies is evaluated.

In order to study rotational isomerism in butadienes and substituted butadienes by nmr spectroscopy it is desirable to have information relating the magnitude of 3J_s and 4J_s coupling constants across the central single bond to the dihedral angle between the planes containing the vinyl groups, and to any other factors affecting these coupling constants. Most acyclic butadienes unsubstituted in C-2 and C-3 appear to be in the *s-trans* conformation and to yield values for 3J_s and 4J_s appropriate to this geometry. A few cases of cyclic butadienes have been examined, and three more are added in this paper.

The choice of compounds for study was dictated by several considerations: (1) the compounds were relatively easily available in a state of good purity, (2) they involved six- and seven-membered rings without unduly strained structures, so that the geometry might readily be estimated, and (3) they yielded spectra amenable to analysis. The three compounds 6-methyl-6-acetoxycyclohexadien-2,4-one (I), 4-fluoro-6-methyl-6-acetoxycyclohexadien-2,4-one (II), and eucarvone (2,6,6-trimethylcycloheptadien-2,4-one, III) met these criteria.

In practice, compound I proved to be somewhat difficult to analyze exactly, because of the small chemical shift between protons 3 and 4. In order to obtain an unambiguous value for J_{24} , the dideuterio derivative was prepared by synthesis from 2-methylphenol-4,6- d_2 (obtained from *o*-cresol by acid-catalyzed exchange with deuterium oxide). An interfering long-range coupling between the methylene and olefinic protons in eucarvone (III) was largely removed by base-catalyzed deuterium exchange to yield eucarvone-7,7- d_2 .

Experimental Section

6-Methyl-6-acetoxycyclohexadien-2,4-one. The compound was synthesized according to the directions of Wessely and Sinwel,² mp 67.5–68° (lit.² 67–68.5°), yield 517 mg from 10 g of *o*-cresol, or 4%.

6-Methyl-6-acetoxycyclohexadien-2,4-one-2,4- d_2 . Heavy water (50 g), 4 ml of PBr₃, and 5.4 g of *o*-cresol were refluxed intermittently for a total of 5 hr. After cooling, the reaction mixture was extracted with five portions of ether, which were combined and washed with water (three times), then dried over MgSO₄. The ether was evaporated under reduced pressure; the residue solidified in the freezer. The nmr spectrum showed methyl and aromatic proton signals with a ratio of areas of 3:1.95. The exchanged cresol, 4 g, was converted by Wessely and Sinwel's procedure to the cyclohexadienone, which was obtained in a yield of 780 mg (8%).

4-Fluoro-6-methyl-6-acetoxycyclohexadien-2,4-one (II). 2-methyl-4-fluorophenol,³ 5 g (0.04 mol) in 100 ml of glacial acetic acid, was heated to 60°. Red lead oxide, 77 g (0.11 mol), was added in portions over a period of 1.5 hr. The mixture, now dark brown, was heated for an additional 0.5 hr, then 300 ml of water was added. The brown precipitate was filtered off and extracted overnight with ether. The filtrate was likewise extracted several times with ether. The extracts were combined, stirred with excess KHCO₃ to neutralize acidity, then filtered and dried over Na₂SO₄. The ether was removed, and the residue distilled under vacuum (10 mm), giving a rough separation into two fractions: the first, boiling at ~115°, crystallized easily, and consisted mainly of toluquinone; the second, boiling at ~135°, was mainly the required ketone. Of this fraction, 570 mg was dissolved in a 5:1 CCl₄-hexane mixture and chromatographed on 100 g of silicic acid. A small amount of yellow impurity passed quickly through the column. The main fraction was eluted with chloroform. Forty-five 20-ml portions were collected. Fractions 31–36 (combined weight after removal of chloroform 461 mg) showed no bands characteristic of toluquinone (or any other extraneous bands) in the nmr spectrum. The compound could not be induced to crystallize. A precise molecular weight determination on the parent ion by mass spectrometric techniques gave a molecular weight of 184.0535 (calculated for C₉H₉O₂F: mol wt, 184.05356).

Eucarvone. Carvone was converted to eucarvone, following the procedure of Corey and Burke.⁴

Eucarvone-7,7- d_2 . Eucarvone, 5.5 g (0.035 mol), was mixed with 27 ml (1.35 mol) of D₂O; 0.2 g of K₂CO₃ was added, and the mixture was heated under reflux for 3 days, at which time the methylene signal was invisible in the nmr spectrum (at least 98% exchanged). No diminution of the olefinic peaks could be detected, in contrast to the behavior when exchange is catalyzed by ethoxide.⁴ The eucarvone was separated and distilled under vacuum. Recovery was 4.075 g (73%), boiling at 89–90° (10 mm). An additional 0.713 g of less pure material boiling at 91–92° was also recovered.

Observation of Spectra. Spectra of samples degassed and sealed under vacuum were obtained by the use of a Varian Associates A-60 spectrometer or a Varian Associates DP-60 spectrometer with an RSI spin decoupler used as a field-frequency locking device. The spectra at 15.085 Mcps were obtained by the use of the DP-60 with an auxiliary 15.085-Mc radiofrequency unit and probe (Varian Model V4311), and were obtained in the field-sweep mode. Spectra were normally recorded four times with sweeps alternately in increasing and decreasing field direction. Line positions were determined by interpolation between calibration side bands.

Spectral Analysis

6-Methyl-6-acetoxycyclohexadien-2,4-one. The 60-Mc proton magnetic resonance spectrum of this compound in CDCl₃ solution is depicted in Figure 1. Preliminary calculations using LAOCN3⁵ revealed that the large coupling and small chemical shift between protons 3 and 4 (for numbering scheme, see Figure 2) made it difficult to determine precisely coupling con-

(3) Aldrich Chemical Co.

(4) E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **78**, 174 (1956); E. J. Corey, H. J. Burke, and W. A. Renner, *ibid.*, **78**, 180 (1956).

(5) A. A. Bothner-By and S. M. Castellano, *J. Chem. Phys.*, **41**, 3863 (1964).

(1) Paper III of this series: A. A. Bothner-By and D. Jung, *J. Am. Chem. Soc.*, **90**, 2342 (1968).

(2) F. Wessely and F. Sinwel, *Monatsh.*, **81**, 1055 (1950).

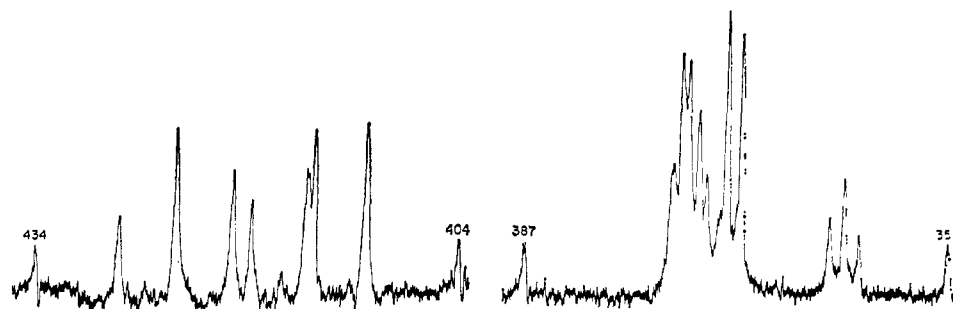


Figure 1. Proton resonance spectrum (60 Mc) of 6-methyl-6-acetoxycyclohexadien-2,4-one (10% in DCCl_3). Numbers above calibration side bands give separation in cycles per second from tetramethylsilane. Left portion (proton 2) at twice the sensitivity of right portion of spectrum.

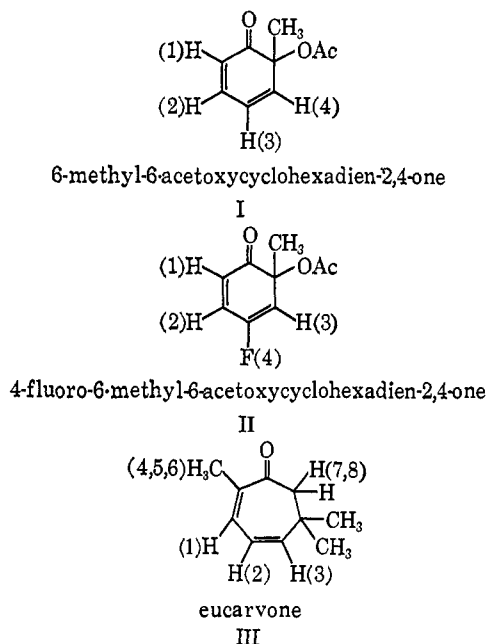


Figure 2. Numbering scheme used for magnetic nuclei.

stants between protons 1 or 2 and 3 or 4. The sums $J_{13} + J_{14}$ and $J_{23} + J_{24}$ were deducible with good precision from the spectrum but the differences $J_{13} - J_{14}$ and $J_{23} - J_{24}$ were poorly determined. Spectra in other solvents (monomethylformamide, acetone) were recorded with the hope that the chemical shift between 3 and 4 might be larger, leading to a better conditioned spectrum; however, these hopes proved in vain. Accordingly the dideuterio derivative, in which protons 1 and 3 were replaced with deuterium, was prepared, and the spectrum redetermined. The signal from proton 4 in the dideuterio derivative consisted of a set of two overlapping 1:1:1 triplets. By the use of a curve analyzer,⁶ it was possible to decompose the observed absorption curve with good confidence into the two sets of triplets. The doublet spacing was 1.12 ± 0.06 cps, the triplet spacing 1.41 ± 0.07 cps. The latter value can be checked, by comparison with the value calculated from J_{34} observed in the fully protonated compound, by division by the ratio of the magnetogyric ratios of protium and deuterium. This calculated value is $9.64/6.5145$ or 1.48 ± 0.01 cps, in good agreement with the 1.41 ± 0.07 measured.

(6) We are grateful to Dr. T. F. Yen, of the Mellon Institute, for instruction in the use of this instrument.

Iterative calculations using LAOCN3 were then performed. The value 1.12 cps was assumed for J_{24} and was not adjusted. All other parameters were adjusted for a least-squares fit of the spectrum. The results for the compound in three solvents are presented in Table I.

Table I. Nmr Parameters Obtained by Least-Squares Analysis of the Spectra of 6-Methyl-6-acetoxycyclohexadien-2,4-one in Three Solvents

Parameters	CDCl_3 (25% w/v)	Acetone (15% w/v)	Monomethyl- formamide (15% w/v)
ν_1^a	369.71 ± 0.02	363.49 ± 0.02	370.10 ± 0.01
ν_2	418.75 ± 0.02	423.60 ± 0.01	429.84 ± 0.01
ν_3	374.42 ± 0.05	376.73 ± 0.03	381.51 ± 0.03
ν_4	373.98 ± 0.05	377.99 ± 0.03	384.06 ± 0.03
J_{12}	9.89 ± 0.03	9.89 ± 0.02	9.84 ± 0.02
J_{13}	0.95 ± 0.05	0.97 ± 0.04	0.95 ± 0.03
J_{14}	0.85 ± 0.04	0.84 ± 0.04	0.86 ± 0.03
J_{23}	6.46 ± 0.05	6.52 ± 0.03	6.58 ± 0.03
J_{24}^b	(1.12 ± 0.06)	(1.12 ± 0.06)	(1.12 ± 0.06)
J_{34}	9.73 ± 0.05	9.61 ± 0.02	9.66 ± 0.02
Rms error ^c	0.068	0.053	0.041

^a Chemical shifts in cycles per second from internal tetramethylsilane. ^b J_{24} not adjusted (see text). ^c In spectral fitting, for all assigned lines.

That all proton-proton coupling constants in this compound are positive could be deduced from the analysis. Calculations with assumed negative signs give poor agreement in line frequencies and intensities with those observed.

4-Fluoro-6-methyl-6-acetoxycyclohexadien-2,4-one. The spectrum of this compound at 60 Mcps is very nearly first order, and can be fitted well with any combination of signs. The best parameters obtained are given in Table II. The appearance expected for the H spectrum at 15.085 Mcps and the F spectrum at 15.085 Mcps was calculated with various sign combinations and shown to be sensitive to choice of sign. Accordingly the spectra at 15.085 Mcps were recorded. The spectra observed matched those calculated with all signs positive, as may be seen in Figure 3.

Eucarvone. Analysis of the spectrum of eucarvone was complicated by a long-range splitting between protons 7 and 8 and protons 2 and 3. Accordingly, protons 7 and 8 were removed by exchange with deuterium oxide, using potassium carbonate as a catalyst. Under these mildly alkaline conditions exchange of protons 7 and 8

Table II. Nmr Parameters for 4-Fluoro-6-methyl-6-acetoxycyclohexadien-2,4-one^a

Parameter	Value
ν_1^b	372.713 \pm 0.003
ν_2	415.890 \pm 0.003
ν_3	342.848 \pm 0.003
J_{12}	10.387 \pm 0.005
J_{13}	0.645 \pm 0.005
J_{14}	5.290 \pm 0.007
J_{23}	3.142 \pm 0.005
J_{24}	7.063 \pm 0.009
J_{34}	9.847 \pm 0.007
Rms error ^c	0.012

^a 25% (v/v) in CDCl₃ with a trace of Si(CH₃)₄ and C₆F₆ to serve as internal references. ^b In cycles per second from internal Si(CH₃)₄. ^c In spectral fitting.

occurs readily, while the slower exchange of proton 2 is not observed. The eucarvone-7,7-*d*₂ thus obtained yields a six-spin spectrum which was readily fitted using LAOCN3. With the parameters thus obtained (Table III, first column) as guides, subspectral analysis was performed. Subspectra corresponding to the three spin states of the methylene protons were picked out of the eucarvone spectrum and analyzed individually. This procedure yields only first-order values of the spin couplings to the 7 and 8 protons. The parameters deduced from the subspectral analysis are given in the second column of Table III.

Table III. Nmr Parameters of Eucarvone (neat)

	Eucarvone-7,7- <i>d</i> ₂	Eucarvone
ν_1^a	386.568 \pm 0.004	387.81 \pm 0.05
ν_2	345.292 \pm 0.007	346.50 \pm 0.01
ν_3	355.891 \pm 0.006	357.21 \pm 0.02
ν_4, ν_5, ν_6	111.946 \pm 0.004	111.90 \pm 0.01
ν_7, ν_8	...	155.20 \pm 0.01
J_{12}	8.152 \pm 0.008	8.12 \pm 0.03
J_{13}	0.339 \pm 0.008	0.26 \pm 0.02
J_{14}, J_{15}, J_{16}	-1.496 \pm 0.004	-1.51 \pm 0.03
J_{17}, J_{18}	...	(0.01 \pm 0.02) ^b
J_{23}	11.614 \pm 0.006	11.63 \pm 0.01
J_{24}, J_{25}, J_{26}	0.387 \pm 0.006	0.38 \pm 0.02
J_{27}, J_{28}	...	\pm 0.12 \pm 0.01 ^c
J_{34}, J_{35}, J_{36}	-0.725 \pm 0.006	-0.70 \pm 0.03
J_{37}, J_{38}	...	\mp 0.78 \pm 0.05 ^c
Rms error ^d	0.042	0.090

^a Cycles per second from internal Si(CH₃)₄. ^b Not observed. ^c Opposite in sign, but not related to signs of other constants. ^d In spectral fitting.

Discussion

In addition to the analyses reported above, analyses of the spectra of a number of other pertinent compounds have been performed in various laboratories.⁷⁻¹² In this study, we are most concerned with the form of the dependence of ³J_s and ⁴J_s on the dihedral angle between the planes containing the vinyl groups of the double

(7) J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3896 (1965).

(8) H. Günther and H. H. Hinrichs, *Tetrahedron Letters*, 787 (1966); *Ann.*, **706**, 1 (1967).

(9) C. Ganter and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 741 (1966).

(10) E. Vogel, R. Erb, G. Lenz, and A. A. Bothner-By, *Ann.*, **682**, 1 (1965); cf. A. Mannschreck, G. Rissman, F. Vogtle, and D. Wild, *Chem. Ber.*, **100**, 335 (1967).

(11) S. M. Manatt and D. Elleman, as quoted in ref 9.

(12) W. Mock, M. P. Williamson, and S. M. Castellano, private communication.

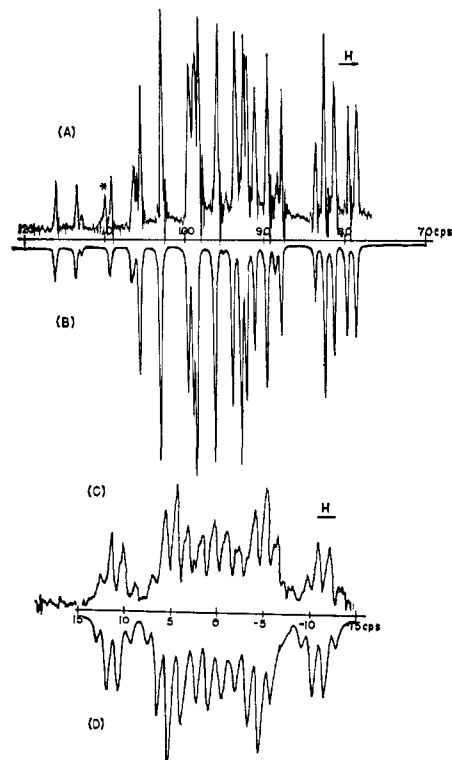


Figure 3. Experimental (A) and calculated (B) 15.085-Mc proton resonance spectrum of II (the signal from CHCl₃ in CDCl₃ marked with an *). Experimental (C) and calculated (D) 15.085-Mc fluorine resonance spectrum of II.

bond ($\phi = 0$ for *cis*-planar, $\phi = 180^\circ$ for *trans*-planar arrangements). In Table IV are presented the values of ³J_s and ⁴J_s obtained in the present study and in these other studies.⁷⁻¹²

With the exception of ³J_s in eucarvone, all of the ³J_s lie well within the range 5-7 cps. While variations within this range have been interpreted in terms of degree of planarity,⁷ there is sufficient scatter to render a correlation on this basis alone dubious. However, if ring size be taken into account, more regularity may be seen in the data. The large ³J_s observed in eucarvone is the result of simultaneous ring flattening (by virtue of partial double-bond character between C3 and C4) and the opening of the C2-C3-C4 and C3-C4-C5 angle as a result of Baeyer ring strain. This fits well with earlier observations of Chapman,¹³ Smith and Kriloff,¹⁴ and Laszlo and Schleyer.¹⁵








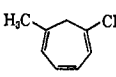


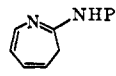

To the extent that ³J_s in the other seven-membered rings are smaller than this, they reflect a larger dihedral angle and less double-bond character. The small values of ³J_s observed in cycloheptatriene (entry 3), 1,6-dimethylcycloheptatriene (entry 12), N-carbethoxyazepin (entry 13), and dibenzamil (entry 15) all reflect a strong noncoplanarity, which in some cases has been confirmed by observation^{7,10} of slow inversion at low temperatures. The larger values observed for 7,7-bistrifluoromethylcycloheptatriene (entry 4), oxepin (entry 14), and thiepin dioxide (entry 16) may be due either to flattening (with concomitant smaller dihedral angles and small values of the HC₁C₂ and C₁C₂H bond

(13) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963).

(14) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).

(15) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

Table IV. Values of 3J_s and 4J_t in Cyclic Dienes: H,H Coupling Constants

Entry	Compound	3J_s	4J_t	Ref
1	I	+6.52 (av)	+0.96; +1.12 (two values)	This work
2	III	+8.14	+0.339	This work
3		+5.26	+0.8	7
		+5.58	+0.68	8
4		+6.86	+0.8	7
5		+5.14	+1.06	11
6		+6.22	+0.84	9
				
7	R, R' = CO ₂ CH ₃ , CO ₂ CH ₃	+5.41	+0.9	8
8	R, R' = COOCO	+5.88	+0.75	8
9	R, R' = CH ₂ OCH ₂	+5.35	+0.89	8
10	R, R' = CH ₂ CH ₂	+5.48	+0.72	8
11		+5.94	+0.58	8
12		+5.39	+0.73	8
13		+5.43	+0.65	8
14		+6.80	-0.73	8
15		+5.2	Unresolved	10
16		+6.96	+1.57, +0.35 (two values)	12
17	II	H-F couplings +7.06	+5.29	This work

angles) or to incursion of norcaradienoid forms, well demonstrated in the case of oxepin.⁸

In the case of six-membered rings, values of 3J_s , ranging from 5.88 (entry 8) to 6.52 (entry 1) are observed for cases where coplanarity is plausible (entries 1, 6, 8, 11), whereas lower values (5.14–5.48 cps) are observed where dihedral angles of $\sim 20^\circ$ are expected (entries 5, 7, 9, 10). Accepting values of ${}^3J_s \approx 6.2$ ($\phi = 0^\circ$), ${}^3J_s = 5.4$ ($\phi = 20^\circ$), and ${}^3J_s = 11.0$ ($\phi = 180^\circ$), the coefficients of a modified Karplus equation¹⁶

$$J_s = A + B \cos \phi + C \cos 2\phi \quad (1)$$

may be evaluated. The values obtained are: $A = 4.5$, $B = -2.4$, $C = 4.1$. It must be understood that these values are approximate, and usable only in unstrained systems.

(16) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

The magnitude of 4J_t fluctuates without a discernible pattern. It assumes especially large or small values in eucarvone (entry 2) and thiepin dioxide (entry 16). However, all values are positive in contrast to the situation where $\phi > 90^\circ$.

Data on the 3J_s coupling between a proton and a fluorine nucleus are rare. Compound II (entry 17) provides one datum, for $\phi \approx 0^\circ$, while fluoroprene,¹⁷ where ${}^3J_s = 25.15$ cps, provides another. From observations reported by Williamson,¹⁸ it may be deduced that H,F coupling constants show a dependence on dihedral angle similar to those of H,H coupling constants. From the two pieces of data cited above, one may deduce $B = -9$, in an equation of form 1, and $A + C = 16$. If one further accepts ${}^3J_s \approx 0$ ($\phi = 60^\circ$),

(17) A. A. Bothner-By and R. K. Harris, *ibid.*, **87**, 3445 (1965).

(18) K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *ibid.*, **88**, 5680 (1966).

as seems probable from studies on 1,1-dichloro-3-fluorobutadiene,¹⁹ approximate constants may be deduced as follows: $A = 8.3$, $B = -9.0$, $C = 7.7$.

To the extent that the numerical values of the coefficients in the Karplus equations estimated above can be confirmed and shown to hold in a wider selection of cases, the determination of the ${}^3J_{\text{HF}}$ coupling constant in

(19) A. A. Bothner-By and D. F. Koster, *J. Am. Chem. Soc.*, **90**, 2351 (1968).

butadienoid systems will be useful in determining conformational preferences in butadienes. The caveat sounded by Karplus must be continually borne in mind, however.

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Nuclear Magnetic Resonance Studies of 1,3-Butadienes.¹ V. Conformations of 1,1-Dichloro-3-fluorobutadiene-1,3 and 1,1-Dibromo-3-fluorobutadiene-1,3

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Abstract: The high-resolution proton magnetic resonance spectra of the title compounds in solution in mixtures of dimethyl ether and dichlorodifluoromethane at temperatures from -130 to $+39^\circ$ have been recorded and analyzed in terms of chemical shifts and coupling constants. The temperature dependence of the ${}^3J_{\text{HF}}$ coupling between the proton on carbon 2 and the fluorine indicates (1) that these compounds exist as mixtures of *s-trans* and skew conformers; (2) that ${}^3J_{\text{HF}}$ in the *s-trans* conformation has the value $+25.7$ cps (dichloro compound) and $+25.2$ cps (dibromo compound), while in the skew conformation ${}^3J_{\text{HF}}$ has the value -1.8 cps (dichloro compound) and -1.9 cps (dibromo compound); (3) that for the dichloro compound $\Delta H = 980 \pm 30$ cal, while for the dibromo compound $\Delta H = 1020 \pm 30$ cal, the *s-trans* form being the more stable at low temperatures in each case.

The finding, that the haloprenes exist practically completely in the *s-trans* conformation, while 1,1,3-trichlorobutadiene-1,3 and 1,1,3-tribromobutadiene-1,3 are entirely in a skew form,² suggested the investigation of butadienes substituted with groups having intermediate steric requirements. Accordingly 1,1-dichloro-3-fluorobutadiene-1,3 and 1,1-dibromo-3-fluorobutadiene-1,3 have been synthesized, and investigated by means of variable-temperature nuclear magnetic resonance spectroscopy. A secondary reason for choosing these compounds was that the ${}^3J_{\text{HF}}$ coupling constant between the fluorine and the proton on carbon 2 can be observed, and is expected to be dependent on the F-C-C-H dihedral angles.³⁻⁵ It should thus be possible to use it as an indicator of conformer population. Initial experiments⁶ over a limited temperature range have confirmed the applicability of the method.

(1) Paper IV of this series: A. A. Bothner-By and E. Moser, *J. Am. Chem. Soc.*, **90**, 2347 (1968).

(2) A. A. Bothner-By and D. Jung, *ibid.*, **90**, 2342 (1968).

(3) J. C. Schug, P. E. McMahon, and H. S. Gutowsky, *J. Chem. Phys.*, **33**, 843 (1960); H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *ibid.*, **36**, 3353 (1962).

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Experimental Section

1,1,1-Trichloro-3-bromo-3-fluorobutane. CBrCl_3 , 1.5 mol, 0.38 mol of 2-fluoropropene, and 5 g of benzoyl peroxide were heated at 100° for 5 hr in a stainless steel bomb.⁷ The bomb was then quickly cooled in ice and the resulting yellowish solution distilled under vacuum. The main product distilled at $87-88^\circ$ (28 mm), giving an 88.4% yield based on the 2-fluoropropene. The nmr spectrum was consistent with the desired product.

1,1-Dichloro-3-fluoro-1,3-butadiene. 1,1,1-Trichloro-3-bromo-3-fluorobutane (0.15 mol) and 0.30 mol of tri-*n*-butylamine were heated quickly in a flask fitted with a condenser for distillation. At a bath temperature of about 125° , the solution turned yellow. A very sudden reaction occurred at about 145° (bath temperature), turning the reaction mixture black. A small amount of a yellowish liquid was collected in the receiver flask. The distillate was washed with dilute HCl, then water, and dried over MgSO_4 , then distilled in a Craig apparatus. Product was collected at a bath temperature of 37° (28 mm). The nmr spectrum was consistent with the expected product. The uv spectrum in cyclohexane gave λ_{max} 242 $\text{m}\mu$ (ϵ 1.8×10^4). Subsequent preparations of the compound gave improved yields if the dehydrohalogenation of the butane was carried out at about 100-mm pressure. This removes the product more quickly from the hot reaction mixture. The most significant impurity, which was evident in the nmr spectrum, was 1,1-dichloro-3-bromo-3-fluoro-1-butene.

1,1,1,3-Tetrabromo-3-fluorobutane. A mixture of 0.22 mol of 2-fluoropropene, 0.75 mol of CBr_4 , 5 g of benzoyl peroxide, and 200 ml of cyclohexane was heated at 70° for about 3 hr in a stainless steel bomb.¹ After cooling, the cyclohexane and most of the CBr_4 were distilled off under vacuum. The desired product was con-

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