[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Electric Moments of Some Aromatic Fluorine Compounds[1]

BY HENRY FREISER,[2] MARCUS E. HOBBS AND PAUL M. GROSS

The unusual and in some cases unique properties of organic fluorine compounds make an interpretation of these properties in terms of molecular structure of importance both because of the end use to which the compounds may be put and because of the insight that such an interpretation may lend to the relations of structure and properties. The present paper gives the results of determinations of the polar properties of a series of organic fluorine compounds in terms of the dipole moments and polarizabilities of the molecules and relates these values to the molecular structures involved.

Materials and Experimental Details

Most of the compounds used in these measurements were made in the Duke University Laboratories in connection with the research being carried on by Messrs. P. Tarrant, L. Rapoport, R. Kittila and G. West under the direction of Drs. L. A. Bigelow and C. K. Bradsher. Their syntheses will be described in other publications. The analyses reported in this section were made by Dr. Rose Davis.

Both the solvents and compounds to be measured were carefully purified. Liquids were purified by careful fractionation while solids were fractionally crystallized. In the absence of other data, constancy of boiling point or freezing point was used as a criterion of purity.

Benzene.—Jones and Laughlin best grade of benzene (did not discolor concentrated sulfuric acid) was dried over anhydrous sodium sulfate, then refluxed over sodium wire for six hours and finally distilled from sodium. Fractions boiling over 0.02° range were used in the measurements. After the benzene had been used for a measurement it was recovered by repeated fractionation from the higher boiling solute and finally redistilled from sodium until

TABLE IA

SUMMARY OF PHYSICAL PROPERTIES OF COMPOUNDS

Compound	B. p. (cor.) °C.	Mm.	n^{30}_D	d^{30}_4	Analyses, % Calcd.	Found
Fluorobenzene	84.8		1.4610	1.0066	*a*	
Chlorobenzene	132.1		1.5197	1.1013	*a*	
Benzotrifluoride	102.7		1.3918	1.1719	*c*	
Benzotrichloride	95.4	14	1.5540	1.3769	*a*	
o-Fluorochlorobenzene	137.6		1.4968	1.2233	*a*	
m-Fluorobenzotrifluoride	100.9		1.3970	1.2769	*b*	
m-Chlorobenzotrifluoride	137.2		1.4432	1.3345	*b*	
m-Fluorobenzotrichloride	119.4	45	1.5310	1.4408		
1,3-bis-(Trifluoromethyl)-benzene	116.1		1.3759	1.3721	53.24 F	53.0
p-Chlorobenzotrifluoride	138.9		1.4430	1.3278	*b*	
p-Fluorobenzotrichloride	93.7	14	1.5311	1.4385		
p-Chlorobenzotrichloride	104.5	4	1.5690	1.4947		
2-Chloro-1,4-bis-(trifluoromethyl)-benzene	148.6		1.4090	1.5043	14.27 Cl	14.31
5-Chloro-1,3-bis-(trifluoromethyl)-benzene	134.9		1.4028	1.4722	14.27 Cl	14.33
4,5-Dichloro-1,3-bis-(trifluoromethyl)-benzene	174.2		1.4372	1.5958		
4-Fluoro-1,3-bis-(trifluoromethyl)-benzene	159	11	1.5661	1.6464	64.30 Cl	64.48
1,3-bis-(Trichloromethyl)-benzene	F. p. 38.8–38.0°		....	....	68.1 Cl	68.0

[a] Best grade obtained from Eastman Kodak Company. [b] No analysis data available, but physical properties check with those described by H. S. Booth, H. M. Elsey and P. E. Burchfield, THIS JOURNAL, **57**, 2066 (1935). [c] Obtained from Hooker Electrochemical Company and treated with boiling sodium bicarbonate solution until no tests for Cl^- were obtained in the solution. This was followed by fractional distillation.

TABLE IB[a]

30.0° C.

Compound	V, cc.	R_D obs., cc.	R_D calcd., cc.	$\Delta R_{D_{o-c}}$
Fluorobenzene	95.37	26.17	26.09	+0.08
Chlorobenzene	112.35	31.03	31.06	− .03
Benzotrifluoride	124.58	29.65	30.50	− .85
Benzotrichloride	141.99	45.49	45.41	+ .09
o-Fluorochlorobenzene	106.68	31.20	30.96	+ .24
m-Fluorobenzotrifluoride	128.44	30.93	30.40	+ .53
m-Chlorobenzotrifluoride	135.26	35.87	35.37	+ .50
m-Fluorobenzotrichloride	148.18	45.85	45.31	+ .54
1,3-bis-(Trifluoromethyl)-benzene	155.97	35.77	34.81	+ .96
1,3-bis-(Trichloromethyl)-benzene	....	...	64.63	....
p-Chlorobenzotrifluoride	135.94	36.04	35.37	+ .67
p-Fluorobenzotrichloride	148.41	45.92	45.31	+ .61
p-Chlorobenzotrichloride	153.88	50.41	50.28	+ .13
2-Chloro-1,4-bis-(trifluoromethyl)-benzene	165.19	40.84	39.68	+1.16
5-Chloro-1,3-bis-(trifluoromethyl)-benzene	168.80	41.17	39.68	+1.49
4,5-Dichloro-1,3-bis-(trifluoromethyl)-benzene	177.34	46.48	44.55	+1.93
4-Fluoro-1,3-bis-(trichloromethyl)-benzene	210.04	65.60	64.53	+1.07

[a] For this table $R_D = \frac{n_D^2 - 1}{n_D^2 + 2}\cdot\frac{M}{d}$. Values of refractivities used were Benzene_D 26.19, H_D 1.100, F_D 0.997, Cl_D 5.967 and C_D 2.418. Values were taken from Fuchs and Wolf, "Dielektrische Polarisation," Akademische Verlagsgesellschaft, Leipzig, 1935, p. 258. V is the molar volume.

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(1) Presented at the Fluorine Symposium at the American Chemical Society Meeting, New York, N. Y., September 17, 1947.

(2) (a) Present address, University of Pittsburgh, Pittsburgh, Pennsylvania. (b) Part of a thesis of Henry Freiser submitted in partial fulfillment of the requirements of the Ph.D. degree in Chemistry at Duke University, June, 1944.

its b. p. was constant. This recovered benzene was also used for some of the measurements: b. p. 80.10–80.12° (cor.); d^{30}_4 0.868143 (av.); n^{30}_D 1.49483.

Heptane.—"Technical" *n*-Heptane from the Phillips Petroleum Company was described by them as "possibly containing up to 4% branched hydrocarbons. The sulfur content is about 0.004% and no olefins are present." The heptane was purified by shaking it with successive portions of concentrated sulfuric acid until the acid remained colorless after four hours of shaking. The product was then washed with dilute sodium hydroxide and finally with water. It was dried over calcium chloride, refluxed for six hours over sodium wire from which the heptane was finally distilled. Fractions boiling over a 0.02° range were used. The heptane was recovered after each measurement in the same manner employed in benzene recovery and was used again in some of the measurements: b. p. 98.52–98.54° (cor.), d^{30}_4 0.677431 (av.).

1,3-bis-(Trichloromethyl)-benzene.—Crystals already partly purified by Mr. G. West were further recrystallized from carbon tetrachloride and a cooling curve obtained: f. p. 38.8–39.0°.

Anal. Calcd.: Cl, 68.1. Found: Cl, 68.0.

All the other compounds used were liquids under ordinary conditions and were purified in the following manner. They were dried over drierite and then fractionally distilled through a nichrome wire-wound spiral column. A summary of their physical properties is given in Tables IA and IB. Where the analysis data are available, they are included.

The procedure has been described previously.[3] The dielectric constant measurements were made with an apparatus of the heterodyne beat type which has been described recently.[4]

Results and Discussion

The experimental results of the electric moment determination are summarized in Table II. In this table μ_D is the value of the moment obtained by means of the usual Debye expression and μ_0 is obtained from the Onsager equation[5] for a polar solute in a dilute solution of a non-polar solvent. The latter equation is

$$\lim. \frac{\Delta\epsilon}{f_2} = \frac{M_2 d_1}{M_1 d_2} \cdot \frac{3\,\epsilon_1 (n_2^2 - \epsilon_1)}{(2\,\epsilon_1 + n_2^2)} + \frac{4\pi N_A d_1}{3kT\,M_1} \left[\frac{\epsilon_1\,(n_2^2 + 2)\,\mu_0}{(2\,\epsilon_1 + n_2^2)} \right]^2 \quad (1)$$

In this expression the subscripts 1 and 2 refer to solvent and solute, respectively. $\Delta\epsilon$ is the increment in the dielectric constant of the solution over that of the solvent, f_2 the mole fraction of the solute, *d* the density, *n* the refractive index which was taken for the sodium D lines, *M* the molecular weight and the other symbols have the usual meaning. Since, in the low concentrations employed, the value of $\Delta\epsilon/f_2$ was constant within experimental error, the average value was employed in the calculations. μ_M was calculated using the empirical extrapolation equation of Müller[6] by insertion of the value μ_D calculated from the Debye dilute solution equation as the value of $\mu_{soln.}$

It can be seen from Table II that agreement between the dipole moment values calculated by the different methods is rather close in most cases, although the Müller value is always somewhat higher than μ_D as would be necessary because of the form of the Müller equation.[6]

TABLE II

Compound	Solvent	Moments (× 10^{18}) μ_D	μ_0	μ_M
Fluorobenzene	Benz.	1.47	1.49	1.57
Chlorobenzene	Benz.	1.58	1.57	1.68
	Hep.	1.58	1.54	1.63
Benzotrifluoride	Benz.	2.56	2.62	2.73
	Hep.	2.63	2.60	2.72
Benzotrichloride	Benz.	2.04	2.01	2.17
	Hep.	2.14	2.06	2.21
o-Fluorochlorobenzene	Benz.	2.38	2.38	2.54
	Hep.	2.40	2.34	2.48
m-Fluorobenzotrifluoride	Benz.	2.19	2.25	2.33
	Hep.	2.24	2.23	2.32
m-Chlorobenzotrifluoride	Benz.	2.22	2.26	2.37
m-Fluorobenzotrichloride	Benz.	1.78	1.77	1.90
	Hep.	1.84	1.78	1.90
1,3-bis-(Trifluoromethyl)-benzene	Benz.	2.43	2.51	2.59
1,3-bis-(Trichloromethyl)-benzene	Benz.	1.99	1.90	2.12
p-Chlorobenzotrifluoride	Benz.	1.15	1.17	1.23
	Hep.	1.22	1.20	1.26
p-Fluorobenzotrichloride	Benz.	0.68	0.68	0.72
p-Chlorobenzotrichloride	Benz.	0.78	0.76	0.83
2-Chloro-1,4-bis-(trifluoromethyl)-benzene	Benz.	1.14	1.17	1.22
5-Chloro-1,3-bis-(trifluoromethyl)-benzene	Benz.	1.29	1.33	1.38
4,5-Dichloro-1,3-bis-(trifluoromethyl)-benzene	Benz.	1.51	1.54	1.61
4-Fluoro-1,3-bis-(trichloromethyl)-benzene	Benz.	1.91	1.88	2.04

A comparison of the values obtained in this work with those available in the literature is given below. In general the agreement is satisfactory.

Substance	Present work	Others	
C_6H_5Cl	1.58	1.56[a,b]	1.57[c]
C_6H_5F	1.47	1.45[a,d]	1.46[e]
$C_6H_5Cl_3$	2.04	2.07[f]	2.15[g]
o-C_6H_4ClF	2.38	2.33[a]	

[a] Bergmann, Engel and Sandor, *Z. physik. Chem.*, **B10**, 106 (1930). [b] L. Tiganik, *ibid.*, **B13**, 425 (1931). [c] A. A. Maryott, Ph.D. Thesis, Duke University, 1940. [d] A. Nukada, *Nia Kemio*, **5**, 41 (1932). [e] Brown, deBruyne and Gross, THIS JOURNAL, **56**, 1291 (1934). [f] L. E. Sutton, *Proc. Roy. Soc.* (*London*), **133**, 668 (1931). [g] A. Parts, *Z. physik. Chem.*, B13, 312 (1931).

The results of the Onsager calculations were in no better agreement with the gas values, where these were known, than were the Debye values. The Müller equation was somewhat better in this regard. Specifically, a comparison[7] may be made for the chlorobenzene gas value of 1.70*D* and the fluorobenzene gas value of 1.57*D*. While the Onsager moments deviated from the gas moments by about 0.10 debye unit, the Müller values agreed with those obtained from gas measure-

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[3] Maryott, Hobbs and Gross, THIS JOURNAL, **62**, 2320 (1940).

[4] Weith, Hobbs and Gross, *ibid.*, **70**, 805 (1948).

[5] L. Onsager, THIS JOURNAL, **58**, 1486 (1936).

[6] H. Müller, *Physik. Z.*, **34**, 689 (1933).

[7] MacAlpine and Smyth, *J. Chem. Phys.*, **3**, 55 (1935).

ments within experimental error. For the Müller equation good agreement is usually obtained in the cases of compounds measured in both solvents. This would indicate the internal consistency of Müller's equation but not its validity and it must be remembered that Müller's equation is empirical. Because of its empirical nature and consequent limitations it should be used only as an expedient for calculating moments when gas values are not available.

In many structural problems, the difference between the observed dipole moment of a molecule and the moment calculated on the basis of vector additivity of the group moments is of considerable interest. For the compounds measured in this study, these differences are fairly independent of the method of calculation used, provided that the same method is used for each molecule considered. Table III lists the results of such a computation.

TABLE III

DEVIATIONS FROM VECTOR ADDITION

Compound	Δ Debye, D	Δ Onsager, D	Δ Müller, D
o-Fluorochlorobenzene	−0.07	−0.09	−0.29
m-Fluorobenzotrifluoride	− .03	− .03	− .04
m-Chlorobenzotrifluoride	− .02	− .01	− .01
m-Fluorobenzotrichloride	− .04	− .05	− .06
1,3-bis-(Trifluoromethyl)-benzene	− .13	− .10	− .14
1,3-bis-(Trichloromethyl)-benzene	− .05	− .17	− .11
p-Chlorobenzotrifluoride	.17	.14	.18
p-Fluorobenzotrichloride	.11	.13	.10
p-Chlorobenzotrichloride	.32	.24	.25
2-Chloro-1,4-bis-(trifluoromethyl)-benzene	− .44	− .39	− .44
5-Chloro-1,3-bis-(trifluoromethyl)-benzene	.31	.28	.29
4,5-Dichloro-1,3-bis-(trifluoromethyl)-benzene	.13	.16	.15
4-Fluoro-1,3-bis-(trichloromethyl)-benzene	.09	.05	.09

The dipole moment of each molecule listed in Table III was calculated by vector addition of the bond moments using as component moments values obtained in the following manner: (1) the Debye value obtained in benzene, since for better comparison, measurements in the same solvent were chosen, (2) the average Onsager value and (3) the average value obtained by calculation using Müller's equation. In all cases, the values of the moments of chlorobenzene, fluorobenzene, benzotrifluoride and benzotrichloride were taken as being those of the C–Cl, C–F, C–CF_3, C–CCl_3 bonds, respectively. The values of the moments obtained in this manner were compared to the actual moments and the deviations listed in Table III. A positive deviation signifies that the measured moment is larger than that calculated by vector addition of the component bond moments. As shown in the table good agreement between the deviations is obtained in most of the cases. The lack of agreement for *o*-fluorochlorobenzene where the value of the deviation calculated by Müller's method is quite different from the other two is the only case where a serious discrepancy is noted. The reason for this discrepancy is not understood.

A general consideration of the origins within the solute molecule of such deviations as shown in Table III have been discussed elsewhere.[8] A cause for deviation extraneous to the solute molecule itself may arise from solvent effects. The theoretical aspects of this effect have been discussed by Frank and Sutton and others.[9] To illustrate the nature of the effect as discussed by Frank and Sutton consider a molecule in which the electric moments completely compensate; *i. e.*, *p*-dichlorobenzene. On the average, in the absence of a field, the solvent molecules arrange themselves in the vicinity of the polar bonds in such a way as to have the moments induced in them by the polar bonds completely cancel one another. In case the moments induced in the solvent molecules by the polar bonds lie in the direction of an imposed field these molecules will be bound more tightly to the solute molecule whereas the solvent molecules with their induced moment directions opposing the field are bound to the solute molecule less tightly than if the field were absent. The net effect of the above is that the solvated solute molecule shows an average electric moment in the direction of the field, *viz.*, an increased polarizability. Such an increased polarizability will, in the usual method of calculation of electric moments from solution measurements, lead to a calculated real dipole moment of the solute molecule. For future reference we will refer to this type of effect as a deviation originating from solvent effects.

Examination of Table III shows that for all of the disubstituted cases the para compounds exhibit a positive deviation and all ortho and meta substituted compounds show negative deviations from vector additivity. The explanation of this difference in sign may well lie in differences in the origins of the observed deviations. It is suggested that the para compounds show positive deviations because the predominating deviation effect is one originating in the solvent effects discussed above. The negative deviations for the ortho and meta cases may be most simply attributed to a preponderance of deviation effects arising from the inductive and space induction effects. However, it may be noted that both the space induction and inductive effects through the ring are expected to be rather small for the meta cases. The distance of separation of the groups minimizes the space effect and the inductive effects through the ring would probably be small if the

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[8] Hobbs and Weith, THIS JOURNAL, **65**, 925 (1943).

[9] (a) Frank and Sutton, *Trans. Faraday Soc.*, **33**, 1307 (1937); (b) S. H. Bauer, *J. Chem. Phys.*, **4**, 458 (1936); (c) H. O. Jenkins, *J. Chem. Soc.*, 910 (1936).

effect is considered to be distributed equally on all carbon atoms of the ring. In the disubstituted cases the electric moments in general corroborate the structure of the isomers considered.

The cause for the observed deviations in the tri- and tetra-substituted compounds is difficult if not impossible to locate because of the complexity and undetermined magnitude of the factors which might cause such deviations. A rather simple consideration of the other reasonable isomers that might have been obtained in the method of preparation leads one to conclude that, in general, the observed moments, considered in light of the deviations from additivity are such as to corroborate the identity of the molecule involved.

In considering the influence of the polar substituents on physical characteristics one of the simplest evidences of this influence is found in Table IB where the values of the molar refraction, R_D, for the sodium D lines are shown. The calculated values are obtained by summing the atomic and bond components of the molecule and this value is compared with the observed value as calculated from the Lorenz–Lorentz expression, *viz.*

$$R_D = \frac{n^2_D - 1}{n^2_D + 2}\cdot\frac{M}{d}$$

The difference between R_D(obs.) and R_D(calcd.) might originate in an effect of the substituents on either the electrical volume fraction term, $(n^2 - 1)/(n^2 + 2)$, or the molar volume term, M/d or on both terms. Thus the electronic transitions responsible for the refractive index may either increase or decrease their strengths, and/or new transitions may become accessible when substituents are attached to the ring. The effect of any of these potential changes on the value of R_D would probably appear most prominently in the $(n^2 - 1)/(n^2 + 2)$ term. If, because of the repulsive or attractive fields of the substituents, the molar volume changes disproportionately to the $(n^2 - 1)/(n^2 + 2)$ term the value of R_D will be affected in direct proportion to the lack of compensatory changes in these terms.

The only data presented which allow a simple evaluation of the relative effects of the above two terms are (1) *m*-chlorobenzotrifluoride and *p*-chlorobenzotrifluoride and (2) *m*-fluorobenzotrichloride and *p*-fluorobenzotrichloride. If we denote $(n^2 - 1)/(n^2 + 2)$ as B, then the following approximate expression may be derived from the equation for R for the meta and para cases

$$\begin{aligned}(R_p - R_m) &= B_pV_p - B_mV_m \\ &\simeq B_p(V_p - V_m) + V_p(B_p - B_m)\end{aligned} \qquad (2)$$

With division by R_p we obtain

$$\frac{\Delta R_{p-m}}{R_p} \simeq \frac{\Delta V_{p-m}}{V_p} + \frac{\Delta B_{m-m}}{B_p} \qquad (3)$$

The values of R, V and B are given for the above compounds in Table IV.

TABLE IV

	R, cc.	V, cc.	B
m-Chlorobenzotrifluoride	35.87	135.26	0.26521
p-Chlorobenzotrifluoride	36.04	135.94	.26520
m-Fluorobenzotrichloride	45.85	148.18	.30939
p-Fluorobenzotrichloride	45.92	148.41	.30944

The values for the terms of eq. (3) taken from the experimental data are shown directly below.

	$\frac{\Delta R_{p-m}}{R_p}$	$\frac{\Delta B_{p-m}}{B_p}$	$\frac{\Delta V_{p-m}}{V_p}$
(*p*-*m*)-Chlorobenzotrifluoride	4.7×10^{-3}	-0.6×10^{-3}	$+5.0 \times 10^{-3}$
(*p*-*m*)-Fluorobenzotrichloride	1.5×10^{-3}	$+0.2 \times 10^{-3}$	$+1.6 \times 10^{-3}$

The discrepancy between $\Delta R_{p-m}/R_p$ and the sum of the other two terms is attributable to lack of precision in the value from which the various terms were obtained and to the approximations used in eq. (3). It is evident from these results that the major fraction of the difference in the R values for the para and meta compounds resides in the molar volume term and as would be expected on the basis of the interdependence of n and V the two terms $\Delta V/V$ and $\Delta B/B$ may be of opposite sign. In general it may be concluded from these results that the repulsive fields of the electronegative atoms cause a volume change that is not compensated for by a corresponding change in n. In view of these results it may be suggested that the probable cause of the other large + ΔR_D values in Table IB lies in volume changes rather than changes in B.

Table IB contains only one serious negative ΔR_D. This value of −0.85 for benzotrifluoride probably shows how significantly the large electronegativity of the $-CF_3$ group can influence the polarizability of the benzene ring. Some evidence for this may be obtained from the data shown for toluene and benzotrifluoride in Table V.

TABLE V

Substance	R_D 30°C	V (30°C.	$\frac{\Delta V(100)}{V}$	$\frac{\Delta B(100)}{B}$
Toluene	31.06	107.58	0	0
Benzotrifluoride	29.65	124.58	+15.8	−17.6
m-Xylene	35.90	124.03	0	0
1,3-bis-(Trifluoromethyl)-benzene	35.77	155.97	+25.8	−20.8

The $\Delta V/V$ and $\Delta B/B$ column data are obtained by using toluene as a reference for the first two cases and *m*-xylene for the latter two. It is evident from the data on toluene and benzotrifluoride that the negative value of ΔR_D for benzotrifluoride probably arises from the overcompensation of the positive volume change by a negative change in the B term. This may be taken as indicative of a tightening of the ring electron system in the benzotrifluoride molecule. This situation is apparently reversed when the cases of *m*-xylene and the 1,3-bis-(trifluoro)-compounds are considered, *viz.*, the fractional positive volume change exceeds the fractional negative change in B. It will be noted in Table IB that the values of ΔR_D are roughly constant for the *m*-fluoro and *m*-chloro compounds and the same applies to the *p*-compounds except for *p*-chlorobenzotrichloride. The latter compound has a rather low ΔR_D in view of the data on the other compounds of similar nature. It is notable that in all cases of the disubstituted compounds in which large $+\ \Delta R_D$ deviations occur one of the substituents is fluorine. This atom because of its small size, large electronegativity and low polarizability would give rise to a large coulombic repulsion for other bonded electronegative atoms and would have low compensatory attraction arising from dispersion forces. The larger chlorine atom has a lower electronegativity and a higher polarizability and as such might give rise to a smaller *relative* volume increment than would the fluorine atom.

The bonded fluorine atom should contribute to the London[10] dispersion forces about the same as bonded hydrogen atoms and yet in spite of the large dipole moment of benzotrifluoride and 1,3-bis-(trifluoromethyl)-benzene the boiling point of the former is roughly 8° lower than that of toluene and of the latter roughly 23° lower than that of *m*-xylene. The first order factor in determining boiling points in normal liquids is the force arising from the interaction of instantaneous atomic dipoles with dipoles induced in neighboring polarizable systems. Since in first approximation this force varies as $1/r^6$, it is evident that a very small change in r will have a considerable influence on the interaction energy, and in cases of systems of essentially the same distribution and magnitude of polarizability within a molecule it may be generally expected that the substance with largest intermolecular distances will have the lower boiling point. In the cases of *m*-xylene and 1,3-bis-(trifluoromethyl)-benzene the ratio of the average intermolecular separations at 30° is about 1/1.15 and for toluene and benzotrifluoride at 30° the ratio is about 1/1.10. The molar volume at the respective boiling points of the compounds would be more instructive in the above connection than the data at 30°; however, to the knowledge of the authors, such data are not available for the fluorine compounds. The fact that the substances listed with largest intermolecular distances are the lowest boiling of the pairs considered can hardly be regarded as coincidence although it is recognized that the entire line of reasoning relating to the boiling point and intermolecular distance has serious quantitative limitations.

Summary

The electric moments of a number of organic fluorine compounds have been measured and discussed in relation to the structure of the molecules. The effect of fluorine on some physical characteristics of molecules is briefly considered.

DURHAM, NORTH CAROLINA RECEIVED AUGUST 14, 1948

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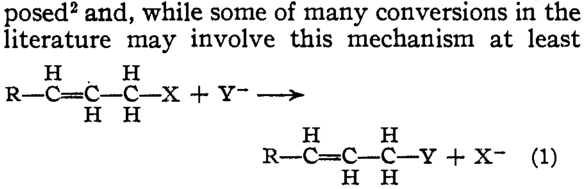
[10] F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

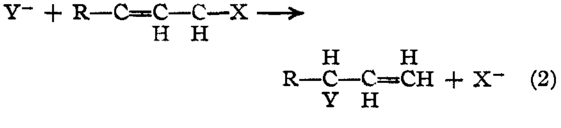
Allylic Rearrangements. XXIV. Abnormal Bimolecular Substitution. The Condensation of Butenyl and Pentenyl Chlorides with Sodium Malonic Ester

BY RICHARD E. KEPNER,[1a] S. WINSTEIN AND WILLIAM G. YOUNG

Recent work[1b,c] on nucleophilic displacement reactions of allylic systems has indicated that bimolecular (S_N2) reactions produce unrearranged products (eqn. 1). An abnormal bimolecular (S_N2') mechanism (eqn. 2) has been proposed[2] and, while some of many conversions in the literature may involve this mechanism at least partly, no completely satisfactory evidence for its operation has so far appeared.



$$\mathrm{R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}X + Y^- \longrightarrow R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}Y + X^-} \quad (1)$$



$$\mathrm{Y^- + R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{-}X \longrightarrow R{-}\underset{Y}{\overset{H}{C}}{-}\overset{H}{C}{=}\underset{H}{CH} + X^-} \quad (2)$$

Thus many reported cases of reactions of allylic halides with nucleophilic reagents such as sodium malonic ester,[3] sodium acetoacetic ester,[4] sodium allyl benzene,[5] potassium phthalimide,[6] sodium

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