

Nuclear Magnetic Resonance Spectroscopy. Conformational Equilibria and Rates of Conformational Interconversion of Halogenated Ethanes^{1a}

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Abstract: The relative ground-state energies of the rotational isomers of some halogenated ethanes and the rates and barriers to interconversions of these isomers have been determined by nuclear magnetic resonance spectroscopy. In the ethanes studied in this research, those with a single fluorine were found to have the ¹⁹F resonance of the least populated conformation at highest field, while that of the most populated conformation was found at the lowest field. All three barriers for interconversion could be determined for the ethanes substituted so as to give three distinguishable conformations. For these cases it was found that the highest barrier separates the two least populated conformations and the lowest barrier separates the most stable conformations. The substances for which complete nmr line-shape analysis have given the equilibrium constants, rates, and barriers for internal rotation include 1,1,2-tribromo-1,2-dichloro-2-fluoroethane, 1,1-dibromo-1,2,2-trichloro-2-fluoroethane, 1-bromo-1,1,2,2-tetrachloro-2-fluoroethane, 1,1,2,2-tetrabromo-1-chloro-2-fluoroethane, 1,2-dibromo-1,1,2-trichloro-2-fluoroethane, 1,1,2-tribromo-1-chloro-2-fluoroethane, 1-bromo-1,1,2-trichloro-2-fluoroethane, and 1,2-dibromo-1,1,2-trichloro-3,3,3-trifluoropropane. For those ethanes carrying five halogens other than fluorine, the barriers (to rotation) range from 13.2 to 14.8 kcal/mol, while for those with four halogens other than fluorine, the barriers range from 9.0 to 10.2 kcal/mol. The ground-state energy differences for all of the ethanes studied did not exceed 0.3 kcal/mol.

The effects of halogen substituents on conformational preferences and barriers for rotation about the C—C bonds of substituted ethanes do not seem as yet to be well understood. One can predict in a qualitative way how increasing the size of all halogens might, through steric interactions, influence the conformational preferences and barriers, but most of the available experimental evidence²⁻⁸ does not accord as simply and directly with variations in sizes of the halogens as do, for example, the rates of racemization of optically active 2,2'-dihalobiphenyls.⁹ The purpose of the present research was to determine whether a consistent pattern of effects could be seen in the conformational equilibria and equilibration of a series of closely related polyhalogen-substituted ethanes in hope, ultimately, of making possible quantitative predictions of conformational populations and barrier heights for such substances by the procedures outlined by Westheimer.^{2,8-12}

Ethanes with relatively symmetrical structures and low barriers to rotation are best investigated by way of the low-energy torsional oscillations which influence infrared and Raman spectra³ or by microwave spectroscopy.¹³ For less symmetrical molecules with higher barriers to rotation, nuclear magnetic resonance is the technique of choice.¹⁴

For the nmr technique to be most useful and reliable, it is desirable to be able to attain a temperature where the rates of rotation are sufficiently slow that distinct spectra from each of the different conformations can be observed.¹⁵ Incorrect conclusions have occasionally been drawn from temperature variations of shifts and/or couplings in spectra where the rotational interconversions are so rapid that only the average properties of the conformations can be determined.¹⁶ Electronic integration of the spectra below the temperature at which exchange is slow can provide accurate values for the ground-state energies of the conformations. These data are vital for detailed analysis of the spectral line shapes in the intermediate temperature ranges wherein one can determine the rate constants for the various interconversion processes.

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(2) See J. D. Roberts, Abstracts of the 20th National Organic Chemistry Symposium of the American Chemical Society, Burlington, Vt., June 1967, p 63.

(3) S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954.

(4) H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962).

(5) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 39 (1963).

(6) T. D. Alger, H. S. Gutowsky, and R. L. Vold, *J. Chem. Phys.*, **47**, 3130 (1967).

(7) R. A. Newmark and C. H. Sederholm, *ibid.*, **43**, 602 (1965).

(8) T. L. Gerig, unpublished work, some of which is quoted in ref 2.

(9) See, for example, F. H. Westheimer in M. S. Newman, Ed., "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956, p 523.

(10) J. A. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961); **84**, 3355 (1962); **86**, 4854 (1964); **89**, 7036, 7047 (1967).

(11) K. B. Wiberg, *ibid.*, **87**, 1070 (1965).

(12) N. L. Allinger and coworkers, *ibid.*, **89**, 4345 (1967); **90**, 1199, 5773 (1968).

(13) E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959).

(14) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1966, p 560.

(15) (a) P. M. Nair and J. D. Roberts, *J. Amer. Chem. Soc.*, **79**, 4565 (1957); (b) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958); (c) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 39 (1963); (d) T. D. Alger, H. S. Gutowsky, and R. L. Vold, *J. Chem. Phys.*, **47**, 3130 (1967).

(16) For example, the spectral parameters assigned by Gutowsky and coworkers⁴ to the conformational isomers of 1,2-dibromo-2-chloro-1,1,2-trifluoroethane from averaged spectra later had to be corrected on the basis of low-temperature spectra by W. S. Brey and K. C. Raney, *J. Chem. Phys.*, **39**, 844 (1963).

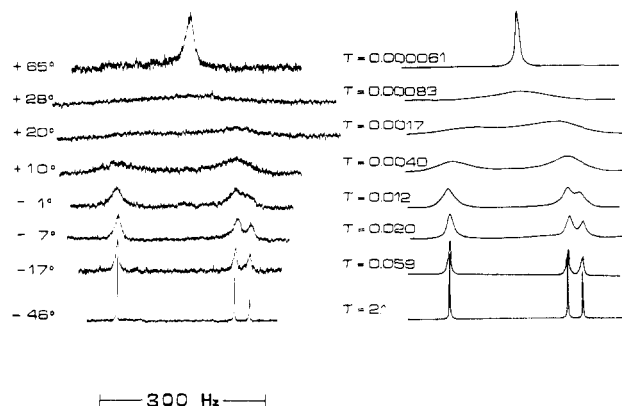


Figure 1. Fluorine nmr spectra of 1,1,2-tribromo-1,2-dichloro-2-fluoroethane (10) at 56.4 MHz. Left, experimental spectra as a function of temperature. Right, calculated spectra as a function of mean lifetime before rotation. The average values of the equilibrium and activation parameters used to compute these spectra are given in Table I. The τ values beside each calculated curve represent the mean lifetime (in seconds) of the predominant rotational isomer before it is converted by rotation about its carbon-carbon bond to either of the lesser isomers. These τ values do not by themselves define the calculated spectra but are appended to show the general order of magnitude of lifetimes of the isomers before rotation occurs.

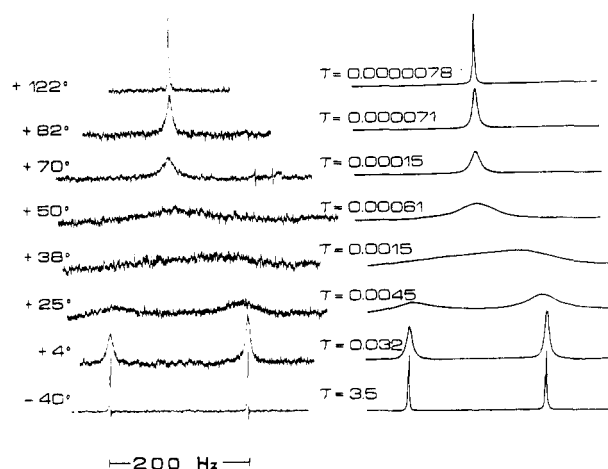


Figure 2. Fluorine spectra at 56.4 MHz of 1,1,2,2-tetrabromo-1-chloro-2-fluoroethane (6). Left, experimental spectra as a function of temperature. Right, calculated spectra as a function of mean lifetime before rotation (seconds). (See legend to Figure 1.)

The equations for variations of line shapes with interconversion rate are relatively simple when the number of magnetic nuclei in the molecules is kept to the minimum. The molecules initially chosen for study here had only a single fluorine nucleus as the significant magnetic nucleus. Later, some substances containing one proton and one fluorine, and a few more complicated systems with trifluoromethyl groups, were also examined.

Syntheses. The preparation of the halogenated ethanes followed conventional lines wherein one begins with ethenes containing fluorine and produces the desired substances by addition of halogen, dehydrohalogenation, and addition of halogen. A summary of the sequences and the compounds prepared is shown in Chart I. The structures of the products are considered to be largely established by the methods of synthesis

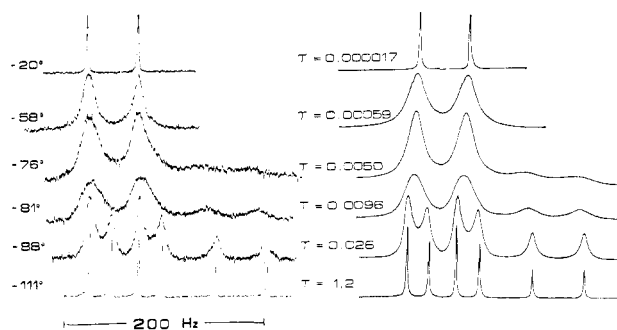
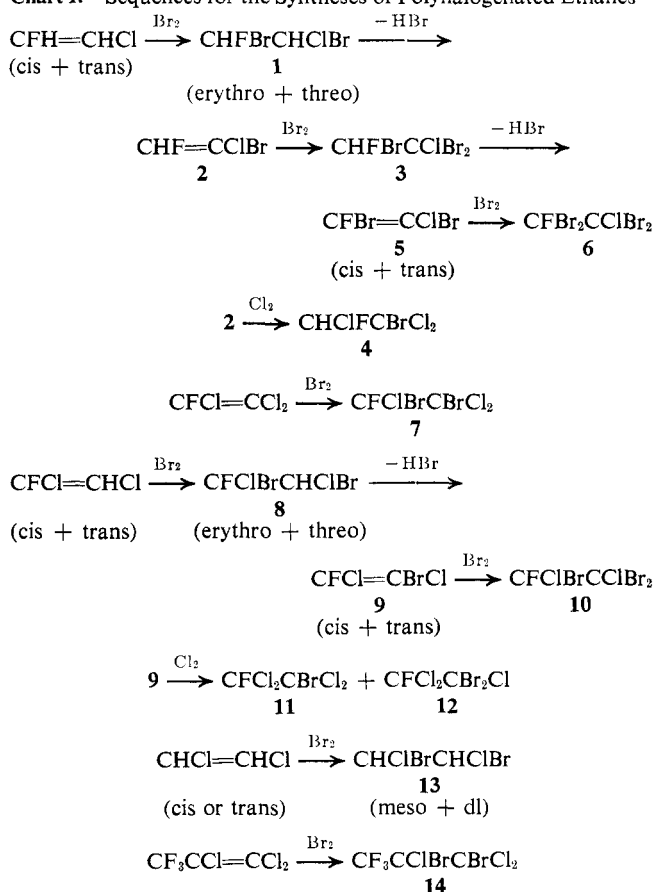


Figure 3. Fluorine spectra at 56.4 MHz of 1,1,2-tribromo-1-chloro-2-fluoroethane (3). Left, experimental spectra as a function of temperature. Right, calculated spectra as a function of mean lifetime before rotation (seconds). (See legend to Figure 1.)

and nmr spectra. In some cases, supporting evidence came from mass spectra.

Chart I. Sequences for the Syntheses of Polyhalogenated Ethanes



We were not able to prepare separate pure samples of *erythro*- and *threo*-1,2-dibromo-1,2-dichloro-1-fluoroethane (8) or *meso*- and *dl*-1,2-dibromo-1,2-dichloroethane (13). Attempts to prepare a single isomer of 13 by addition of bromine to either pure isomer of 1,2-dichloroethene and destruction of any excess bromine with bisulfite and distillation gave nearly 50:50 mixtures of the *dl*- and *meso*-bromides. Careful integration of the nmr peaks of the dibromide mixture revealed small but significant deviations from exactly equal proportions of *meso* and *dl* which depended on the configuration of the starting ethenes. On addition of bromine to the dichloroethenes at -30° , one product

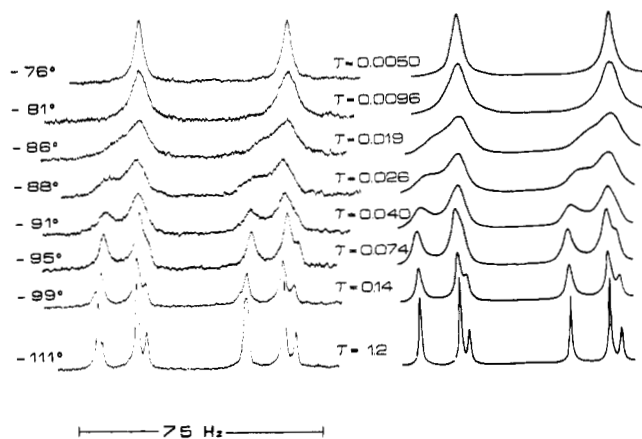
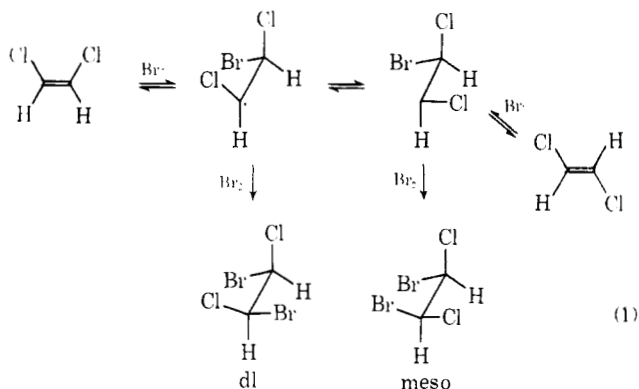


Figure 4. Proton spectra at 60.0 MHz of 1,1,2-tribromo-1-chloro-2-fluoroethane (3). Left, experimental spectra as a function of temperature. Right, calculated spectra for rotation about the 1,2 bond as a function of mean lifetime before rotation (seconds). (See legend to Figure 1.)

predominated from each to the extent of 2:1. However, the rates of bromination became inconveniently slow below this temperature. That the starting ethenes are isomerized at a rate comparable to the addition reaction¹⁷ is suggested by the observation that a single drop of bromine added to either *cis*- or *trans*-1,2-dichloroethene in the dark at room temperature catalyzes *cis*-*trans* equilibration before the bromine color disappears. It appears most likely that addition occurs by a free-radical chain process involving reversible addition of a bromine atom as shown in eq 1. At low



temperatures, apparently combination of the second bromine competes successfully with interconversion of rotational isomers of the intermediate. Several attempts to separate the two dibromides by gas chromatography were unsuccessful.

Of the four possible products which could form from 1,2-dibromo-1-chloro-2-fluoroethane (1) by loss of hydrogen bromide, apparently only one is produced because the product shows only one doublet resonance in both the pmr and fmr spectra. From the magnitude of the proton-fluorine coupling constant and the products of further synthetic transformations, it appears that dehydrohalogenation involves loss of the proton α to chlorine. This is reasonable because α chlorine usually seems to be more effective than α fluorine in stabilizing carbanions. A common carbanion inter-

(17) Equilibration of the *cis*-*trans* isomers of 1,2-dichloroethylene has been reported to be catalyzed by iodine at 150° by R. E. Wood and R. G. Dickenson, *J. Amer. Chem. Soc.*, **61**, 3259 (1939).

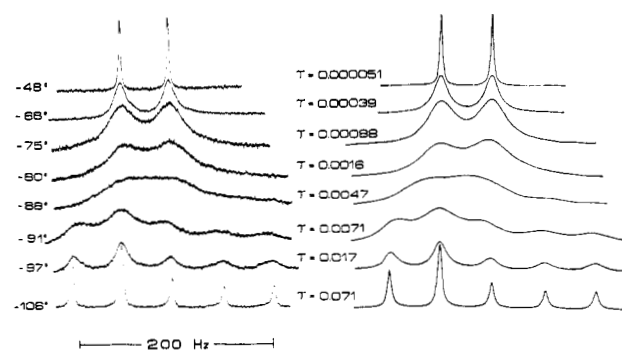


Figure 5. Fluorine spectra at 56.4 MHz of 1-bromo-1,1,2-trichloro-2-fluoroethane (4). Left, experimental spectra as a function of temperature. Right, calculated spectra as a function of mean lifetime before rotation (seconds). (See legend to Figure 1.)

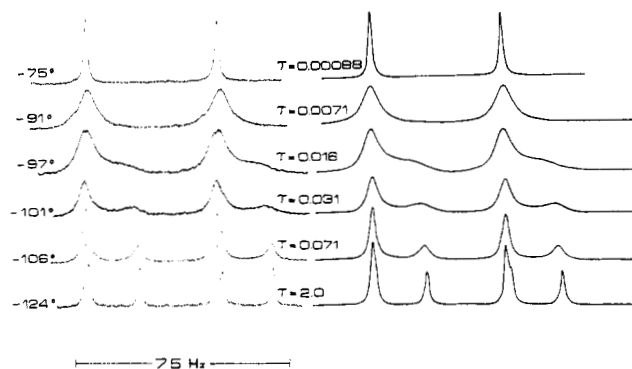


Figure 6. Proton spectra at 60.0 MHz of 1-bromo-1,1,2-trichloro-2-fluoroethane (4). Left, experimental spectra as a function of temperature. Right, calculated spectra as a function of mean lifetime before rotation (seconds). (See legend to Figure 1.)

mediate rather than a concerted E2 elimination must be involved in dehydrohalogenation of 1 because the same elimination product is formed from either the erythro or the threo isomers. The stereochemistry of the resulting alkene 2 is not known.

Spectra. Proton and fluorine magnetic resonance spectra were determined with a Varian A56-60A spectrometer equipped with a V-6040 temperature controller. A Varian C-1024 CAT computer was used to record spectra which extended over more than 1 kHz, and also to define better some of the less intense broad spectra near the coalescence point. Spectra as a function of temperature for some halogenated ethanes with a single fluorine are shown in Figures 1 and 2, and for some ethanes with one proton and one fluorine in Figures 3-6. Calculated spectra are shown on the right, which utilize the relative ground- and transition-state energies given in Table I.

The relative ground-state energies of the various rotational isomers were obtained by direct integration of the resonance peaks below the temperatures where exchange processes produce significant line broadening. In general, ten to twenty separate integrations were made at at least two such temperatures. The activation energies for rotation can be determined by comparison of the experimental spectra in the region of temperature where rotation affects the line shapes, with theoretical spectra calculated by Alexander's equation for line

Table I. Chemical Shifts and Equilibria and Free Energies of Activation for Interconversion of Rotational Isomers of Halogenated Ethanes

Compd	Most stable conformation	$\theta = 0^\circ$ ^a δ_F^e	$\Delta G^\ddagger (0 \rightarrow 120^\circ)^{b,c}$	$\theta = 120^\circ$ ^a $\Delta G^{b,d}$ δ_F^e	$\Delta G^\ddagger (120 \rightarrow 240^\circ)^{b,c}$	$\theta = 240^\circ$ ^a $\Delta G^{b,d}$ δ_F^e	$\Delta G^\ddagger (0 \rightarrow 240^\circ)^{b,c}$
6		2652	14.8	0.26 2863	<i>f</i>	0.26 2863	14.8
11		3031	<i>f</i>	0.0 3031	13.1	0.20 3299	13.1
12		2868	13.2	0.14 3111	<i>f</i>	0.14 3111	13.2
10		2729	13.9	0.16 2938	14.7	0.28 2965	14.0
7		2899	13.8	0.17 2923	14.5	0.30 3153	14.2
14		3311	13.7	0.13 3360	14.1	0.25 3363	13.9
3		6573 396 ^g 46.0 ^h	9.6	0.07 6595 408 ^g 47.8 ^h	10.2	0.30 6699 392 ^g 48.7 ^h	10.0
4		6713 389 ^g 48.8 ^h	9.0	0.12 6766 368 ^g 50.2 ^h	9.4	0.22 6876 388 ^g 48.0 ^h	9.1

^a Angle of clockwise rotation of the *rear* carbon of the structure with respect to the front carbon. ^b In kilocalories per mole. ^c Free energy of activation for indicated rotational isomer interconversion. ^d Free energy relative to the most stable conformation as measured below the coalescence point. ^e Fluorine chemical shift in hertz at 56.4 MHz upfield from dichlorodifluoromethane as measured below the coalescence point, normally rather temperature dependent. ^f This barrier is between rotational isomers which are mirror-image isomers and cannot be measured by the nmr method. ^g Proton chemical shift in hertz at 60.0 MHz downfield from TMS. ^h J_{HF} in hertz as determined from the low-temperature fluorine spectra.

shapes for systems undergoing intermolecular exchange.¹⁸

For a molecule which has three mutually interconvertible rotational states, each giving a single resonance line with different chemical shifts, the steady-state approximation can be applied to the set of three coupled differential equations (eq 2) relating the various density matrix elements p_i , wherein t_{ij} is the lifetime of state i before it is transformed to state j ; δ_i is the chemical shift of species i ; ω is the frequency at which the intensity of absorption is being calculated, and T_{2i} is the relaxation time of species i , including contributions from field inhomogeneities, unresolved

couplings, viscosity, and possible quadrupole relaxation effects.

$$\frac{dp_i}{dt} = 0 = \sum_{j \neq i}^3 \frac{p_j - p_i}{t_{ij}} - i(\delta_i - \omega)p_i - p_i/T_{2i} + iC \quad (2)$$

The intensity $I(\omega)$ is calculated from the density matrix elements by eq 3, where pop_i is the population of species i , and the function Imag selects only the imaginary part of p_i . Because each line in the low-

$$I(\omega) = \sum_{i=1}^3 \text{pop}_i [\text{Imag}(p_i)] \quad (3)$$

temperature spectrum can be the subject of an independent equation, the number of simultaneous equations to be solved for the intensity at any point in the spectrum becomes quite large as the number of magnetic nuclei increases and as the spectral symmetry decreases. The exchange of three ABC patterns with 15 possible transitions for each rotational isomer requires solution of up to 45 equations in 45 unknowns for *each* point in the spectrum. Some simplification is available

(18) S. Alexander, *J. Chem. Phys.*, **37**, 975 (1962). Although rotation about the C—C bond of a halogenated ethane is an intramolecular process, there being no disassociation followed by recombination to a different rotational isomer involving fragments from the same or different molecules, use of Alexander's equations for *intermolecular* processes is appropriate because there is a dynamic equilibrium among several species with different populations. Rotation of a trifluoromethyl group relative to the rest of the molecule may be treated mathematically as an intramolecular process because no population changes are involved. The equations of Sack¹⁹ are not applicable to the ethane rotations studied here because there is more than one characteristic exchange lifetime.

(19) R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

through factoring, but the problem remains quite formidable.²⁰

For molecules which have three different rotational states, each of which gives a different AX spectrum such as 1,1,2-tribromo-1-chloro-2-fluoroethane (**3**) and 1-bromo-1,1,2-trichloro-2-fluoroethane (**4**), an algorithm identical with that used for three interconverting rotational isomers giving single lines may be used to calculate each half of the A part and each half of the X part because rotation about the C—C bond does not cause the spin state of the X nucleus to change. Thus, the twelve-line system presented by **3** may be treated as two independent three-line systems for either hydrogen or fluorine. For example, if we consider the fluorine spectra, one system will have the proton in spin state α , and the fluorine chemical shifts for each of the three conformations can be corrected by the proper value of $+^3J_{\text{HF}}/2$ for that conformation. The other system with spin state β will be corrected correspondingly by $-^3J_{\text{HF}}/2$. The individual calculated spectra are summed to give the final spectrum. For the fluorine portion of the AX system, the chemical shifts are larger than the proton-fluorine coupling constants and considerable overlap of the lines from the α and β proton spin sets usually occurs. In the proton spectrum the lines corresponding to the α and β fluorine spin sets are widely separated and the two halves may be solved completely independently. The slight asymmetry in the proton spectra of **3** and **4** arises from the slightly different values for the proton-fluorine coupling constants in the three rotational conformations. Although there is little doubt about what to expect in these kinds of cases, the observed changes in the line shapes are in accord with spin sets assigned on the basis that proton-fluorine coupling constants have the same sign in all three conformations.

The input for the calculated spectra includes the relative ground-state free energies of the three conformations, the chemical shifts, relaxation times, and estimates of the free energies of activation for the various interconversion processes. The six interconversion lifetimes τ_{ij} are calculated by the program from the free energies of the ground and transition states. In the preliminary stages, an approximate match to the observed spectra in the coalescence temperature region was sought on the basis that the ΔG^\ddagger for the three barriers were equal. After an approximate "average barrier" was thus obtained, matches to the spectra below the coalescence temperature were investigated wherein all ΔG^\ddagger values were varied independently. Above the coalescence temperature, many combinations of ΔG^\ddagger values could be found to reproduce the observed spectra, but below coalescence this was not the case. Usually, changes of any of the ΔG^\ddagger values by 0.1 kcal/mol from the values given in Table I had an adverse effect on the match between the calculated and experimental spectra below coalescence point. Errors in the temperature measurements or sweep calibrations could cause the absolute values of ΔG^\ddagger for interconversion of the conformations to be uncertain by ± 0.5 kcal/mol, but this does not affect the

fact that values for three barriers can be obtained with a relative accuracy of ± 0.1 kcal/mol.

The uniqueness of the ΔG^\ddagger values given in Table I has not been rigorously established. If δ is some measure of the goodness of fit, the ΔG^\ddagger 's given are in accord with the relations $\partial\delta/\partial\Delta G_i^\ddagger = 0$ and $\partial\delta^2/\partial\Delta G_i^\ddagger < 0$, but no comparable study was made of $\partial\delta^2/\partial\Delta G_i^\ddagger\Delta G_j^\ddagger$ or related quantities.

On the basis of earlier work,⁷ the entropies of activation for rotation were expected to be small and the free energy of activation independent of temperature. For some compounds, such as 1,2-dibromo-1,1,2-trichloro-2-fluoroethane (**7**) and 1,1,2-tribromo-1,2-dichloro-2-fluoroethane (**10**), this expectation appeared to be incorrect because the spectra immediately above the coalescence temperature could not be matched with the same free energies as those below coalescence (see Figure 1). For this reason, a more detailed study of some of the possible effects which might influence the temperature dependence of the spectra of **10** was made.

The chemical shifts of the three rotational isomers used as input to the computer program in the intermediate- and high-temperature regions were extrapolated from values determined at several temperatures below the low-temperature limit. Although there were significant changes in shift relative to the internal standard, only minor changes in shift were observed for one conformation relative to another, and it is only shifts of this kind which influence the line shapes. The changes in relative shifts required to produce the effects observed for **7** and **10** seem much too large to explain the observed discrepancies.

Possible influences on the line widths of the resonances of the individual conformations such as partially relaxed couplings between fluorine and either chlorine or bromine were considered but were discarded because the differential variations required again seemed excessively large. It is our opinion that for **7** and **10** there are, in fact, significant entropies of activation for the rotation process. Because of the insensitivity of the line shapes to relative free energies above the coalescence temperature, the entropy of activation was assumed to be the same for three possible rotational interconversions. For **10**, the only compound investigated in detail, an average entropy of activation of -6.2 eu was found for observations spanning a temperature range of 105° . The Arrhenius plot corresponding to these observations is shown in Figure 7. The temperature range which could be studied below coalescence was limited and no change of the free energy of activation with temperature could be discerned (see dotted line in Figure 7). On the whole, it seems desirable to consider barriers given in Table I as free energies of activation at temperatures below coalescence.

So far we have not considered the problems of assigning the observed resonances below coalescence to particular rotational isomers or the barriers to particular rotational interconversions. These will be discussed next.

Assignments. The proper assignment of the observed resonances to particular rotational conformations is not immediately obvious. In most of the previous investigations^{4-8,15} of conformational isomerization several magnetic nuclei were present in the

(20) (a) See R. A. Newmark, Ph.D. Thesis, University of California at Berkeley, 1964, for discussion of this kind of problem. (b) See also G. Binsch, *Mol. Phys.*, **15**, 469 (1968), and *J. Amer. Chem. Soc.*, **91**, 1304 (1969), for a different and efficient approach to calculation of nmr spectra, which has great power when applied to exchanging systems.

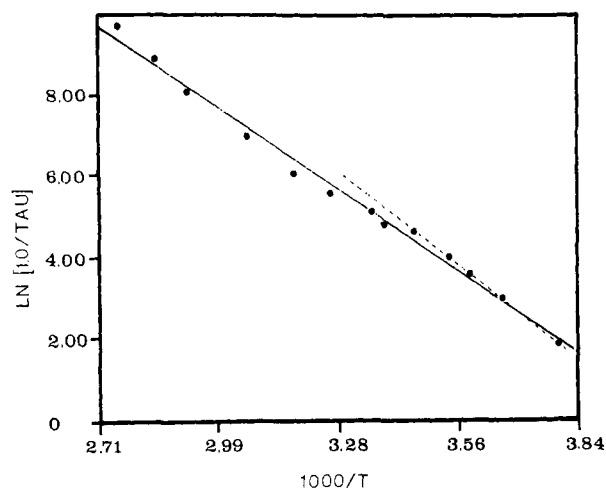
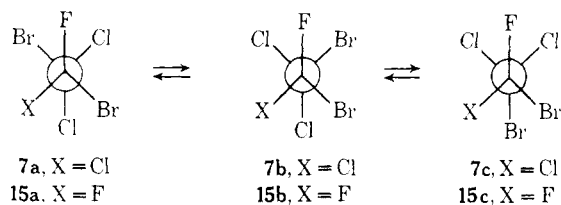


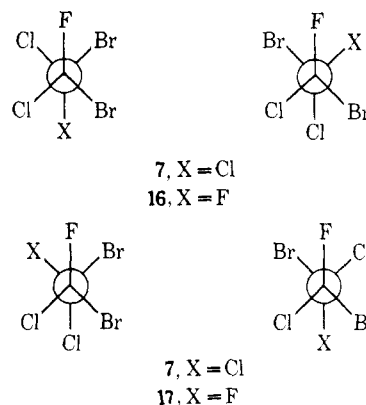
Figure 7. Arrhenius plot for rotation about the 1,2 bond between rotational isomers **1** and **2** of 1,1,2-tribromo-1,2-dichloro-2-fluoroethane (**10**).

molecule and assignments could often be made on the basis of spin-spin splitting patterns. In the present work, the same spectral simplicity which simplified the detailed kinetic investigation also makes the assignments more difficult. With polyfluoroethanes, the degree of symmetry of the multiplets arising from spin-spin interactions between fluorines usually provides a reliable indication of how the resonances should be assigned.^{21,22} Study of the assignments made in this way shows that there are some regularities in chemical shifts. Especially important for us is the observation that a fluorine resonance is shifted farther upfield by a gauche chlorine than by a gauche bromine.²¹ This permits identification of many of the resonances in the present work. For example, it allows differentiation of **7c** from both **7a** and **7b**. However, identification of



the members of such pairs as **7a** and **7b** requires further information.

More or less tentative assignments can be made on the expectation that in these highly halogenated compounds the conformations with gauche bromines should be less stable than those with trans bromines, e.g., that **7b** would be less stable than **7a**. This idea is supported by the knowledge that for 1,2-dibromo-1,1-dichloro-2,2-difluoroethane (**15**) conformation **15b** is less stable (by 0.32 kcal/mol) than conformation **15a**.^{15a,23} The observed difference in energy between **7a** and **7b** is 0.17 kcal/mol. Two further model compounds where a fluorine is substituted for one chlorine in **7** are the dl and meso forms of 1,2-dibromo-1,2-dichloro-1,2-difluoroethane (**16** and **17**, respectively). With these also, the conformations with gauche bromines are less stable than the ones having the



bromines trans.²¹ We shall assume that this trend is general in the perhalogenated ethanes and assign the remaining resonances accordingly.²⁴ The assignment of barriers to specific interconversions is straightforward when the resonances have been assigned but, of course, will be subject to the same uncertainties.

Chemical Shift and Equilibrium Constant Correlations. The ¹³C chemical shifts of methyl groups in sterically perturbed environments come at higher fields of methyls than in electronically similar but uncrowded environments.²⁵⁻²⁷ These upfield shifts have been interpreted in terms of hydrogen-hydrogen repulsions which create electric-field gradients at the carbon.²⁸ However, data are available showing the carbon resonances of methyl groups are also shifted upfield by other substituents,^{29,30} and fluorine resonances are often (but not always) shifted to higher fields by sterically proximate vicinal methyl groups,³¹ and it may well be that such shifts are to be expected for elements other than hydrogens. This is quite reasonable because the important influence on both fluorine and carbon chemical shifts involve the so-called paramagnetic interactions.³²

Without exception for the compounds studied in the present investigation, the fluorine resonance which comes farthest upfield has been assigned by one means or the other to the least populated conformation and the resonance farthest downfield to the most populated conformation. However, there does not seem to be any very quantitative relationship between the chemical-shift differences and the energy differences and, obviously, ambiguities are possible for those ethanes with more than one fluorine per carbon. Nonetheless, the correlation does provide one more piece of confirmatory evidence for the assignment of the two resonances of 1,2-difluorotetrachloroethane,^{7,33} wherein

(24) We do not believe that this procedure should be taken to have general validity for ethanes, especially when it is known that the gauche isomer of 1,1,2,2-tetrabromoethane is somewhat more stable than the trans in the liquid state; cf. N. Sheppard, *Advan. Spectrosc.*, **1**, 288 (1959).

(25) D. M. Grant and W. R. Woolfenden, *J. Amer. Chem. Soc.*, **88**, 1496 (1966).

(26) D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967).

(27) However, see J. I. Kroschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *ibid.*, **91**, 5927 (1969), for somewhat different effects in some long-range interactions.

(28) D. M. Grant and B. V. Cheney, *ibid.*, **89**, 5315 (1967); B. V. Cheney and D. M. Grant, *ibid.*, **89**, 5319 (1967).

(29) T. D. Brown, Ph.D. Thesis, University of Utah, Salt Lake City, Utah, 1965.

(30) F. J. Weigert, J. I. Kroschwitz, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 1338 (1970).

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the only way the upfield resonance can arise from both the least stable and the most populated conformation is for it to represent the double degenerate gauche form.

The fluorine spectra of **3** and **4** (Figures 3 and 5) which have a single proton on the same carbon as the fluorine follow the trend of stability and chemical shift noted for the other compounds. As might be expected from the other differences between proton and fluorine spectra, the proton resonance lines (Figures 4 and 6), which can also be observed at low temperatures, do not show similar patterns. In fact, the order of the resonances is not even the same for the two compounds. However, the proton spectra are consistent with the configurational assignments. Thus, with **3**, the proton resonance of the isomer with the proton gauche to two bromines is found at a substantially lower field than those of the two isomers in which the proton is gauche to one chlorine and one bromine. With **4**, the proton resonance of the isomer with the proton gauche to two chlorines is found considerably upfield from those in which the proton is gauche to one chlorine and one bromine.

Barrier Heights. The energy barriers to rotation in heavily halogenated ethanes are generally interpreted in terms of nonbonded repulsions between proximate atoms in the eclipsed form. If the differences in the ground-state energies can likewise be attributed to repulsions between the gauche halogen atoms in the staggered form, some degree of correlation might be expected between the ground-state energies and the energies of the corresponding eclipsed forms through which they are interconverted. With the compounds investigated in the present study, the highest barrier separates the two least stable conformations, and the lowest barrier separates the two conformations of lowest energy.

The fact that all three barriers influence the spectral line shapes shows that each rotational interconversion in these compounds is followed by immediate deactivation (Figure 8a).⁷ Clearly, if the "free-rotor" concept is correct for interconversion of these isomers (Figure 8b), the spectra would be independent of the highest energy barrier.^{34,35}

It has not so far been possible to correlate rotational barriers in halogenated ethanes from pairwise interaction constants²¹ or a complete Westheimer-type⁹ calculation with the currently available free and nonbonded interaction constants.² Detailed calculations² indicate that it does not seem likely that the difficulties arise from deviations from perfect staggering or eclipsing in the ground or transition states, although the small fluorine chemical-shift differences between the conformations such as **10a** and **10b** may result from such deviations in the ground state.

One of the more notable observations in this series of compounds is the fact that replacement of chlorine by bromine has little effect on either the relative ground-state energies or the barrier heights (compare **7** with **10** and **3** with **4**). This appears to be a consequence of the fact that, although bromine is larger than chlorine,

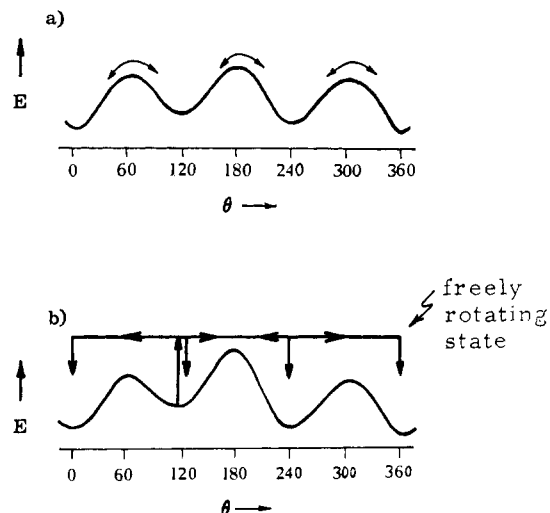


Figure 8. Schematic potential energy surface for the rotation about the C—C bond of ethane derivatives: (a) activation followed by immediate deactivation; (b) activation followed by free rotation before deactivation.

the carbon–bromine bond distances are greater than the carbon–chlorine bond distances, thus tending to keep the vicinal interactions constant.²

Some Halogenated Ethanes with Vicinal Hydrogens and/or Fluorines. With 1,1,2,2-tetrachloroethane⁴ or 1,1,2,2-tetrachloro-1-fluoroethane^{15c,d} the gauche conformations are the most stable. However, for 1,1,2,2-tetrachloro-1,2-difluoroethane, the conformation with the fluorines trans is the most stable.^{7,33} This generalization apparently does not apply throughout the analogous series of 1,2-dibromo-1,2-dichloroethanes, wherein the situation is rendered more complex by having two asymmetric carbons. Thus, for either the *meso*- or *dl*-1,2-dibromo-1,2-dichloro-1,2-difluoroethane the conformations with the bromines trans are already known to be the most stable.²¹ In the *meso* isomer, the fluorines are also trans while the most stable conformation of the *dl* isomer has the fluorines gauche.

The preferred conformations of the *meso* and *dl* forms of **13** can be deduced from the vicinal three-bond proton–proton coupling constants obtainable from the ¹³C satellites of the proton spectra. These couplings are small, 2.8 Hz for the *meso* and 2.3 Hz for the *dl* isomer, and indicate that the conformations are favored wherein the protons are gauche, just as for the other 1,1,2,2-tetrachloro- or tetrabromoethanes (see Table II).

Table II. Coupling Constants in 1,1,2,2-Tetrahaloethanes

Compound —CHXYCHXY—		J_{HCH} , Hz	J_{CH} , Hz	J_{CCH} , Hz
X	Y			
Cl	Cl	3.0	181 ^a	+1.2 ^a
Br	Br	3.0	181 ^a	+1.1 ^a
Cl	Br (<i>meso</i>) ^b	2.8	181.9	1.54
Cl	Br (<i>dl</i>) ^b	2.3	181.9	1.26

^a E. Sackmann and H. Dreeskamp, *Spectrochim. Acta*, **21**, 2005 (1965). ^b Although the proton resonance of the *meso* isomer of 1,2-dibromo-1,2-dichloroethane (**13**) is 0.045 ppm upfield from the resonance of the *dl* isomer, the ¹³C resonance is 0.24 ppm downfield. The ¹³C chemical shifts and two-bond, carbon–proton coupling constants were determined using the Varian DFS-60 spectrometer [F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2627 (1967)].

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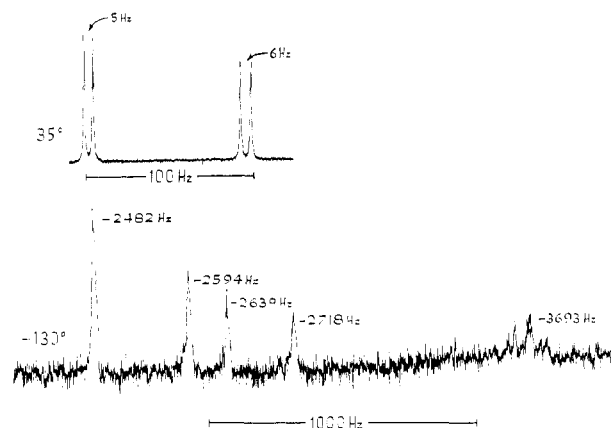


Figure 9. High- and low-temperature limiting spectra for a mixture of *erythro*- and *threo*-1,2-dibromo-1,2-dichloro-1-fluoroethane (**8**). The chemical shifts at low temperatures are relative to fluorotrichloromethane.

The ambient-temperature proton and fluorine spectra of a mixture of isomers of 1,2-dibromo-1,2-dichloro-1-fluoroethane (**8**) each showed two doublets with proton-fluorine couplings of 5 and 6 Hz. Only the fluorine spectrum was examined at low temperatures and is shown in Figure 9. Below -130° , two groups of resonances are seen, separated by over 1000 Hz. The four most intense resonances, at lowest field, have line widths of less than 10 Hz which are indicative of gauche proton-fluorine couplings. The proton-fluorine coupling constants of the *trans* conformations could not be evaluated because of the low populations of these conformations. Clearly, for these compounds, the conformations with hydrogen and fluorines gauche are most favorable, irrespective of whether this brings changes in the number of chlorine-chlorine, chlorine-bromine, or bromine-bromine interactions. This is not surprising because, as we have already pointed out, substitution of bromine for chlorine causes little change in the conformational preferences or rotational barriers. No analysis of the line shapes in the intermediate temperature regions was attempted because of the serious overlap of the spectra from the *erythro* and *threo* isomers. As with the other compounds studied, the fluorine resonances of the least stable conformation come at the highest fields.

Halogenated Propanes. The two C—C bond rotations which are possible for 1,2-dibromo-1,1,2-trichloro-3,3,3-trifluoropropane (**14**) can be separately investigated by the nmr method. At ambient temperatures, a single line is observed because rotation about both C—C bonds is fast on the nmr time scale. At -62° , the spectrum (Figure 10) shows three singlets which are indicative of slow rotation about the 1,2 bond but rapid rotation about the 2,3 bond on the nmr time scale. As with the monofluoroethanes, the chemical shift of the trifluoromethyl group in the least populated conformation comes at highest field and that of the most populated conformation at lowest field. However, there is one anomaly between the -62° spectrum and that of the related compound **7**. With **7**, the conformation in which the fluorine is flanked by two chlorines **7a** has been assigned to the high-field resonance, and the two conformations **7b** and **c** in which the fluorine is flanked by one chlorine and one bromine

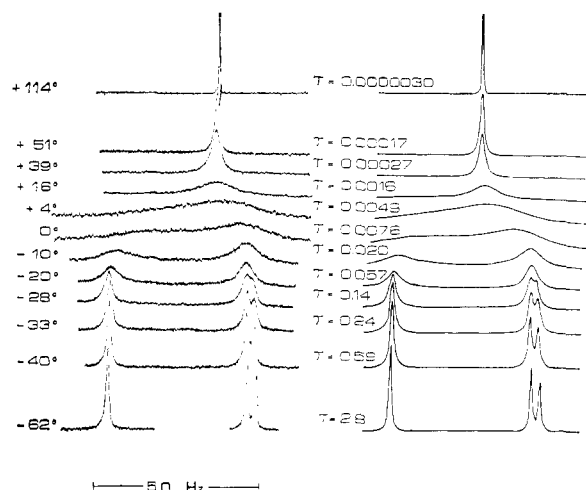
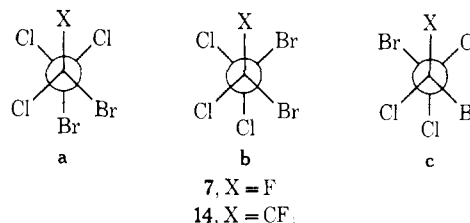


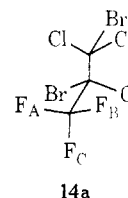
Figure 10. Fluorine spectra at 56.4 MHz of 1,2-dibromo-1,1,2-trichloro-3,3,3-trifluoropropane (**14**). Left, experimental spectra as a function of temperature. Right, calculated spectra for rotation about the 1,2 bond as a function of mean lifetime before rotation (seconds). (See legend to Figure 1.)

have been assigned to the low-field proximate resonances. With **14**, the two close chemical shifts come at high fields, which suggests that these should be assigned to **14b** and **14c**. This is all the more tempting



because a reversal of the direction of the methyl substituent effect on ^{19}F resonances appears to occur, going from interactions involving β - to interactions involving γ -methyl groups.³¹ However, the barrier heights and ground-state energies for **7** and **14** are so similar (see Table I) as to indicate that perhaps the chemical-shift argument should be ignored. No final decision is possible on the basis of the present evidence. The determination of the barriers to rotation about the 1,2 bond was carried out in the same manner as for the simpler fluoroethanes.

Below -60° , the three resonance lines of **14** begin to broaden again and at -140° (the lowest temperature for which we were able to obtain reasonable spectra), there were two very broad, structureless peaks in the ratio of 1:2, separated by about 850 Hz. When rotation about both the 1,2 and 2,3 bonds is slow, the spectrum is expected to be a superposition of three individual ABC spectra with a possible total of 45 lines. With the resolution generally attainable at these low temperatures, a detailed interpretation would be very difficult. The peak with the larger intensity probably arises from the two fluorines, F_A and F_B (**14a**), which are gauche

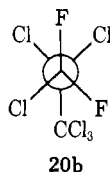
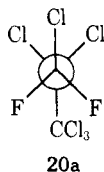


to the dichlorobromomethyl group and either chlorine or bromine, while the less intense resonance comes from the unique fluorine, F_C , which is gauche to bromine and chlorine.

An at least semiquantitative determination of the average barrier to rotation about the 2,3 bond from the line shape changes is possible with our computer programs if the geminal fluorine-fluorine couplings are neglected. At temperatures much below -140° , this is certainly a very poor approximation, but above the coalescence temperature where there is a single very broad line which sharpens with temperature, the approximation seems reasonably valid—all the more so because the calculated line shapes over a considerable range of mean lifetimes are quite insensitive to the chemical-shift differences and the limiting line widths, as well as to whether the high-temperature limit corresponds to three closely spaced fluorine resonances or just one. Over the temperature range from -140 to -104° , the line shape changes correspond to an average activation energy of 6.5 ± 1 kcal/mol for rotation about the 2,3 bond.

With 1,1,1-trifluoropentachloropropane (**18**) at -140° , two broad peaks were observed in the ratio of 1:2, separated by about 850 Hz. Again, it is clear that the low-temperature limit has not been reached. The results with **14** and **18** are in sharp contrast to what has been found with bis(trifluoromethyl)tetrachloroethane (**19**) for which rather sharp spectra are observed even at -120° for the gauche form.³⁶ Here, however, there is the possibility of interference between the two trifluoromethyl groups which would certainly be expected to result in a higher barrier to rotation of the CF_3 groups.

The fluorine spectrum of 1,1-difluorohexachloropropane (**20**) is a sharp singlet at -120° . The lack of any temperature dependence of the spectrum suggests that the substance exists in a single preferred conformation (**20a**) with the two fluorines in magnetically equivalent locations because the barrier to rotation about the 1,2 bond would be expected to be at least as high as that of **18** or **19**, and the chemical-shift difference between the two fluorines in the gauche conformation (**20b**) would be on the order of 850 Hz.



Experimental Section

Proton and fluorine spectra were taken with a Varian A56-60A spectrometer operating at 60 MHz for protons and 56.4 MHz for fluorine. A Varian Model V6040 temperature controller was used for variable-temperature studies. In all of the spectra in the figures the field increases to the right. Temperature calibrations were made with ethylene glycol and methanol samples, and for temperatures below -100° , linear extrapolations of calibrations made with methanol at higher temperatures were used. The temperature measurements are believed to be accurate to $\pm 2^\circ$ but, in any case, are most likely to be the source of error in determining the barriers to rotation. Sweep-width calibrations by the side-band technique were made several times each day, using a Hewlett-Packard 4204A

digital oscillator monitored with a Hewlett-Packard 5425L frequency counter. Mass spectral studies were carried out using a Consolidated Electrochemical Corp. mass spectrometer, Type 21-103C. Melting points were obtained in sealed capillaries using a Büchi apparatus, and are uncorrected. Boiling points are uncorrected.

Trichlorofluoroethene, 1-chloro-2-fluoroethene, and 1,2-dichlorofluoroethene were obtained from the Pierce Chemical Co., Rockford, Ill. Trifluoroperchloropropane and 1,1-difluoroperchloropropane were obtained from Columbia Organic Chemicals, Inc., Columbia, S. C.

The ^{19}F nmr spectra of the halogenated ethanes were taken as about 30% solutions in carbon disulfide with fluorine and proton internal standards added as required. For the spectra of the propanes down to -140° , the solvent was dichlorodifluoromethane. Fluorine chemical shifts (ϕ^*) are upfield from chlorotrifluoromethane, and proton chemical shifts (δ) are downfield from tetramethylsilane. Some of the compounds studied are potent lachrymators and should be handled with care.

1,2-Dibromo-1-chloro-2-fluoroethane (1). 1-Chloro-2-fluoroethene (25 g, 0.3 mol) was dissolved in 30 ml of carbon disulfide in a 100-ml flask equipped with magnetic stirrer and Dry Ice condenser. The mixture was stirred and a carbon disulfide solution of bromine was added dropwise until decolorization of the bromine required longer than 5 min. Distillation gave 60 g (81%) of pale yellow product having bp $148-149.5^\circ$. The proton and fluorine nmr spectra were consistent with the two ABX patterns expected of a mixture of the erythro and threo forms.

1-Bromo-1-chlorofluoroethene (2). Compound **1** (24 g, 0.1 mol) as prepared above was added dropwise over a period of 1 hr to 18.6 g (0.2 mol) of aniline stirred and heated in an oil bath. The temperature was gradually raised to 150° and the product allowed to distill, bp $45-60^\circ$. Redistillation gave 13.6 g (85%) of **2**, bp $52-58^\circ$. Either *cis*- or *trans*-1-bromo-1-chlorofluoroethene was the exclusive product of this dehydrobromination because the proton and the fluorine spectra each showed only a single doublet with $J_{HF} = 82$ Hz, $\delta_H = 7.12$ ppm, and $\phi^* = 110.2$ ppm.

1,1,2-Tribromo-1-chloro-2-fluoroethane (3). Bromination of **2** in carbon disulfide followed by distillation gave an 80% yield of **3**, bp $63-65^\circ$ (42 mm). The parent peak in the 70-V mass spectrum was not observed. Fragmentation peaks were found at m/e 239 (C_2HBr_3ClF), 207 (CBr_2Cl), and 112 ($CHBrF$).

1-Bromo-1,1,2-trichloro-2-fluoroethane (4). Chlorine was slowly bubbled into a stirred solution of **2** in carbon disulfide for 6 hr, or until the proton nmr spectrum indicated that all of the starting alkene had disappeared. Distillation gave **4**, bp 56° (50 mm). The parent peak in the mass spectrum was found at m/e 229 (C_2HBrCl_3F) and fragmentation peaks at m/e 194 (C_2HBrCl_2F), 162 ($CBrCl_2$), 149 (C_2HCl_3F), and 67 ($CHClF$).

1,2-Dibromo-1-chloro-2-fluoroethene (5). To a solution of 1 g of potassium hydroxide in 5 ml of warm ethylene glycol was added 3.2 g (0.01 mol) of **3**. The mixture was stirred and heated at 90° for 1 hr, then distilled under reduced pressure to give **2** g (83%) of **5**, bp 50° (95 mm). The fluorine nmr spectrum showed two singlets separated by 28 Hz.

1,1,2,2-Tetrabromo-1-chloro-2-fluoroethane (6). A stirred solution of **5** in carbon disulfide was irradiated with a 100-W light and 1 equiv of bromine added. Evaporation of the solvent and sublimation of the residue gave a 56% yield of **6** which melted at 150° after some initial softening. The colorless solid was a potent lachrymator. The parent peak (m/e 398) was not evident in the 70-V mass spectrum of **6**, but the fragmentation pattern was consistent with the assigned structure including peaks at m/e 318 (C_2Br_3ClF), 238 (C_2Br_2ClF), 158 (C_2BrClF), 191 (CBr_2F), and 207 (CBr_2Cl).

1,2-Dibromo-1,1,2-trichloro-2-fluoroethane (7). Bromination of trichlorofluoroethene in the usual way gave **7**, mp 122° (lit.³⁷ mp 122.5°).

1,2-Dibromo-1,2-dichloro-1-fluoroethane (8). A stirred solution of 1,2-dichloro-1-fluoroethene in carbon disulfide was irradiated with a 100-W bulb and 1 equiv of bromine added. Distillation gave a mixture of isomers of the *erythro-threo*-**8**, bp $160-161^\circ$ (lit.³⁸ bp 163.5°).

1-Bromo-1,2-dichloro-2-fluoroethene (9). Dehydrobromination of **8** with aniline in the manner described for **2** produced on subsequent redistillation a 40% yield of **9**, bp $89-91.5^\circ$. The fluorine spec-

(36) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 3577 (1968).

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trum of the product showed two singlets at $\phi^* = 72.5$, separated by 0.029 ppm.

1,1,2-Tribromo-1,2-dichloro-2-fluoroethane (10). Photochemical addition of bromine to **9** as for **6**, followed by evaporation of the solvent and sublimation, gave a 55% yield of **10**, mp 148.5–149°. The parent peak in the mass spectrum was seen at m/e 354.

1-Bromo-1,1,2,2-tetrachloro-2-fluoroethane (11). A stirred solution of **9** in carbon disulfide was irradiated with a 100-W bulb and chlorine bubbled in. A mixture of substances was produced with the desired product predominating. The solvent was evaporated and the residue sublimed, giving white lachrymatory crystals of mp 105–107°. The product appeared to be mainly a mixture of **11** and 1,1-dibromo-1,2,2-trichloro-2-fluoroethane (**12**) with perhaps some pentachlorofluoroethane as judged from the mass spectrum (see below). The origin of **12** remains obscure.

The mass spectrum of the product showed no parent peaks for **11**, **12**, or pentachlorofluoroethane but there were fragmentation peaks for **11** at m/e 228 (C_2BrCl_3F), 183 (C_2Cl_4F), 244 (C_2BrCl_4), 101 (CCl_3F), and 162 ($CBrCl_2$); for **12** at 228 (C_2BrCl_3F), 101 (CCl_3F), and 207 (CBr_2Cl , weak); and for C_2Cl_5F at 117 (CCl_3), 101 (CCl_2F), and 183 (C_2Cl_4F , weak).

1,2-Dibromo-1,2-dichloroethane (13). Bromine was added to a stirred solution of either *cis*- or *trans*-1,2-dichloroethene until

the solution remained colored. The excess bromine was destroyed by addition of the required bisulfite solution; the organic layer was then taken up in ether, dried over magnesium sulfate, and distilled at the water aspiration pressure, bp 88–92° (lit.³⁹ bp 84° (45 mm)).

1,2-Dibromo-1,1,2-trichloro-3,3,3-trifluoropropane (14). A mixture of equivalent amounts of 1,1,2-trichlorotrifluoropropene and bromine and 0.1 g of anhydrous ferric chloride was stirred and heated at 90° for 2 days. The reaction mixture solidified on cooling and the product was recrystallized from aqueous ethanol. Sublimation gave colorless lachrymatory crystals of mp 155–156° dec (lit.⁴⁰ mp 151–152°).

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