diaminopyridine[16] and aminotriazines.[17] Clearly, the unshared electron pairs of the amino nitrogen atoms are not fully available for reactions of the electrophilic type. Similar unusual boron trifluoride adducts of a 3:1 molar ratio are also known in the aliphatic series.[18]

---

[16] A. E. Tschitschibabin and O. A. Seide, *J. Russ. Phys. Chem. Soc.*, **46**, 1233 (1914); A. I. Titov, *J. Gen. Chem. USSR*, **8**, 1483 (1938).

[17] C. Broche, *J. prakt. Chem.*, [2] **50**, 116 (1894).

[18] E. L. Muetterties, *Z. Naturforsch.*, **12b**, 264 (1957).

Structure and Stability of Isomeric Fluorobromoethylenes. I. The Geometrical Isomers of 1-Bromo-2-fluoro- and 1,2-Dibromo-1-fluoroethylene

ARYE DEMIEL

Israel Institute for Biological Research, Ness-Zionah, Israel

Received March 2, 1962

The *cis-trans* isomeric forms of 1,2-dibromo-1-fluoroethylene have been prepared and their structures determined from the infrared spectra and dipole moments. These have been correlated with the corresponding data for the *cis-trans* isomeric 1-bromo-2-fluoroethylenes. Certain regularities in the series of the 1,2-dihalogenoethylenes are discussed.

In a recent publication,[1] the two known[2] *cis-trans* isomeric 1-bromo-2-fluoroethylenes (*cis:* b.p. 40°, dipole moment 1.9 D.; *trans:* b.p. 20°, dipole moment 0.3 D.) have been described in detail; the *cis* form is the more stable one, the equilibrium lying at 75% *cis* isomer. This equilibrium has been reached by heating of the pure isomers at 100° in the presence of acid.

In the framework of a larger project, the two above isomers were also studied in this laboratory some three years ago. The constants measured fully agree with those reported by Viehe[1]: *cis* isomer: b.p. 39.8° (760 mm.); dipole moment 1.95 D.. *trans* isomer: b.p. 19.8° (760 mm.), dipole moment ~0. The infrared spectra observed in solution (Fig. 1a and 1b) agree with those published by Viehe,[1] which refer to the vapor phase. The *trans* compound is characterized by a lower intensity of the C═C band and a smaller number of absorption bands[3]; furthermore, it shows the out-of-plane vibration of the C—H bond at 890 cm.$^{-1}$, while that frequency lies in the *cis* isomer at 730 cm.$^{-1}$. There is also a difference between the two isomers in the position of the C—F frequency: *cis*-1035, *trans*-1100 cm.$^{-1}$. This appears to be a more general effect; in the spectra published by Viehe,[1] one finds the following peaks for the C—F absorption of other 1-fluoro-2-halogenoethylenes studied: 1,2-Difluoroethylene: *cis* 1120 and 1140, *trans*-1168 and 1149 cm.$^{-1}$. 1-Chloro-2-fluoroethylene: *cis*-1073 and 1057, *trans*-1139 and 1125 cm.$^{-1}$. 1-Iodo-2-fluoroethylene: *cis*-1038 and 1027, *trans*-1102 and 1092 cm.$^{-1}$. The C—F frequency is always *lower* in the *cis* isomer, and the magnitude of the shift increases with the increase in atomic weight of the second halogen atom.

The infrared spectrum of the two isomeric 1-bromo-2-fluoroethylenes can be used to advantage for a study of their isomerizability. The *cis* isomer is fairly stable and can, therefore, be obtained very easily by distillation from the mixture of the isomers. In sealed glass ampoules, it can be kept at room temperature for several months without significant isomerization; transformation into the equilibrium mixture does take place but very slowly. The *trans* compound, on the other hand, polymerizes during distillation to oily and solid products and is much more easily isomerized; transformation into the equilibrium mixture (Fig. 1c) takes place within three to four days at room temperature (without added external catalyst). (This is somewhat at variance with the description of the isomerization given by Viehe.[1]) Both compounds isomerize more quickly in carbon tetrachloride solution than in the isolated state, as can be seen from the infrared spectrum of their solutions (Fig. 1d). At the same time, the compounds appear to add carbon tetrachloride to the double bond, as evidenced by the following observations (although we have not isolated the adduct): (a) While the C—H stretching frequency in the unsaturated compounds lies at 3120 cm.$^{-1}$, in the solution a peak gradually appears at 3020 cm.$^{-1}$, corresponding to that frequency in a *saturated* molecule. (b) The intensity of the C═C band (1640 cm.$^{-1}$) decreases gradually. (c) A peak at 1260 cm.$^{-1}$ appears and increases gradually in intensity; it is also due to a C—H vibration of the saturated compound. (d) In the 1020–1150-cm.$^{-1}$ region the peaks become less clear, probably because of the appearance of new C—F vibrations—*viz.* those of saturated fluorine compounds.

These results have made it possible to arrive at

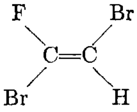
---

[1] H. G. Viehe, *Ber.*, **93**, 1697 (1960).

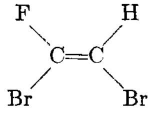
[2] F. Swarts, *J. Chim. Phys.*, **20**, 49 (1923).

[3] H. J. Bernstein and J. Powling, *J. Am. Chem. Soc.*, **73**, 1843 (1951).

definite conclusions in the more complex case of 1,2-dibromo-1-fluoroethylene, which has been prepared from 1,1,2,2-tetrabromo-1-fluoroethane and zinc. The two isomers isomerize spontaneously, so that distillation of the crude product only gives the equilibrium mixture (Fig. 2a). However, it was found possible to separate the two isomers as their azeotropes with ethanol: The azeotropes boiled at 70.2 and 73.3°, respectively, under 760 mm. pressure. Either azeotrope showed the charac-



F—Br isomer
B.p. of azeotrope, 73.3°



F—H isomer
B.p. of azeotrope, 70.2°

teristic infrared absorption (Fig. 2b, 2c) of the respective isomer only, and was thus completely free of the other isomer. However, an attempt at isolating the isomer by addition of water to the azeotropes resulted in instantaneous transformation to the equilibrium mixture. The olefins can be obtained in the form of dilute solutions (<10%) in carbon disulfide or carbon tetrachloride from the azeotropes by addition of these solvents and treatment of the mixture with calcium chloride, or by distillation of the alcohol in the form of its azeotrope with carbon disulfide. In carbon tetrachloride (as well as in carbon disulfide) the isomerization is slow, and the rate of addition of carbon tetrachloride to the double bond is low enough to permit the infrared spectra (Fig. 2d and 2e) and the dipole moments of the two isomers to be determined. Again, evaporation of the solvents (even *in vacuo* at −20°) brought about immediate equilibration of the two isomers.

In the infrared spectrum of the compound giving the 70.2° azeotrope two characteristic bands lie at 816 and 1116 cm.$^{-1}$; in the azeotrope of the other isomer they appear at 712 and 1059 cm.$^{-1}$. The dipole moments are 1.20 ± 0.05 and 1.36 ± 0.05 D., respectively. It is obvious that the two isomers would have about the same dipole moment, as the specific moments of the C—F and the C—Br bond are close to each other. If the observed difference in the two moments is considered significant, the following argument may be applied leading to the above-postulated configuration of the two isomers: In the F—Br isomer, the two C—Br moments cancel each other, and the resulting moment should be identical with that of vinyl fluoride, for which $\mu = 1.5$ D. has been calculated.[4] In the F—H isomer, on the other hand, the moment of the molecule results from the vectorial addition of one C—Br moment and of the difference between one C—Br and one C—F moment; the moment of this isomer should, therefore, be smaller than that of vinyl bromide (1.41) and also than that of the other isomer. The higher moment should, then, be ascribed, to the F—Br isomer. These considerations presuppose that the molecule is planar and that the valency angles are not distorted, conditions which probably do not strictly apply. This may be the cause for the fact that the moments of both isomers are lower than that of vinyl bromide.

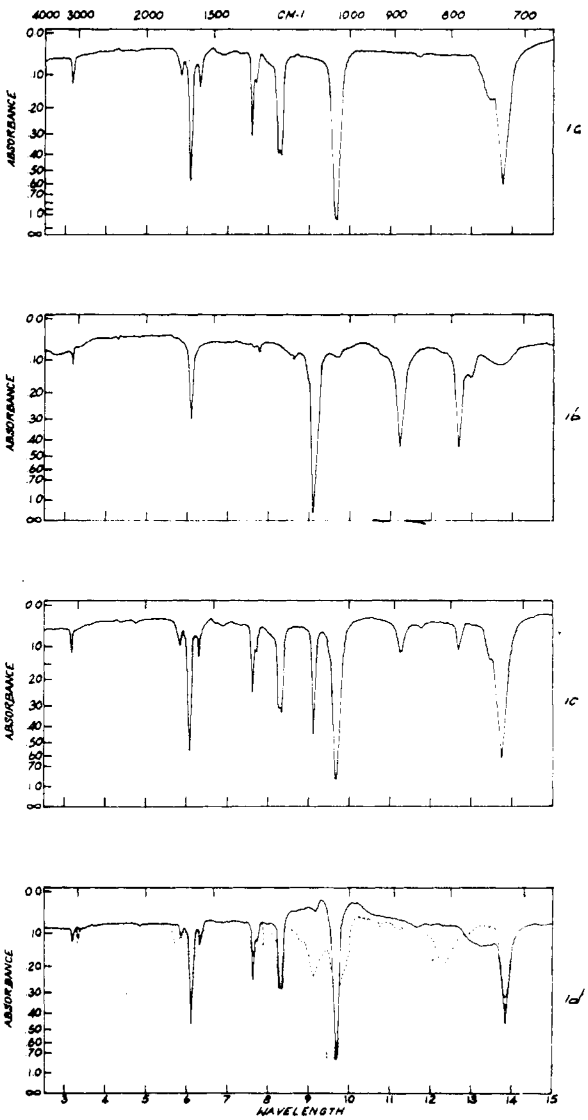


Fig. 1.—Infrared spectra of the 1-bromo-2-fluoroethylenes (850–4000 cm.$^{-1}$ in carbon tetrachloride, 675–850 cm.$^{-1}$ in carbon disulfide). a. *cis* isomer; b. *trans* isomer; c. equilibrium mixture; d. *cis* isomer, measured immediately after preparation of the solution in CCl_4 (————); after 5 days (- - - - -); after 20 days (. . .).

The infrared spectra support the conclusion that the 70.2 azeotrope compound is the F—H, the 73 azeotrope compound the F—Br isomer: 1) The F—H isomer has the higher C—F frequency (1110, as compared with 1060 cm.$^{-1}$), the F—Br isomer the lower one; in 1-bromo-2-fluoroethylene, the closeness of Br and F (*cis* compound) lowers the C—F frequency, and the latter (1035 cm.$^{-1}$) is similar to

---

[4] V. W. Laurie, *J. Chem. Phys.*, **34**, 293 (1961).

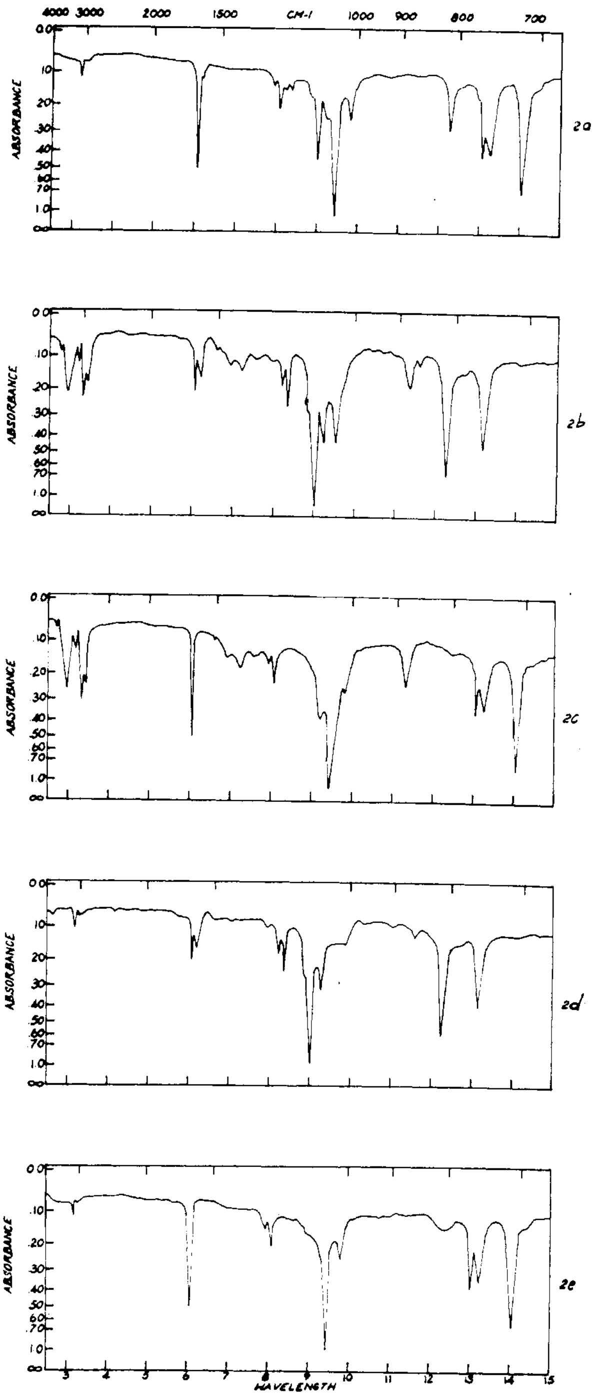


Fig. 2.—Infrared spectra of the 1,2-dibromo-1-fluoroethylenes (850–4000 cm.$^{-1}$ in carbon tetrachloride; 675–850 cm.$^{-1}$ in carbon disulfide). a. equilibrium mixture of isomers; b. azeotrope of ethanol with the F—H isomer (b.p. 70.2°); c. azeotrope of ethanol with the F—Br isomer (b.p. 73.3°); d. F—H isomer; e. F—Br isomer.

that of the F—Br isomer (1060 cm.$^{-1}$). *trans*-1-Bromo-2-fluoroethylene shows the C—F stretching mode at exactly the same frequency (1110 cm.$^{-1}$) as the F—H isomer. 2) The C═C band in the F—H isomer is a doublet (1630, 1650 cm.$^{-1}$), whilst in the F—Br isomer we have a band at practically the same wave length as the higher component of the doublet, but with greater intensity. Similar doublets have been observed in the infrared spectra of tribromo-[5] and *cis*-1,2-dibromoethylene,[6] in which the two bulky Br atoms are on the same side of the double bond. 3) The band due to C—H in-plane deformation (1200–1300 cm.$^{-1}$) has a lower frequency for the F—H isomer. If one compares this vibration in the compounds CF_2═CHF,[7] CF_2═CHCl,[8] CF_2═CHBr[9] with that in CCl_2═CHCl[10] and CBr_2═CHBr,[5] one finds that it lies, in the first three compounds, in which fluorine and hydrogen are on the same side of the double bond, at a lower frequency than in the last two ones, in which the hydrogen atom is on the same side of the double bond as the chlorine or bromine atom.

If one compares the intensities of the absorption bands characteristic of the two isomers in the spectrum of the equilibrium mixture, the F—Br isomer appears to be thermodynamically favored. This conclusion is supported by the results of vapor phase chromatography, according to which the equilibrium mixture is composed of 82% of the F—Br isomer and 18% of the F—H isomer. This relationship would seem reasonable, as the two largest atoms (bromine) linked to the two carbon atoms would thus be *trans* to each other; however, in 1,2-dibromoethylene, the *cis* structure is the more stable one, and, therefore, the size of the substituent atoms cannot be the determining factor. The same conclusion follows from the fact that in 1,2-dihalogenoethylenes in general the *cis* structure is thermodynamically favored. In all these cases the two most electronegative substituents are on the same side of the plane. In fact, the difference in stability between the two isomers in this series increases with increasing electronegativity of the halogen atom. According to Coyle, Stafford, and Stone[11] only the *cis* form is formed in the preparation of 1,2-difluoroethylene. Our own experiments have shown that in the dehalogenation of 1-bromo-1,2,2-trifluoroethane with zinc mainly *cis*- and very little *trans*-1,2-difluoroethylene is formed, as shown by fractionation of the product (b.p. *cis:* −25.0°; *trans:* −51.0°) and the infrared spectrum (this is at variance with the results of Viehe[1]).

The energy difference between the two isomeric 1-chloro-2-fluoroethylenes is 0.6 kcal./mole,[1]) that

---

(5) J. C. Evans and H. G. Bernstein, *Can. J. Chem.*, **33**, 1177 (1955).

(6) J. M. Dowling, P. G. Puzanik, and A. G. Meister, *J. Chem. Phys.*, **26**, 233 (1957).

(7) D. E. Mann, N. Acquista, and E. K. Plyler, *ibid.*, **22**, 1586 (1954).

(8) J. R. Nielsen, C. Y. Liang, and D. C. Smith, *ibid.*, **20**, 1090 (1952).

(9) R. Theimer and J. R. Nielsen, *ibid.*, **27**, 264 (1959).

(10) H. J. Bernstein, *Can. J. Research, B*, **28**, 132 (1950).

(11) (a) T. D. Coyle, S. L. Stafford, and F. G. A. Stone, *J. Chem. Soc.*, 743 (1961). (b) After the completion of this manuscript, N. C. Craig and E. A. Entemann [*J. Am. Chem. Soc.*, **83**, 3047 (1961)] published a study of the *cis-trans*-isomerization of the 1,2-difluoroethylenes.

between the two 1,2-dichloroethylenes is 0.45 kcal./mole,[12] between the two 1,2-dibromoethylenes 0.13–0.3 kcal./mole,[13] while in the case of 1,2-diiodoethylene the *trans* form is more stable. Thus one obtains the following series: 1,2-difluoro- > 1-chloro-2-fluoro- > 1,2-dichloro- > 1-bromo-2-fluoro- > 1,2-dibromo- > 1-fluoro-2-iodo- > 1-chloro-2-iodo- > 1-bromo-2-iodo- > 1,2-diiodoethylene.

It is interesting that a similar sequence appears if one compares the boiling point differences in the various pairs of isomers: 1,2-difluoroethylene 26°, 1-chloro-2-fluoroethylene about 20°, 1-bromo-2-fluoroethylene 20°, 1,2-dichloroethylene 11.7°, 1,2-dibromoethylene 2°.

It seems that the above series, but in the opposite direction, also represents the ease of interconversion of the two isomers. From that series and the close similarity of the moments of the C—Br and C—F bonds one would expect that the F—Br isomer of 1,2-dibromo-1-fluoroethylene would be more stable and the interconversion very easy. This expectation is, indeed, borne out by the instantaneous interconversion of the two pure isomeric 1,2-dibromo-1-fluoroethylenes, which tends to point to a low energy difference between them and to a low activation energy. The reaction takes place without any external catalyst, and its rate is proportional to the concentration of the halogen–olefin. Unlike the case of 1-bromo-2-fluoroethylene, carbon tetrachloride reduces in this case the rate of reaction of the pure isomer—the higher the dilution, the lower the velocity of the isomerization.

The configurations ascribed to the two pairs of isomers discussed above have been confirmed by a study of the n.m.r. spectra. Details of this study which involved all fourteen bromofluoroethylenes, will be published elsewhere; the following data are pertinent to the present study: For *cis*-1-bromo-2-fluoroethylene, the spin-spin coupling in the proton resonance spectrum gives rise to eight lines (two quartets). The splitting constants are $J_{H_1,H_2} = 3.5$ c.p.s., $J_{H_1,F_1} = 79$ c.p.s. and $J_{H_2,F_1} = 31$ c.p.s. The first and last point to the *cis* configuration of the two hydrogen atoms and the *trans* configuration of hydrogen and fluorine, respectively. In the F^{19} resonance spectrum, the expected four lines were found with the same values $J_{H_2,F_1} = 31$ and $J_{H_1,F_1} = 79$ c.p.s.

For the *trans* isomer, eight lines were found in the proton resonance spectrum with the splitting constants: $J_{H_1,H_2} = 11$ c.p.s. and $J_{H_1,F_1} = 79$ c.p.s., corresponding to two hydrogen atoms in *trans* to each other, while $J_{H_2,F_1} = 12.5$ c.p.s. The second and third values appear also in the F^{19} resonance spectrum. J_{H_2,F_1} is somewhat higher for the *trans*, J_{H_1,H_2} somewhat lower for the *cis* compound than one would expect from previous experience, but the assignments appear to be unambiguous.

For the case of the F—H isomer of 1,2-dibromo-1-fluoroethylene, there appears both in the proton and in the F^{19} resonance spectrum a pair of lines with a distance of 8 c.p.s., which is characteristic of hydrogen and fluorine *cis* to each other. In the F—Br isomer, the distance between the lines is 22.5 c.p.s., corresponding to *trans* configuration of hydrogen and fluorine.

In conclusion, it seems worthy of note that also in the case of 1-bromo-1,2-difluoroethylene two isomers have been isolated, one boiling at 12°, the other at 15.7°. To judge from the infrared spectrum, in this case, too, the higher boiling compound which is thermodynamically favored, contains the two most electronegative atoms (fluorine) in *cis* to each other. A detailed study of this case will form the subject of a forthcoming publication.

Experimental

The two isomers of **1-bromo-2-fluoroethylene** (*cis:* b.p. 39.8° (760 mm); $n^{11}D$ 1.4233; d^{11}_4 1.761; *trans:* b.p. 19.8° (760 mm); $n^{12}D$ 1.4090; d^{10}_4 1.727) have been prepared in the same manner as described by Viehe.[1] The distillation was carried out in an atmosphere of nitrogen in a column packed with glass helices or, preferably, copper turnings which prevented polymerization; for the same reason, some hydroquinone was added to the pot.

The **dipole moments** were determined both in benzene and carbon tetrachloride solution; each dilution was checked by means of the infrared spectrum to ensure that no isomerization had taken place.

1,2-Dibromo-1-fluoroethylene.—(a) In an atmosphere of nitrogen and with vigorous stirring, 62 ml. of 1,1,2,2-tetrabromo-1-fluoroethane was added slowly to a mixture of 150 ml. of anhydrous ethanol, 55 g. of zinc dust, and 1 g. of zinc bromide. As a by-product a gaseous halogenoacetylene is formed (especially in the first stages of the reaction) which has to be trapped at −70°; it ignites explosively on contact with air. Its formation decreases the yield of the halogenoethylenes to 60–65%.

During the reaction, the azeotropes of the two isomers with ethanol distil; they are distilled again (in order to remove traces of the acetylene compound) and then fractionated repeatedly in a Todd column (nitrogen atmosphere). The two azeotropes boil at 70.2 and 73.3° (760 mm.), respectively.

In order to obtain the pure (solvent-free) compound as **equilibrium mixture**, either azeotrope was diluted with water and the oil dried over calcium chloride and fractionated in a Todd column in a nitrogen atmosphere. The product boiled at 88.3° (760 mm.) and had $n^{30}D$ 1.4885, d^{30}_4 2.255.

Anal. Calcd. for C_2HBr_2F: C, 11.8; Br, 78.4; F, 9.3. Found: C, 11.8; Br, 78.5; F, 9.2.

(b) A 20% aqueous solution of potassium hydroxide was added slowly and in equivalent amount to a suspension of 1,1,2-tribromo-1-fluoroethane in boiling water, using an efficient stirrer and a nitrogen atmosphere. At the end of the addition, the reaction mixture was refluxed for 1 hr., cooled, and separated into two phases; the organic product was dried over calcium chloride and distilled, yield 60%.

Separation of the Isomers.—The removal of the ethanol from the two azeotropes can be carried out in two ways:

---

(12) (a) K. S. Pitzer and J. L. Hollenberg, *J. Am. Chem. Soc.*, **76**, 1493 (1953). (b) A. R. Olson and W. Maroney, *ibid.*, **56**, 1320 (1934). (c) R. E. Wood and D. P. Stevenson, *ibid.*, **63**, 1650 (1941).

(13) R. M. Noyes and R. G. Dickenson, *ibid.*, **65**, 1427 (1943).

TABLE I

DIPOLE MOMENT MEASUREMENTS

Substance	Molar fraction	$\epsilon_{15°}$	$v_{15°}$	P	μ
CHBr=CHF, *cis* (in C_6H_6)	0.0042813	2.3199	1.13049		
	.0067949	2.3329	1.12602		
	.0115237	2.3557	1.12112		
	.0165635	2.3745	1.11714	97.65	1.94
CHBr=CHF, *trans* (in CCl_4)	.0039703	2.2448			
	.0088673	2.2427			
	.0143844	2.2413			0[a]
CHBr=CBrF, F—Br isomer	.004678	2.26139	0.62250		
(in CCl_4)	.008177	2.26867	.62171		
	.013469	2.28054	.62131		
	.017496	2.29114	.61969		
	.021423	2.29858	.61821	65.2	1.36
CHBr=CBrF, F—H isomer	.004891	2.2533	.622186		
(in CCl_4)	.009255	2.2580	.620643		
	.013624	2.2696	.619792		
	.017996	2.2724	.619007		
	.022283	2.2860	.618471	56.57	1.20

[a] The small change in ϵ in the various solutions proves that the dipole moment of this compound is practically zero.

(a) Over a mixture of 1 ml. of the azeotrope and 10 ml. of carbon disulfide a slow current of nitrogen is passed which causes the evaporation of the azeotrope of carbon disulfide and ethanol (b.p. 40°). The resulting solution in which the infrared analysis could not detect any trace of ethanol was used for the determination of the infrared spectra of the isomers.

(b) **Molecular Distillation in a High Vacuum.**—One distils 30 ml. of carbon disulfide or carbon tetrachloride and 10 ml. of the azeotrope quickly onto 40 g. of granulated calcium chloride, which had been dried *in vacuo*. After 10 min., dry air is admitted into the vessel and the solution is filtered through sintered glass in a closed system. The solution so obtained is so concentrated that at room temperature isomerization is fairly quick; it has to be diluted to a convenient concentration and kept at Dry Ice temperature.

The **dipole moment** measurements were carried out in carbon tetrachloride.

1-Bromo-1,2,2-trifluoroethane.—In a stainless steel autoclave, 1,1-dibromo-2,2-difluoroethane was heated with mercuric fluoride at 200°, according to Henne and Renoll.[14] The same effect is obtained by the use of antimony pentafluoride; this method will be described elsewhere.

1,2-Difluoroethylene.—In a three-necked flask, mounted with an ice water-cooled condenser, a mixture of 50 g. of zinc dust, 150 ml. of anhydrous ethanol, and 1 g. of zinc bromide was heated at 50° with vigorous agitation, and 114 g. of 1-bromo-1,2,2-trifluoroethane added slowly. Under these conditions, the bromo compound and the ethanol were returned continuously to the reaction vessel, while the gaseous 1,2-difluoroethylene escaping through the condenser was liquefied by means of a Dry Ice–acetone mixture. The distillate was then fractionated in a column[6]: *trans* isomer, b.p.–51.0° (1.5 g.); *cis* isomer, b.p. −25° (23.5 g.). In the distillation flask, there remained 26 g. of the starting material, so that the yield of the ethylene is 70%.

Dipole Moment Measurements.[15]—The dielectric constants and densities of the solutions were measured as usual, and moments calculated according to the method of Halverstadt and Kumler.[16]

In order to determine the exact concentration of 1,2-dibromo-1-fluoroethylene in the solutions, a large excess of a standard solution of bromine in carbon tetrachloride was added to the sample and the solution irradiated with ultraviolet light for 2 hr. In parallel, equal volumes of the standard bromine solution were irradiated. The excess bromine was titrated, the difference between the two values indicating the concentration of the olefin. This method had been shown to give reliable results with weighed quantities of the **equilibrium mixture** of the two isomers.

The **infrared spectra** were determined both in carbon tetrachloride and carbon disulfide; an Infracord apparatus model 137 of Perkin-Elmer was employed and an 0.1-mm. cell used.

The **vapor phase chromatography** of the 1,2-dibromo-1-fluoroethylenes was carried out in a column (1.50 m. length) charged with 10% tricresyl phosphate on "Chromosorb."

Acknowledgment.—This paper forms parts of a thesis submitted to the Hebrew University in partial fulfilment of the requirements for the Ph.D. degree.

---

[14] A. L. Henne and M. W. Renoll, *J. Am. Chem. Soc.*, **58**, 887 (1936).

[15] The dipole moments measurements have been carried out by Mrs. H. Feilchenfeld-Weiler, Department of Organic Chemistry, Hebrew University.

[16] L. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).