Structure and Stability of the Bromofluoroethylenes. II. The Geometric Isomers of 1-Bromo-1,2-difluoro- and 1,2-Dibromo-1,2-difluoroethylene

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The two isomeric 1-bromo-1,2-difluoroethylenes have been prepared in pure state; their configurations have been determined, using the n.m.r. and infrared spectra as indicators. In the absence of oxygen, no interconversion of the two isomers takes place. The two isomeric 1,2-dibromo-1,2-difluoroethylenes could only be prepared in the form of their equilibrium mixture; however, the presence of both compounds in this mixture has been established unambiguously by the n.m.r. and infrared spectra. Thermal interconversion of the isomers is extremely fast; the *cis* isomer has the lower energy, the *trans* isomer predominating at room and elevated temperature. The existing data on the steric stability of the various halogenated ethylenes are summarized and discussed.

In continuation of the study of the *cis–trans* isomeric 1-bromo-2-fluoro- and 1,2-dibromo-1-fluoroethylenes[1] the two remaining pairs of isomers of the bromofluoroethylene series have been investigated, *viz.*, 1-bromo-1,2-difluoroethylene and 1,2-dibromo-1,2-difluoroethylene. Both compounds have been prepared 68 years ago by Swarts,[2] but no attempt has been reported of isolating the geometrically isomeric forms. The first product obtained by the Swarts procedure (fluorination of 1,1,1,2-tetrabromo-2-fluoroethane and treatment of the product, presumed to be 1,1,2-tribromo-1,2-difluoroethane, with zinc dust in alcohol) boiled between −6.0 and 16.0° and could be resolved into four compounds, characterized by their infrared and n.m.r. spectra. The lowest boiling (small) fraction could not be identified. The other three had the expected formula C_2HBrF_2: (a) b.p. 5.7°, 1-bromo-2,2-difluoroethylene; (b) b.p. 13°, *trans* isomer of 1-bromo 1,2-difluoroethylene; (c) b.p. 16°, *cis* isomer of 1-bromo-1,2-difluoroethylene (*trans* and *cis* refer to the spatial relation of the two fluorine atoms).

The structure of 1-bromo-2,2-difluoroethylene for the 5.7° fraction was derived from the form and coupling constants of the n.m.r. spectra. The eight lines in the F^{19} resonance typically display the AB part of an ABX spectrum while the four lines found in the proton resonance represent the X part of that spectrum. The calculated coupling constants[3] are $J_{HF} = 0.3$ c.p.s., $J_{HF} = 19.0$ c.p.s., and $J_{FF} = 34.5$ c.p.s. From the small chemical shift between the two fluorine nuclei (see Table I) it may be concluded that they are in *gem* position to one another and the above coupling constants can be assigned to $J_{HF(cis)}$, $J_{HF(trans)}$, and $J_{FF(gem)}$, respectively, in agreement with previous data for compounds of this kind.[4]

The structure was confirmed by the infrared spectrum identical with that described in the literature for this compound[5,6] and finally by direct comparison with an authentic specimen, prepared as described in the Experimental section of this paper. The unexpected formation of this *structural* isomer is due to the presence of some 1,1,2-tribromo-2,2-difluoroethane in 1,1,2-tribromo-1,2-difluoroethane; it is probable that the starting material 1,1,1,2-tetrabromo-2-fluoroethane loses and adds successively hydrobromic acid under the catalytic influence of antimony trifluoride, before the latter exerts its fluorinating activity. In any event,

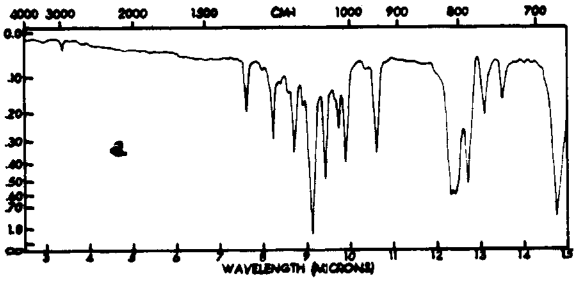

Figure 1a.—Infrared spectrum of $CHBrFCBr_2F$.

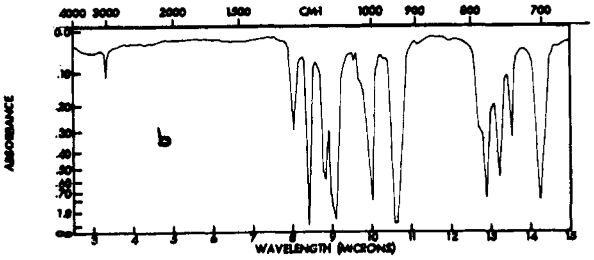

Figure 1b.—Infrared spectrum of $CHBr_2CBrF_2$.

$$CHBrF{-}CBr_3 \xrightarrow{-HBr} CBrF{=}CBr_2 \xrightarrow{+HBr}$$
$$CBr_2F{-}CHBr_2 \xrightarrow{SbF_3} CBrF_2{-}CHBr_2$$

the two isomeric ethanes can hardly be separated by distillation [b.p. 42.6° (18 mm.) and 46.4° (23 mm.)]; the spectrum of the fluorination product shows the presence of both isomers, if compared with that of the two compounds isolated in pure form (Figure 1a,b). Furthermore, it was shown that pure 1,1,2-tribromo-1,2-difluoroethane, prepared by addition of bromine to 1-bromo-1,2-difluoroethylene, regenerates, upon dehalogenation, this olefin only, without any trace of 1-bromo-2,2-difluoroethylene.

If oxygen is strictly excluded, the two isomers of 1-bromo-1,2-difluoroethylene do not isomerize spontaneously and can be separated in pure form by a laborious sequence of fractional distillations. The n.m.r. spectra have permitted a practically unequivocal assignment of the structures.

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(1) A. Demiel, *J. Org. Chem.*, **27**, 3500 (1962).

(2) F. Swarts, *Bull. Acad. Roy. Belg.*, [3] **34**, 307 (1897).

(3) All coupling constants are given in cycles per second.

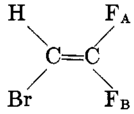
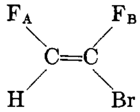
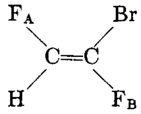
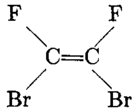
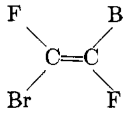
(4) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959, pp. 85–86, and unpublished observations from this laboratory. See also D. Seyferth and T. Wada, *Inorg. Chem.*, **1**, 78 (1962); D. Seyferth, T. Wada, and E. Maciel, *ibid.*, **1**, 232 (1962); G. Andreades, *J. Am. Chem. Soc.*, **84**, 864 (1962).

(5) R. Theimer and J. R. Nielsen, *J. Chem. Phys.*, **27**, 264 (1957).

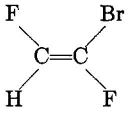
(6) G. Pavlow, *Dissertation Abstr.*, **19**, 2475 (1959).

TABLE I

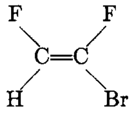
N.M.R. SPECTRA

Compd.	Chemical shifts, p.p.m.[a]			Spin–spin coupling constants, c.p.s.[b]					
	H	F_A	F_B	J_{HF} (*gem*)	J_{HF} (*cis*)	J_{HF} (*trans*)	J_{FF} (*gem*)	J_{FF} (*cis*)	J_{FF} (*trans*)
	5.1	81.9	82.8		0.3	19.0	34.5		
	6.4	145.4	102.8	72.9		13.5		8.4	
	7.5	167.7	129.2	75.0	0				137.3
		95.3	95.3					34.3	
		113.1	113.1						141.4

[a] Chemical shifts of protons are relative to tetramethylsilane, chemical shifts of fluorine atoms to CCl_3F. The resonance of all fluorine atoms in these compounds lies in an *higher* field than that of the reference compound. [b] J_{HF} values are the mean values measured from the proton and F^{19} n.m.r. spectra.



b.p. 13.0°, *trans* isomer



b.p. 16.0°, *cis* isomer

A. *cis* **Isomer.**—The proton resonance is the X part of a first-order ABX spectrum and consists of four lines arranged in two pairs, the distance 13.5 and 73.1 each appearing twice. The latter corresponds to $J_{F_1H_1}$, the former to $J_{F_2H_1}$, fluorine and hydrogen being *trans* to each other.[4] (The subscript 1 refers to carbon atom 1.)

The F^{19} resonance spectrum which is the AB part of the spectrum consists of eight lines of equal intensity which appear as two groups of two doublets with a distance of 8.4 between the lines in each of these four doublets. A distance of 13.4 appearing twice in one of the groups and a distance of 72.7 appearing twice in the other correspond to the two distances assigned above in the proton resonance spectrum. The figure 8.4 must therefore be attributed to $J_{F_1F_2}$, the two fluorine atoms being *cis* to each other, although this figure is lower than the value quoted in the literature.[4]

B. *trans* **Isomer.**—The n.m.r. spectrum of this isomer is less unequivocal, but the following data together with the definite assignment of the *cis* configuration to the higher boiling substance lead to the *trans* structure for the other isomer (b.p. 13°). This uncertainty stems from the fact that in the proton resonance spectrumon ly two instead of the expected four lines appear, and in the F^{19} resonance spectrum only six out of the expected eight lines appear. The former are of equal intensity and are separated by a distance of 74.9 ($J_{F_1H_1}$). The latter are distributed as follows: one pair is separated by a distance of 137.3, and the two other doublets (the intensity of which is half that of the first pair) are separated by distances 137.3 and 75.1 ($J_{F_1H_1}$), each appearing twice. The figure of 137.3 corresponds to $J_{F_1F_2}$ with the two fluorine atoms *trans* to each other. The splitting caused by spin–spin coupling between the fluorine and hydrogen *cis* to each other appears to be less than 0.6 c.p.s. (the experimental line width) so that the expected four lines appear as two, but of double intensity.

The data mentioned are summarized in Table I.[7]

In a forthcoming paper the n.m.r. spectra of all 14 bromofluoroethylenes will be discussed in detail. It will then become clear that values of the chemical shift and coupling constants cited in Table I fit well into the general framework and above all that the assignment made here for the two 1-bromo-1,2-difluoroethylenes is unambiguous on the basis of the n.m.r. spectra.

The infrared spectra (Figure 2) summarized in Table II strongly support the conclusions drawn from the n.m.r. spectra.

TABLE II

INFRARED SPECTRA

ν, cm.$^{-1}$	
Isomer of b.p. 13.0°	Isomer of b.p. 16.0°
3120 (C–H stretching)	3120 (C–H stretching)
1275 (C–H in-plane deformation)	1725 (C=C stretching)
1165 (vs) 1120 (m) } (C–F stretching)	1310 (C–H in-plane deformation)
775 (C–H out-of-plane[a] and/or C–Br stretching)	1135 (m) 1070 (vs) } (C–F stretching)
	775 (C–H out-of-plane stretching)
	825 (C–Br stretching)

[a] In other trihaloethylenes, this frequency lies at 750 (trifluoro-), 754 (1-chloro-2,2-difluoro-), 767 (tribromo-), and 760 (1,2-dibromo-1-fluoro-) cm.$^{-1}$. See ref. 1 and D. E. Mann, N. Acquista, and E. R. Plyler, *J. Chem. Phys.*, **22**, 1586 (1954); J. R. Nielsen, C. H. Liang, and D. C. Smith, *ibid.*, **20**, 1090 (1952); J. C. Evans and H. J. Bernstein, *J. Can. Chem.*, **33**, 1177 (1955).

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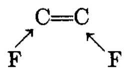
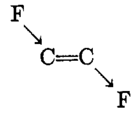
[7] The data for this table anticipate a forthcoming publication by J. Reuben, Y. Shvo, and A. Demiel.

The C=C stretching frequency appears only in the *cis* isomer and is completely absent in the solution of the *trans* isomer. This is unexpected, as the latter is not completely symmetrical, and therefore, that frequency should be permitted. For reasons discussed in the case of the two 1,2-dibromo-1-fluoroethylenes[1] one would expect that the *cis* isomer has a higher dipole moment in the case under discussion. If one then assumes that in the two isomers the extent of stretching of the C=C bond is about equal, the change in dipole moment caused by the stretching will be greater, and the corresponding infrared absorption intensity larger for the *cis* isomer.

The differences in the relative intensities of the C–F stretching frequencies in the two isomers point to the same conclusions, if one remembers that of the two frequencies the *lower* frequency is due to the *symmetrical*, the *higher* to the *antisymmetrical* mode. In the *cis* isomer the symmetrical mode of vibration is the one



associated with a greater change in the dipole moment and therefore, the peak at 1070 cm.$^{-1}$ is stronger than that at 1135 cm.$^{-1}$. The inverse is true for the *trans* isomer for which the intensity of the band at 1165 cm.$^{-1}$ is stronger than at 1020 cm.$^{-1}$; in this case the *antisymmetrical* mode of vibration is the one associated with a more significant change in the dipole moment.



As expected in view of previous experience,[1] the in-plane deformation frequency of the hydrogen is lower in the isomer in which fluorine and hydrogen are *cis* to each other (*trans* isomer) than in the isomer in which bromine and hydrogen are in the *cis* configuration (*cis* isomer).

The C–Br stretching frequency in the *cis* isomer (825 cm.$^{-1}$) is higher than in the *trans* isomer (775 cm.$^{-1}$ or lower). A similar effect has been observed in the case of the isomeric 1-fluoro-2-bromoethylenes, the configurations of which have been established independently.[1] The C–Br stretching frequency in that case is higher when bromine is *cis* to hydrogen (790 cm.$^{-1}$) than when it is *cis* to fluorine (730 cm.$^{-1}$ or lower).

1,2-Dibromo-1,2-difluoroethylene was also prepared according to Swarts,[2] *viz.*, by dehydrobromination of 1,1,2-tribromo-1,2-difluoroethane which was carried out with aqueous potassium hydroxide and not with potassium ethoxide, to prevent ether formation.[8] Two fractions were obtained, both of the expected formula $C_2Br_2F_2$: a small one, boiling at 68°, which was identified by infrared analysis as 1,1-dibromo-2,2-difluoroethylene,[9] and a main one boiling at 71.8°. The infrared spectrum of the 68° fraction was identical with that of authentic 1,1-dibromo-2,2-difluoroethylene, prepared by the dehydrobromination of 1,1,2-tribromo-2,2-difluoroethane.

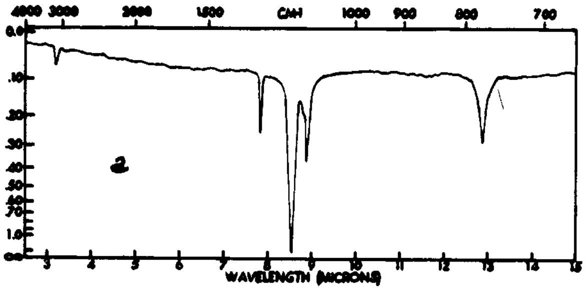


Figure 2a.—Infrared spectrum of *trans*-1-bromo-1,2-difluoroethylene, b.p. 13.0°.

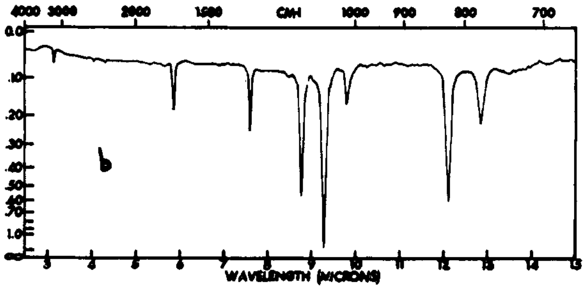


Figure 2b.—Infrared spectrum of *cis*-1-bromo-1,2-difluoroethylene, b.p. 16.0°.

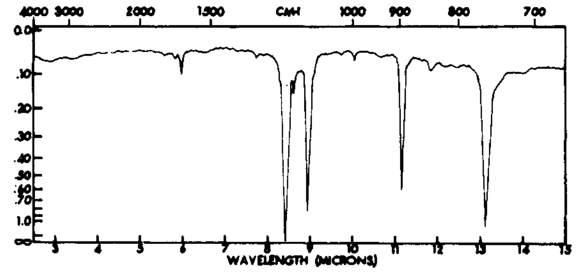


Figure 3.—Infrared spectrum of the equilibrium mixture of the isomers of CBrF=CBrF.

As in the recently published case[10] of 1,2-dichloro-1,2-difluoroethylene, vapor phase chromatography of the main fraction (on several different columns) revealed only one peak, instead of the expected two of the *cis–trans* isomers of 1,2-dibromo-1,2-difluoroethylene. However, unlike the above case, even the most careful fractionation of our product neither separated nor enriched the two isomers, all subfractions tested showing the same infrared spectrum (Figure 3).

The usual methods employed for *cis–trans* isomerization of olefins (*e.g.*, by heating at 200° with iodine) did not bring about any change in the relative intensities of the infrared bands, nor was it possible to obtain more than one constant-boiling azeotrope with any of a number of alcohols tested.[11]

It seemed, therefore, plausible that in this case only one geometrical isomer was formed, that it is very

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(8) A. Demiel, *J. Org. Chem.*, **25**, 993 (1960).

(9) J. R. Nielsen and R. Theimer, *J. Chem. Phys.*, **30**, 103 (1959). This compound is obviously formed by dehydrobromination of the isomeric ethane, the presence of which in the starting material has been proven above.

(10) G. V. D. Tiers and P. C. Lauterbur, *ibid.*, **36**, 1110 (1962).

(11) This method proved to be effective in the separation of other pairs of *cis–trans* isomers. See ref. 1 and (a) H. Van de Walle, *Bull. soc. chim. Belges*, **29**, 322 (1920); *Chem. Abstr.*, **16**, 2109 (1922); (b) H. Van de Walle and A. Henne, *Bull. soc. chim. Belges*, **34**, 399 (1925); *Chem. Abstr.*, **20**, 1394 (1926); (c) H. Van de Walle and A. Henne, *Bull. Sci. Acad. Roy. Belg.*, [5] **11**, 360 (1925); *Chem. Abstr.*, **20**, 1050 (1926); (d) H. Van de Walle, *Bull. soc. chim. Belges*, **45**, 726 (1936); *Chem. Abstr.*, **31**, 3000 (1937); (e) H. Van de Walle, *Bull. soc. chim. Belges*, **47**, 217 (1938); *Chem. Abstr.*, **32**, 5371 (1938).

much more stable than the other isomer, and furthermore that it is the *cis* form (four infrared bands in the region 750–1200 cm.$^{-1}$ and a weak C=C stretching band at 1168 cm.$^{-1}$; in the *trans* isomer no C=C stretching frequency is allowed in the infrared spectrum, and the number of bands in the 750–1200-cm.$^{-1}$ region should be smaller). Nevertheless, we have shown beyond doubt that the product of constant boiling point 71.8° is a mixture of the two geometrical isomers which we have not been able to resolve into its components.

Mann, *et al.*,[12] have calculated the fundamental bands of the two isomers: *cis* 910, 1111, and 1235 cm.$^{-1}$; *trans* 768, 1168 (forbidden in the infrared), and 1228 cm.$^{-1}$. Figure 3 shows that the product in question has bands both at 895 and 760 cm.$^{-1}$ corresponding to the two lower frequencies calculated for the two isomers; however, of the C–F stretching bands only the value 1115 cm.$^{-1}$ corresponds to the calculated one, and only one more absorption (not two) has been observed at 1185 cm.$^{-1}$. In spite of its low value, we assume that this band corresponds to *both* the predicted frequencies (1235 and 1228 cm.$^{-1}$). This assignment is supported by the fact[12,13] that, in the infrared spectrum of the mixture of the two 1,2-dichloro-1,2-difluoroethylenes, only two (instead of the expected three) C–F stretching modes were found. In this case, as well as in the present case, the observed frequency (1214 cm.$^{-1}$) was lower than the calculated ones (1234 and 1260 cm.$^{-1}$) for the two isomers.

The n.m.r. spectrum of our product supported our assumption that the latter is a mixture of the two isomers. Because of the equivalence of the two fluorine atoms, either isomer studied should show only one single fluorine resonance peak. Our product has *two* such peaks at a distance of 17.8 p.p.m. from each other at room temperature (chemical shift). The ratio of the intensities of these two lines was 1:3.75, so that undoubtedly one of the isomers is likely to be present in larger quantities. That this is the *trans* isomer may be concluded from the infrared spectrum of the mixture on the strength of the observation that the peak at 1680 cm.$^{-1}$ (C=C stretching) is very weak; this line must be that of the *cis* isomer, and it is unlikely that it would be so weak if the *cis* isomer were the predominant constituent of the mixture.

The n.m.r. spectrum of the C^{13} satellites in 1,2-dibromo-1,2-difluoroethylenes furnished the final proof that the above assignment is correct: by the technique used by Tiers and Lauterbur[10] for 1,2-dichloro-1,2-difluoroethylene, it was found[7] that for our product the more intense line (which is also in a higher field) belongs to the *trans* isomer (J_{FF} = 141.4 c.p.s., $J_{C^{13}F}$ = 355.0 c.p.s., and $J_{C^{13}C^{12}F}$ = 102.5 c.p.s.), the weaker to the *cis* isomer (J_{FF} = 34.3 c.p.s., $J_{C^{13}F}$ = 324.7 c.p.s., and $J_{C^{13}C^{12}F}$ = 35.8 c.p.s.).

Our inability to separate the two 1,2-dibromo-1,2-difluoroethylenes or even to enrich the mixture with one of the isomers led us to conclude that either of the two isomers is transformed practically instantaneously into the mixture boiling at 71.8°. In this connection it may be useful to recall that also in the case of 1,2-dibromo-1-fluoroethylene[1] the two geometrical isomers interconverted spontaneously when their azeotropes were decomposed or when the solvent was removed from their solutions. Also the mixture of the two 1,2-dichloro-1,2-difluoroethylenes[10] has proved to be inseparable by careful fractionation which only led to a slight shift in the ratio of the two isomers in the various fractions of the distillate. It is in keeping with previous experience that the dibromo analog should be even more refractory to attempts at separation than the dichloro compound.

The hypothesis of fast interconversion and equilibration of the two 1,2-dibromo-1,2-difluoroethylenes is supported by the observation that the intensities (and the areas) of the lines, in both the infrared and n.m.r. spectra, changed instantaneously and reversibly by just varying the temperature of the mixture. Semiquantitative results of the n.m.r. spectroscopy at various temperatures show that the equilibrium constant (*cis/trans*) changes from about 0.28 at room temperature to 0.23 at 80°, so that the energy difference between the two isomers, calculated by the van't Hoff isochore, is about 750 cal./mole, the *cis* isomer having the lower energy. Although this figure seems to be rather high, it is in the range of values found for 1,2-dihaloethylenes.[14] However, 1,2-dibromo-1,2-difluoroethylene is exceptional in this series inasmuch as the "less stable" *trans* isomer predominates largely (about 77% of the equilibrium mixture) at room temperature.[15]

The facts reported here point not only to a low value of ΔH, but also to an unusually low potential barrier between the two geometrical isomers which makes possible a very fast interconversion at room or higher temperatures. However, this interconversion is slow enough to allow detection, by means of the n.m.r. spectrum, of the two distinct species (and not an average)[16] with a distinct chemical shift, which becomes smaller with rising temperature.

It may be of interest to summarize the pertinent data on the halogenated ethylenes, although this summary must by necessity be somewhat speculative. For the 1,2-dihalogenoethylenes it has been shown[1] that the isomer containing the two most electronegative substituents *cis* to each other is the more stable one and that the inverse of the sequence of stabilities represents the relative ease of isomerizability of the geometrical isomers into the equilibrium mixture; for the tri- and tetrasubstituted ethylenes the data are scanty and do not appear always reliable. Van de Walle has prepared the isomers of 1-bromo-1,2-dichloro- and 1,2-dibromo-1-chloroethylene[11a,d] and has concluded that the *cis* isomers are the more stable ones in both cases. This is in line with our experience[1] as far as the first pair of compounds is concerned, but not for the second pair; it would be interesting to verify the proposed configurations by more unambiguous methods

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[12] D. E. Mann, L. Fano, J. H. Meal, and T. Shimanochi, *J. Chem. Phys.*, **27**, 51 (1957).

[13] D. E. Mann and E. K. Plyler, *ibid.*, **26**, 773 (1957).

[14] For the pertinent literature, see ref. 1.

[15] A rational explanation of this phenomenon is given by T. L. Hill, "An Introduction to Statistical Thermodynamics," Addison-Wesley Publishing Co., Reading, Mass., and London, 1960, pp. 182–184.

[16] See J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 365.

and to study the energy relations and ease of isomerization in this series.[17]

In any event our experience with 1,2-dibromo-1-fluoro- and 1-bromo-1,2-difluoroethylene seems to show that the "electronegativity rule"[1] applies to them, as evidenced by the fact that in both cases the equilibrium mixture of isomers, reached from both sides at room or higher temperatures, is richer in the isomer in which the two most electronegative substituents are on the same side of the double bond (the *trans* isomer in the first, the *cis* isomer in the second case); in either case these isomers are also the higher boiling ones.[18]

For the tetrahaloethylenes it has been claimed that mixtures of the 1,2-dibromo-1,2-dichloro- and 1,2-dichloro-1,2-difluoroethylenes can be resolved into the isomers. Van de Walle[11e] assigned in the first case the *cis* configuration to the more stable isomer—as the "electronegativity rule" demands—but no isomerization studies have been carried out. In the second case Henne, *et al.*,[19] have stated that the higher boiling isomer has the *trans* structure. This has been proven by Tiers and Lauterbur[10]; however, it has not yet been shown which isomer is the more stable.

The 1,2-dibromo-1,2-difluoroethylene studied in the present paper would be expected to occupy an intermediate position between the two above tetrahaloethylenes. This is, however, not the case so far as the separation of isomers is concerned. One might, therefore, draw the following conclusions. For the 1,2-dihaloethylenes the configuration is determined not by the size of the substituents, but by their ability to withdraw or to supply electrons by inductive or mesomeric effects, respectively.

In the trihaloethylenes there are always two halogens *cis* to each other and the electronic properties and the steric factor act in the same direction. Obviously in the tetrahaloethylenes, in which there are in every case two pairs of halogens *cis* to each other, the steric factor will play a more important role in determining the relative stability of the configuration. Thus, in the case of 1,2-dibromo-1,2-difluoroethylene, one could not foresee which isomer is the more stable. In the *cis* form, the two more voluminous bromine atoms would be on the same side of the double bond; in the *trans* isomer, the "electronegativity rule" would not be obeyed.

Experimental

1,1,1,2-Tetrabromo-2-fluoroethane.—This compound was prepared by addition of bromine to 1,1-dibromo-2-fluoroethylene, as described by Swarts,[20] but was purified by distillation at lower pressure in order to avoid decomposition: b.p. 42.5° (0.25 mm.), d^{18}_{4} 2.933, n^{18}_{D} 1.5958, MR 42.14 (calcd. 42.15[21]).

Anal. Calcd. for C_2HBr_4F: C, 6.6; H, 0.3; Br, 87.9; F, 5.2. Found: C, 6.8; H, 0.4; Br, 87.3; F, 4.9.

There was no change in the infrared spectrum on further distillation; this spectrum in CS_2 or CCl_4 contained only seven peaks between 675 and 4000 cm.$^{-1}$ at 2990, 1305, 1210, 1080, 1005, 767, and 750 cm.$^{-1}$.

1,1,2-Tribromo-1,2-difluoroethane.—A mixture of 372 ml. of 1,1,1,2-tetrabromo-2-fluoroethane, 140 g. of antimony trifluoride,[22] and 50 ml. of bromine was heated for 6 hr. at 110–115° in a stainless steel vessel with vigorous stirring. The product was washed several times with concentrated hydrochloric acid and with water, dried over calcium chloride, and distilled *in vacuo:* b.p. 44° (19 mm.). It is advisable to treat the product with a small quantity of bromine (to remove unsaturated impurities), to destroy the excess of the halogen with sodium hydrogen sulfite, and to wash, dry, and distil the product again. The yield was 610 g. (67%). A small quantity of 1,2-dibromo-1,1,2-trifluoroethane (b.p. 75.3°) was also obtained, and 102 ml. (27%) of the starting material was recovered.

In order to prepare the desired substance in an absolutely pure state, gaseous (b.p. 13–16°) 1-bromo-1,2-difluoroethylene was bubbled through bromine in water and the product was worked up as above: b.p. 42.6° (18 mm.), d^{16}_{4} 2.612, n^{16}_{D} 1.5078, MR 34.54 (calcd. 34.53).

Anal. Calcd. for $C_2HBr_3F_2$: C, 7.9; H, 0.3; Br, 79.2; F, 12.5. Found: C, 8.1; H, 0.3; Br, 79.0; F, 12.3.

1,1,2-Tribromo-2,2-difluoroethane.—In the manner described above, pentabromoethane or 1,1,2,2-tetrabromo-1-fluoroethane were fluorinated. A very pure product was obtained by bromination of 1-bromo-2,2-difluoroethylene (see below) with bromine in water: b.p. 46.4° (24 mm.), d^{22}_{4} 2.591, n^{22}_{D} 1.4985, MR 34.29 (calcd. 34.53).

Anal. Calcd. for $C_2HBr_3F_2$: C, 7.9; H, 0.3; Br, 79.2; F, 12.5. Found: C, 8.1; H, 0.5; Br, 79.0; F, 12.6.

1-Bromo-2,2-difluoroethylene. A.—A well-stirred mixture of 50 g. of zinc dust, 1 g. of zinc bromide, and 150 ml. of anhydrous ethyl alcohol was refluxed in an atmosphere of nitrogen, a descending condenser being connected to the top of the reflux condenser. While the latter was being cooled with water, the former was cooled with a Dry Ice–acetone mixture, and a separatory funnel containing cold water (to remove the entrained alcohol) served as receiver. The bottom of the separating funnel was connected to a Dry Ice–acetone cooled flask.

To the boiling reagent mixture, 70 g. of 1,1,2-tribromo-2,2-difluoroethane was added gradually. After an induction period, the exothermic reaction did not require any external heating; only toward the end of the reaction was the mass heated for a short while. The product, withdrawn from time to time from the separatory funnel into the cooled flask, was dried by refluxing it over calcium chloride (condenser packed with Dry Ice), cooled, filtered quickly, and fractionated: b.p. 5.7° (760 mm.), yield 78 g. (91%).

B.—In the same type of apparatus as that used in part A, a solution of 35 g. of potassium hydroxide in 150 ml. of water was added to a suspension of 112 g. of 1,2-dibromo-1,1-difluoroethane in 50 ml. of boiling water. The reaction needed only a little external heating; the yield was 44 g. (63%), b.p. 5.7° (760 mm.). The infrared spectra of the two preparations were identical.

1,2-Dibromo-1,2-difluoroethylene.—A solution of 70 g. of potassium hydroxide in 300 ml. of water was added—in an atmosphere of nitrogen—to a well-stirred suspension of 116 ml. of 1,1,2-tribromo-1,2-difluoroethane in 116 ml. of boiling water. The external heating was regulated so that the mixture boiled gently. After 30 min. of additional heating, the reaction product was distilled, dried over calcium chloride, and fractionated in a good column, all operations being carried out under nitrogen: b.p. 71.8° (760 mm.), yield 165 g. (74%), d^{24}_{4} 2.296, n^{24}_{D} 1.4482, MR 25.89 (calcd., 25.49).

Anal. Calcd. for $C_2Br_2F_2$: C, 10.8; Br, 72.0; F, 17.1. Found: C, 10.7; Br, 71.1; F, 17.1.

The azeotropes of the olefin were prepared by dissolving it in an equal volume of the alcohol and repeated fractionation in an efficient column. The following boiling points were observed for the azeotropes: methanol, 54.3°; ethanol, 62.9°; 1-propanol, 70.0°; and *t*-butyl alcohol, 68.5°.

1-Bromo-1,2-difluoroethylene.—In the apparatus used for the preparation of the isomeric 1-bromo-2,2-difluoroethylene, a

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(17) K. Lakshmi [*Dissertation Abstr.*, **20**, 2856 (1960)] has recently separated the isomers of 1-bromo-2-chloro-2-fluoroethylene, without indicating their relative stability.

(18) The temperature dependence of the equilibrium constants in these cases is being studied at present.

(19) E. G. Lock, W. R. Brode, and A. L. Henne, *J. Am. Chem. Soc.*, **56**, 1726 (1934); *cf.* R. F. Sullivan, *Dissertation Abstr.*, **18**, 1650 (1958).

(20) F. Swarts, *Bull. Acad. Roy. Belg.*, [3] **33**, 439 (1897).

(21) For the calculation of the molecular refractions, the values, C = 2.418, H = 1.100, Br = 8.865, have been employed. An unpublished study of 26 bromofluoroethanes and -ethylenes has shown that, if these figures are being kept constant, the atomic refraction of fluorine varies between the extreme values 0.25 and 1.10, which is obviously due to constitutional factors. In accordance with the results of this study the fluorine value for the monofluoroethane compounds in the present paper was taken as 0.75, for the difluoroethane compounds as 1.00, and for the difluoroethylene compounds as 0.60.

(22) The quantity is less than theoretical, in order to repress the formation of 1,2-dibromo-1,1,2-trifluoroethane.

mixture of 40 g. of zinc dust, 1 g. of zinc bromide, and 150 ml. of anhydrous alcohol was heated to the boiling point and 58 ml. of 1,1,2-tribromo-1,2-difluoroethane was added dropwise. The work-up gave 68 g. (94%) of the mixture of geometric isomers, which was resolved in two (in series) vacuum-jacketed Todd columns (metal spiral) with a vacuum-jacketed distilling head; the latter was connected to a reflux condenser cooled with a mixture of Dry Ice and acetone. The descending condenser was cooled also in this manner.

Fractionation of the above product gave after repeated distillations one isomer, boiling at 13.0°, and a second, boiling at 16.0°. The fractionation was repeated until either of the two compounds boiled within a 0.1° range and further distillation did not cause any change in the infrared spectrum.

The infrared spectra were determined using a Perkin-Elmer infrared spectrophotometer, Model 137, with sodium chloride prisms. The samples (solutions in carbon tetrachloride for the range 850–4500 cm.$^{-1}$, in carbon disulfide for the range 675–850 cm.$^{-1}$) were prepared as follows[23]: the compound was distilled directly into a small glass ampoule of known weight; the ampoule was sealed; the two glass parts were cleaned and weighed, so that the weight of the substance measured was known. For the measurements, the ampoules were broken under the solvent in a suitable vessel.

The vapor phase chromatography of 1,2-dibromo-1,2-difluoroethylene was attempted in a column of 1.5 m., packed with tricresyl phosphate (10%) on Chromosorb W, which was effective in the separation of the two isomers of 1,2-dibromo-2-fluoroethylene,[1] and also in columns of 3.5 m., packed with either Dow Corning 550 fluid (10%) or Cambridge Industries Co. LAC-2-R446 polyester (10%) on Chromosorb W; temperatures were 25–100°.

The n.m.r. studies were carried out with the Varian high resolution n.m.r. spectrometer, Model HR-60, at a frequency of 56.4 Mc./sec. using the side-band technique. For the proton resonance spectra, a 0.5% solution of tetramethylsilane in carbon tetrachloride, for the F^{19} resonance spectra, a solution of Freon 11 (trichlorofluoromethane) in the same solvent served as internal reference standard.[24]

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(23) This method proved most useful for all substances boiling below room temperature.

(24) G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

Bridgehead Dehydrohalogenation in the Photodimer of 9-Chloroanthracene

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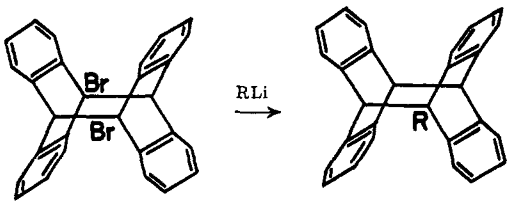
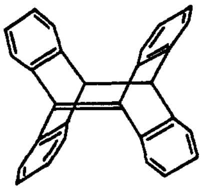
The previously reported reaction of the photodimer of 9-bromoanthracene with alkyllithiums to give alkylated dianthracenes is shown by deuterium labeling not to be an elimination–addition mechanism as previously supposed. The photodimer of 9-chloroanthracene, however, does react with aryllithiums through an elimination–addition–elimination sequence to give aryldehydrodianthracenes. The intermediate olefin formally violates the Bredt rule. Efforts to isolate it have been thus far unrewarded.

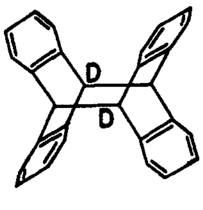
It was reported a few years ago[1] that the photodimer (**1**) of 9-bromoanthracene reacted with alkyllithiums to produce, among other products, 9-alkyldianthracenes (**2**). It was felt that the most probable mechanism for such a conversion was an elimination–addition through an intermediate 9,9′-dehydrodianthracene (type **3**), followed by protolysis of the bridgehead lithium. One of the halogens was removed by some reductive process, and in fact a common product was the parent dianthracene.



1 **2**, R = $n\text{-}C_4H_9$, CH_3



3



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It has now been found that the dimer of 9-bromoanthracene-10-*d* reacts with *n*-butyllithium in pentane–benzene to give **2** (R = $n\text{-}C_4H_9$) with no loss of deuterium. The elimination–addition mechanism is thus unequivocally ruled out.

The question of mechanism of formation of **2** is not settled, although a free-radical coupling of the sort proposed to explain random coupling products in simple alkyl cases[2] seems most attractive. The bridgehead free radical in the present case is almost certainly not seriously destabilized by strain.[3] The radical could also serve conveniently to account for reduction, since it could abstract hydrogen atoms from solvent or butyl radicals.

Perhaps a more difficult mechanistic question is raised by the reduction of **1** with lithium aluminum hydride. It has been found that reduction with lithium aluminum deuteride in THF gives dianthracene-9,10′-d_2 (**4**), identified by its conversion to anthracene-9-*d* upon melting. On the other hand, reduction with lithium aluminum hydride with a D_2O isolation procedure gave unlabeled dianthracene.[4] If we exclude frontside S_N2 reaction as a reasonable mechanism, then we are left with reagent-promoted ionization of the bridgehead bromide and hydride transfer to the carbonium ion, or some free-radical path like that proposed above for alkyl coupling. The present data do not distinguish these possibilities.

For the reasons earlier given,[1] substances of structure type **3** still seemed attractive research objectives,

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(1) D. E. Applequist, R. L. Litle, E. C. Friedrich, and R. E. Wall, *J. Am. Chem. Soc.*, **81**, 452 (1959).

(2) (a) D. E. Applequist and D. F. O'Brien, *ibid.*, **85**, 743 (1963); (b) D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

(3) D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 2194 (1965).

(4) Professor P. D. Bartlett has informed us that the opposite labeling pattern emerges in reductions of 9-bromotriptycene; *i.e.*, the bridgehead proton comes from the water added after the reduction.