The Addition of Bromine Monofluoride to Acetylenes

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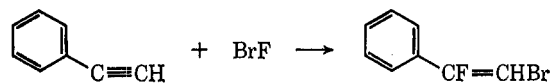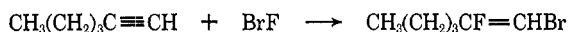
The addition of the elements of bromine monofluoride to a variety of olefinic substrates has been achieved in several different ways. Schrader[1] claimed the production of 1-bromo-2-fluoroethane by the reaction of a mixture of bromine and fluorine with ethylene. Bowers[2-4] showed that it was more convenient to use a mixture of anhydrous hydrogen fluoride and N-bromoacetamide in an ether solvent. In this manner additions of BrF to cyclohexene and unsaturated steroidal molecules were attained in good yields. Subsequently, Pattison and coworkers extended the reaction to the production of vicinal fluorobromides from aliphatic alkenes.[5]

To date, no reactions have been reported between acetylenes and BrF. Although there is a structural relationship between carbon–carbon double bonds and triple bonds, the reactivities of the two systems are quite different. Thus a triple bond is much less reactive than a comparably situated double bond toward electrophilic reagents such as halogens. This difference is probably due to respective electron distributions within the linkages.[6] In view of these considerations it was not certain that BrF would add to acetylenic compounds at all. Therefore a brief study was undertaken to establish this point.

It was found, using the anhydrous hydrogen fluoride–N-bromoacetamide (HF–NBA) system, that BrF could be added to several simple acetylenic molecules, giving bromofluoro olefins. In no case was the addition of a second molecule of BrF observed. This undoubtedly is due to the deactivation of the double bond caused by the α halogens. There may also be a slight steric effect, since it is known that under the appropriate conditions two molecules of chlorine can be added to triple bonds, whereas only one molecule of bromine or iodine will react under similar conditions.[6a]

The HF–NBA procedure worked moderately well for 1-hexyne, 3-hexyne, 1,4-dichloro-2-butyne, and phenylacetylene, confirming the lower reactivity of triple bonds over double bonds. In the case of terminal alkynes the addition followed the Markovnikov rule;

$$CH_3(CH_2)_3C\equiv CH + BrF \longrightarrow CH_3(CH_2)_3CF=CHBr$$

the magnitude of the H–F coupling constants (Table II) clearly indicate that hydrogen and fluorine cannot be attached to the same carbon atom.[7] When the triple bond was deactivated by electron-withdrawing groups, no reaction occurred. For example, $CH_3OC(CF_3)_2C\equiv CH$ and $CH_3OC(CF_3)_2C\equiv CCl$[8] were recovered unchanged and the parent alcohols[9] added bromine only slowly at 25°, in contrast to the vigorous reaction normally observed between acetylenes and bromine. Dimethylacetylene dicarboxylate and diphenylacetylene gave intractable products.

From a study of the products isolated, the principal mode of addition appeared to be *trans*, i.e., F⁻ entering from the least hindered side. Use of the terminal acetylenes resulted in initial orientations of the type

1-Hexyne produced 95% *trans* and 5% *cis* isomer. The composition of the mixture was observed to change slowly over a period of months, from 95:5 to 40:60 (*trans* to *cis* ratios), indicating the former to be a kinetically produced mixture and the latter to be a thermodynamically produced composition. These changes were reflected in the change in intensities of the proton nmr signals. The product ratios were determined by measurement of the areas of the olefinic proton peaks. The styrene example was relatively unstable and no examination could be made for composition changes. 1,4-Dichloro-2-butyne and 3-hexyne both gave isomers of the type

as the principal product. In the case of 3-hexyne 22% of the alternate structure was formed. No isomerization was observed in these examples over a 15-month period.

The sensitivity of the reaction to the structure of the acetylenes indicates that the process is initiated by attack of a weakly electrophilic species at the triple bond. In view of the stereospecificity observed in the products it is probable that the intermediate species has more of the character of an oriented π complex, and should be distinguished from a discrete carbonium ion, where less selectivity would be anticipated. The reaction is completed by fluoride addition from HF. When the presence of electron-withdrawing groups prevents the first step from occurring, the reaction cannot take place.

One anomalous reaction was noted in this series of experiments. Methyl propiolate, $HC\equiv CCOOCH_3$, did not participate in the addition reaction. Instead, $BrC\equiv CCOOCH_3$ was formed in 36% yield, indicating that initial addition of Br⁺ had taken place followed by collapse of the intermediate to the observed product. A less likely explanation is that BrF addition was followed by spontaneous dehydrofluorination.

Recently a new method, involving the use of a silver

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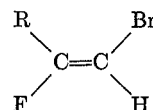(3) A. Bowers, L. C. Ibanez, E. Denot, and R. Becerra, *ibid.*, **82**, 4001 (1960).

(4) A. Bowers, E. Denot, and R. Becerra, *ibid.*, **82**, 4007 (1960).

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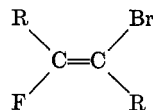
(6) (a) R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworth and Co. Ltd., London, 1955, pp 21, 35; (b) T. F. Rutledge, "Acetylenic Compounds," Reinhold Publishing Corp., New York, N. Y., 1968, p 2.

(7) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1966, pp 910, 911.

(8) R. E. A. Dear and E. E. Gilbert, U. S. Patent 3,450,773 (1969).

(9) R. E. A. Dear and E. E. Gilbert, *J. Org. Chem.*, **33** 819 (1968).

TABLE I
PROPERTIES OF NEW COMPOUNDS

Compd	Registry no.	Bp (mm), °C	$n^{25}D$	—Calcd, %—		—Found, %—	
A. BrF Additions							
$CH_3(CH_2)_3CF=CHBr$	*cis-*, 23680-35-5;	34 (12)	1.4361	C	39.80	C	39.67
	trans-, 23680-34-4			H	5.57	H	5.74
				Br	44.13	Br	43.96
$ClCH_2CF=CBrCH_2Cl$	*trans-*, 23680-36-6	49 (1.5)	1.5123	H	1.82	H	2.16
				Br	36.19	Br	35.86
				Cl	31.96	Cl	31.82
$CH_3CH_2CF=CBrCH_2CH_3$	*cis-*, 23680-38-8;	37 (30)	1.4372	C	39.79	C	39.92
	trans-, 23680-37-7			H	5.57	H	5.60
$C_6H_5CF=CHBr$	*trans-*, 23680-39-9	48-50 (0.1)	1.5699	C	47.79	C	48.06
				H	3.01	H	3.13
B. Br₂ Additions							
$HOC(CF_3)_2CBr=CHBr$	23754-52-1	56.6-57 (12)	1.4328	C	17.04	C	17.32
				H	0.57	H	0.71
				Br	45.42	·Br	45.26
$HOC(CF_3)_2CBr=CClBr$	23668-74-8	90-92 (30)	1.4514	C	15.45	C	15.64
				H	0.26	H	0.33
				Br	41.37	Br	41.08

fluoride–halogen system, was reported.[10] Since it is operative at ambient temperatures, gives high yields, and does not employ corrosive materials, such as hydrogen fluoride, it would appear to be the method of choice for many BrF additions. However, in experiments using AgF–Br₂ in acetonitrile, only a trace of the BrF addition product of 1-hexyne was obtained. The major product was $CH_3(CH_2)_3C\equiv CBr$, probably formed *via* the silver salt and its subsequent reaction with bromine. Under similar conditions 3-hexyne gave only 3,4-dibromo-3-hexene.

In many cases the structure of the products was deduced from spectral data. The conformation assigned to the terminal hexenes, based on the position and magnitude of their nmr signals, is in full accord with analogies described in the literature.[7] In the styrene derivative the order of magnitude of the coupling constant J_{HCCF} (15.8 Hz) suggests a *cis* relationship between F and H. In the absence of the other isomer this conclusion can be only tentative, although formation of the molecule by approach of fluoride from the least hindered side also leads to the proposed structure in preference to the alternate. The structure of the isomers formed from 3-hexyne may be designated with some confidence, since it is known[7] that a fluorine located *trans* to another halogen and *cis* to an alkyl group generally has a larger chemical shift than one positioned conversely. The structure proposed for the 1,4-dichlorobutene is that anticipated from the addition of fluoride to the least hindered side. Since the *cis* isomer was not detected in this product, no definite conclusions can be drawn from the nmr assignments.

Experimental Section

Physical constants and analytical data for the new compounds are presented in Table I. Significant infrared bands and nmr data are reported in Table II. The nonfluorinated acetylenic chemicals were purchased from Farchan Research Laboratories. Nmr spectra were recorded on Varian A-60 and DP-56 instruments. The ¹⁹F spectra were calibrated by generating side bands of Cl_3CF. All elemental analyses were made by Schwarzkopf Microanalytical Laboratory.

(10) L. D. Hall, D. L. Jones, and J. F. Manville, *Chem. Ind.* (London), 1787 (1967).

TABLE II
SPECTROSCOPIC PROPERTIES OF THE PRODUCTS[a]

A. $CH_3(CH_2)_2CF=CHBr$ [1667 cm⁻¹ (s, C=C)][b]

	trans (95%)	*cis* (5%)
δ_{CF}	100	96.3
δ_{CH}	5.8	5.23
δ_{CH_2CF}	2.42	c
$\delta_{CH_2CH_2}$	1.4-1.6	
δ_{CH_3}	0.9	
J_{FC-CH}	13	27.5
J_{FCCH}	21	16.5
J_{HC-CCH}	1.0	
J_{HCCH}	7.0	

B. $ClCH_2CF=CBrCH_2Cl$ [1669 cm⁻¹ (s, C=C)]

	trans (100%)
δ_{CF}	104
δ_{CH_2CF}	4.33
δ_{CH_2CBr}	4.39
J_{FCCH}	21
J_{FCCCH}	3.5

C. $CH_3CH_2CF=CBrCH_2CH_3$ [1689 cm⁻¹ (s, C=C)]

	trans (78%)	*cis* (22%)
δ_{CF}	110	96.3
δ_{CH_2}	2.45	2.45
δ_{CH_3}	1.05	1.07
J_{FCCH}	23	21
J_{HCCH}	7.6	7.6

D. $C_6H_5CF=CHBr$ [1689-1587 cm⁻¹ (s, C=C)[d]]

	trans (100%)
δ_{CH}	6.11
δ_{CH} (phenyl)	7.3, 7.8
J_{HCCF}	15.8

E. $HOC(CF_3)_2CBr=CHBr$ [1593 cm⁻¹ (s, C=C)][e]

F. $HOC(CF_3)_2CBr=CClBr$ [1550 cm⁻¹ (s, C=C)][e]

G. $BrC\equiv CCOOCH_3$ [2252 cm⁻¹ (s, C=C)]

[a] Chemical shifts expressed as parts per million (δ) from Cl_3CF and $(CH_3)_4Si$ as internal references; coupling constants expressed in hertz. [b] C—F stretching bands also present at 1144 and 1079 cm⁻¹. The expected range for $RCF=CR_1R_2$ is 1700-1630 cm⁻¹: J. K. Brown and K. J. Morgan, *Advan. Fluorine Chem.*, **4**, 253 (1965). [c] Peaks for this isomer masked. [d] Includes aromatic C=C bands. [e] Analogous chlorinated materials absorb in the 1570-1600-cm⁻¹ range (Brown and Morgan); so the frequencies observed are to be expected when the heavier bromine atoms are substituted for chlorine.

Typical experimental procedures are described below. No differences in product yield or composition were observed when diethyl ether was replaced by tetrahydrofuran. Similarly, it did not matter if the reagents were added alternately in small portions or consecutively in one portion each. An attempt to improve the yield by making fluoride ion more readily available as pyridine hydrofluoride was unsuccessful.

1-Bromo-2-fluoro-1-hexene.—Anhydrous hydrofluoric acid (50 g, 2.5 mol) was condensed into a 500-ml polyethylene bottle and the bottle was cooled to $-78°$. To the cooled acid was added ether (120 ml), N-bromoacetamide (34.5 g, 0.25 mol), and 1-hexyne (20.5 g, 0.25 mol). The pale yelow slurry so produced was stirred at $-78°$ for 3 hr; then, after overnight storage at $-20°$, it was poured slowly into a mixture of sodium carbonate (250 g), water (200 ml), ice (200 g), and ether (60 ml). The ether layer was separated and the residue was extracted with ether (three 50-ml portions). The combined ether extracts were washed with nitrous acid solution to destroy any residual acetamide, washed with sodium carbonate solution and then with water, dried, and distilled. There was obtained 10.8 g (47.9%) of 1-bromo-2-fluoro-1-hexene, bp $34°$ (12 mm), $n^{25}D$ 1.4361. The product was characterized by elemental analysis (Table I), a C=C stretching frequency in the infrared spectrum (Table II), and by nmr spectroscopy. Infrared spectroscopy also revealed the presence of C—F stretching frequencies at 1144 and 1079 cm^{-1}. The original 1-hexyne does not have any bands in this region.

3-Bromo-4-fluoro-3-hexene.—Anhydrous hydrogen fluoride (80 g, 4.0 mol) was condensed into a 500-ml polyethylene bottle cooled to $-78°$. Cold tetrahydrofuran (200 ml) was added together with pyridine (2 ml). N-bromoacetamide (70 g, 0.508 mol) and 3-hexyne (32.8 g, 0.4 mol) were added alternately in small portions over a 20–30-min period. The mixture was stirred at $-78°$ for 2 hr, then at $0°$ for 3 hr. The pale yellow solution was poured onto a mixture of sodium carbonate (300 g, 2.8 mol), water (300 ml), ice (300 g), and methylene chloride (100 ml). The aqueous layer was extracted with a further 100 ml of methylene chloride. The organic extracts were washed with water, nitrous acid, and finally with water, After drying and distillation, 20.2 g (27.9%) of 3-bromo-4-fluoro-3-hexene was obtained. The product was characterized as described above.

Silver Fluoride–Bromine Procedure.—Silver fluoride (14 g, 0.11 mol) was finely ground and added to dry acetonitrile (25 ml) in a 100-ml, three-necked flask. 1-Hexyne (8.29 g, 0.1 mol) was added in one portion. Some heat was evolved. Bromine (16 g, 0.1 mol) in acetonitrile (20 ml) was added very slowly, with stirring, through a dropping funnel. Complete addition required 1.5 hr. The solution was pale yellow and contained a yellow-gray sludge. The solid was removed by filtration and the acetonitrile was removed from the product by water washing. The residue was dried and distilled. Unreacted 1-hexyne (2.5 g) was recovered together with a fraction boiling at 52–53° (29 mm). Nmr examination showed that there was a trace of the BrF addition product, but that the major product was 1-bromo-1-hexyne. A similar reaction with 3-hexyne gave only 3,4-dibromo-3-hexene.

Mesomorphic Properties of Alkoxybenzylideneaminoacetophenones

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Compounds of the alkoxybenzylideneaminoacetophenone series are of special interest, as many of them

have a wide range of smectic phase A below 130°. Four homologs of this series with C_1, C_2, C_4, and C_8 in the n-alkoxy chain length have been reported by Castellano, *et al.*[1]

Their observation of a nematic phase in 4-n-octyloxybenzylidene-4'-aminoacetophenone we believe to be in error. The only phase we observe between the melt and the isotropic liquid is a smectic phase. The possibility of a nematic phase in the aforementioned compound is, further, ruled out because no nematic phase is observed in the lower homolog with C_7 in the chain length. The absence of the nematic phase in these two compounds is further confirmed by our optical and differential thermal analysis studies.

Of the 11 compounds synthesized by us in this series, the lowest homolog with C_1 in the alkyl chain shows no liquid crystalline phase. A nematic phase is observed in compounds with n-alkoxy chain lengths of C_3, C_4, C_5, and C_6 only. All other compounds from C_3 to C_{10}, C_{12}, and C_{14} show an enantiotropic smectic 1 phase. Monotropic smectic 2 is observed in compounds with chain lengths of C_3–C_9. A plot of phase transition temperatures *vs.* the number of carbon atoms in the alkyl chain is shown in Figure 1. For comparison, the data of Castellano, *et al.*,[1] is shown by dotted lines.

Smectic 1 shows the focal-conic texture typical of smectic A of Sackmann and Demus.[2] Monotropic smectic 2 appears to be identical with smectic 1, and it is not possible to distinguish this phase from smectic 1 by optical methods.

In Figure 1, one observes an unusually marked alternation of the nematic–isotropic transition temperatures for odd and even numbers of carbon atoms in the alkyl chain of this homolog's series. The plot for even carbon chain homologs lies above that for odd carbon chain members. Further, this extent of alternation decreases as the chain length increases. The alternation of nematic–isotropic transition temperatures in such a series is similar to that found by Gray[3] in alkoxybenzoic acids and alkoxy Schiff bases.

The nematic–isotropic transition curve (Figure 1) for both odd and even alkyl chain homologs appears to merge with the rising smectic–nematic transition curve at a point which lies below the point for the homolog with C_7 in the alkyl chain. When such a merging of the nematic–isotropic and smectic–nematic curves takes place, then it is well known that all other higher homologs above the merger do not show a nematic phase. This behavior is indeed observed in 4-n-heptyloxybenzylidene-4'-aminoacetophenone which does not exhibit a nematic phase but has only one enantiotropic smectic mesophase which passes directly into the isotropic liquid. Hence, on this basis, it is unlikely for C_8 to have a nematic phase when its predecessor homolog does not show such a phase.

The absence of a nematic phase in C_8 is further confirmed by our differential thermal analysis (DTA) of this compound. In Figure 2, the thermograms of homologs with alkyl chain length of C_6, C_7, and C_8 are shown. An examination of these establishes one enantiotropic liquid crystal phase between the melt and

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(2) H. Sackmann and D. Demus, *Mol. Cryst.*, **2**, 81 (1966).

(3) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, London and New York, 1962, p 197.