

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Addition of Hydrogen Fluoride to Acetylenic Compounds

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The addition of hydrogen fluoride to acetylene homologs has been described recently by Grosse and Linn.¹ In general they operated on one-half or one-quarter gram mole, in closed vessels, at temperatures ranging between -40 and -70° and obtained yields from 46 to 76%.

In the treatment of larger quantities (5–10 moles), we have found it desirable to resort to different procedures in order to avoid localized hot spots which cause resinification, as well as excessively low temperatures where reagents tend to accumulate unreacted, and create a considerable hazard. The choice of procedure depends on the nature of the alkyne treated.

With low-boiling alkynes, such as 1-butyne in the preparation of 2,2-difluorobutane, one mole of the liquefied gas is allowed to boil off through a mercury bubble-counter and a copper tube into a 25% excess (2.5 moles of hydrogen fluoride) of liquefied hydrogen fluoride contained in an ice-cold copper flask surmounted by a dry-ice reflux condenser. The last traces of the gas are swept over with a stream of dry nitrogen. After an hour's standing, the mixture is allowed to boil off into the base of a tall column of cracked ice and the small residue at the end is poured directly on top of the ice. The ice-water mixture drains into a separatory funnel and, after decantation and washing, is distilled. The yields are 0.75 mole of difluoride, 0.18 mole of oily residue, and 0.07 mole of handling losses.

For pentyne or hexyne, it is more convenient to drop the alkyne at a rate not exceeding two drops per second through the reflux condenser into well-stirred hydrogen fluoride cooled to -50° ; as the reaction proceeds, the reacting mixture is allowed to warm up progressively to room temperature.

For higher boiling alkynes, a solution of 5 moles of hydrogen fluoride in one mole of an ether or a ketone is used as the agent of hydrofluorination.² This procedure is not merely one of diluting the reagents but depends on the formation of oxonium derivatives, containing one mole of oxygenated material linked to two moles of hydrogen fluoride.

These oxonium derivatives are good solvents for both reagents as well as for the reaction product. It should be remembered that the two moles of hydrogen fluoride linked in the oxonium compound are not available for addition to the alkyne. Therefore, a mixture of five moles of hydrogen fluoride in one mole of ether can hydrofluorinate no more than one and one-half moles of alkyne, and in practice saturates only one mole of alkyne satisfactorily. The synthesis of 2,2-difluorooctane from 1-octyne illustrates the method.

One mole of ether or acetone is placed in an ice-cooled copper container. Hydrogen fluoride vapors are led in until the weight increase indicates the absorption of five moles of acid. One mole of 1-octyne is then dripped into the mixture which is allowed to warm up slowly to room temperatures as the reaction proceeds. After one hour of standing, the reaction mixture is poured directly into ice water, decanted and washed. Distillation gives first a small amount of wet material which is easily decanted. This is a better method of drying than the use of solid desiccating agents. The yield is 0.75 to 0.80 mole of difluoride, 0.15 mole of an oily material, and 0.05 mole of handling losses. There is no resinous or tarry material.

Whenever the difluoro-octane proves contaminated with unsaturated material (original octyne or 2-fluorooctene), it is treated with one-quarter mole of hydrogen fluoride without solvent, per mole of product, allowed to stand overnight, then worked up as before. It is convenient to use the extremely low refractive index of the polyfluorides (see table) to follow the progress of the reaction.

Identical yields are obtained with ketones and with ethers, *i. e.*, 70 to 75% when the reactions are run as swiftly as possible, and 85 to 90% when the addition is performed very slowly. The reason for not using this procedure with low boiling alkynes is the need for elaborate precautions against handling losses while removing the solvent.

The compounds listed in Table I were made by hydrogen fluoride addition to the proper

(1) Grosse and Linn, *THIS JOURNAL*, **64**, 2289 (1942).

(2) In collaboration with Dr. A. M. Whaley.

TABLE I
 GENERAL TABLE OF PHYSICAL PROPERTIES

Compounds	F. p., °C.	P, mm.	B. p., °C.	t, °C.	n_D^t	d_4^t	MR	A. R. F.	Remarks
CH ₃ CF ₂ C ₂ H ₅	-117.3	760	30.92	10	1.3192	0.9159	20.32	0.92	
	-116.9	747	30.4-.6	20	1.3133	Grosse ¹
	-117.1	747	30.4-.6	20	1.3140	Grosse
	-114.0	760	31.0	10	1.3189	.9170	20.29	.91	Renoll ³
CH ₃ CF ₂ C ₃ H ₇	-93	760	59.7	20	1.3350	.8932	24.99	.95	
	-98.1	760	60.1	20	1.3360	.8987	24.95	.93	Renoll
	749	58.2-.8	20	1.3352	.8904	25.15	1.03	Grosse
C ₂ H ₅ CF ₂ C ₂ H ₅	-94.0	760	60.2	20	1.3370	.9023	24.89	0.90	
	-94.0	760	60.8	20	1.3390	.9106	24.83	.87	Renoll
CH ₃ CF ₂ C ₄ H ₉	-82.5	760	87.4	20	1.3526	.8922	29.62	.95	
	750	86.0-.2	20	1.3535	.8923	29.71	1.00	Grosse
C ₂ H ₅ CF ₂ C ₃ H ₇	-89.3	760	87.4	20	1.3545	.9027	29.42	0.85	
	742	86.0	20	1.3546	.9024	29.46	.87	Grosse
CH ₃ CF ₂ C ₅ H ₁₁	-62.2	760	112.7	20	1.3653	.8885	34.26	.96	
	749	111.7-.9	20	1.3659	.8889	34.29	.97	Grosse
CHF ₂ C ₆ H ₁₃	-82	760	119.7	20	1.3710	.8959	34.47	1.07	
CH ₃ CF ₂ C ₆ H ₁₃	-53.2	760	137.5	20	1.3763	.8854	38.91	0.98	
	-50.0	760	136.3-.6	20	1.3766	.8867	-38.92	.99	Renoll
		60	66.2-.6	20					
C ₃ H ₇ CF ₂ C ₄ H ₉	-45.9	760	137.3	20	1.3780	.8919	38.79	.91	
CH ₃ CF ₂ (CH ₂) ₅ CF ₂ CH ₃	-2.3	20	82	20	1.3712	1.0507	43.22	.96	
CH ₂ =CF(CH ₂) ₅ CF=CH ₂	1.19	4	87	20	1.4036	0.9978	39.21	..	

Analyses. C₃H₇CF₂C₄H₉: 25.2% F, calculated 25.3%.
F, calculated 23.7%.

C₂H₅CF₂: 37.8% F, calculated, 38.0%. C₃H₇CF₂: 23.2%
F, calculated 23.7%.

alkyne, except 3,3-difluoropentane and 1,1-difluoroheptane, which were made from the corresponding dichlorides. The quantities were large enough to permit adequate purification and physical measurements which are believed to be more precise than those of the literature with which they are compared.^{1,3} This belief is based on the constancy of the observed atomic refraction increment for fluorine (A. R. F. in Table I) and on the shape of the freezing curves which showed a range of 0.1° or less between appearance of the crystals and complete solidification. Only two compounds (CHF₂C₆H₁₃ and CH₃CF₂C₃H₇) were of a lower standard of purity, and their freezing point is therefore listed with less precision.

Direction of Addition.—Hydrogen fluoride adds strictly in accordance with the rule of Markownikow. When the triple bond is not located at the end of the chain, addition could occur in two directions, except when the molecule is symmetrical. To illustrate: 2-octyne could give 2,2- and/or 3,3-difluorooctane, while 4-octyne can give only 4,4-difluorooctane. To find out if a directing effect exists, hydrogen fluoride

was added to 2-pentyne; a mixture of the 2,2- and the 3,3-difluoropentanes freezing at -109° resulted. With 3-octyne, a mixture of isomers was also obtained. With 2-octyne, the shape and location of the freezing plateau indicated the formation of a preponderance of the 2,2-isomer. Progressive additions of pure 2,2-difluorooctane were made to this reaction product, and the improvements of the freezing curve were noted. From the trend so established, it was estimated that the original composition was 87% of 2,2- and 13% of 3,3-difluorooctane.

Miscellaneous Experiments.—Hydrogen fluoride was added to various acetylene derivatives with a second chemical function in their molecule. This led frequently to much difficulty.

The addition of hydrogen fluoride to 1,8-nonadiyne was performed successfully in an oxygenated solvent, to yield 2,2,8,8-tetrafluorononane (see table). An appreciable amount of 2,8-difluoro-1,8-nonadiene (see table) was obtained as by-product.⁴ In contrast, all efforts to treat 1,6-heptadiyne resulted in complete resinification.

Orientation results were obtained with phenylacetylene, 5-chloropentyne, propiolic and hexyl-

(3) Renoll, THIS JOURNAL, 64, 1115 (1942).

(4) In collaboration with A. M. Whaley and W. J. Zimmerschied.

propiolic acid and their esters. Details will follow.

Summary

Hydrogen fluoride has been added to a number of acetylene homologs and has yielded generally 70 to 80% of the difluorides expected from

Markownikow's rule. A technique is offered which uses a complex between hydrogen fluoride and an oxygenated compound able to form an oxonium addition product, as the agent of hydrofluorination. The physical properties of the fluorides are tabulated.

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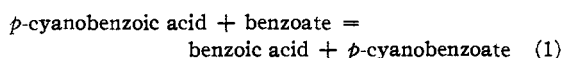
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Effect of Substituents on the Acid Strength of Benzoic Acid. VI. The Cyano Group

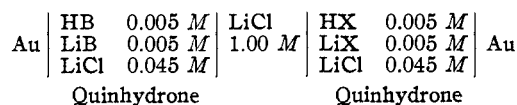
BY MARTIN KILPATRICK AND R. DEAN EANES

In order to test recent theoretical predictions on the effect of substituents on acid strength, the equilibrium constants for the reaction



and the corresponding reaction for *m*-cyano-benzoic acid have been determined in the solvents water, ethylene glycol, methyl alcohol, ethyl alcohol, and in the mixed solvent dioxane-water.

The experimental technique involving the measurement of the e. m. f. of concentration cells of the type



has been described in the earlier papers of this series.¹ These papers also describe the purification of the solvents and the preparation of the lithium chloride.

***p*-Cyanobenzoic Acid.**—The acid was dissolved in water, treated with norite, filtered and crystallized. This treatment was repeated several times, and after five recrystallizations from water the white product was dried in an Abderhalden pistol at room temperature. The product melted between 218.5 and 219° in agreement with the findings of Valby and Lucas.² A portion of the product was heated to 100° in the pistol, after which the melting point was found to be 214°, indicating decomposition as reported by Sandmeyer.³ Titration with sodium hydroxide gave

(1) Elliott and Kilpatrick, *J. Phys. Chem.*, **45**, 454, 466, 472, 485 (1941).

(2) Valby and Lucas, *THIS JOURNAL*, **51**, 2718 (1929).

(3) Sandmeyer, *Ber.*, **18**, 1497 (1885).

an equivalent weight of 147.3. The theoretical value is 147.1.

***m*-Cyanobenzoic Acid.**—This compound was prepared⁴ from *m*-aminobenzoic acid by means of the Sandmeyer reaction, following closely the procedure described by Valby and Lucas² for the preparation of *p*-cyanobenzoic acid. The product was recrystallized four times from water (after treatment with decolorizing charcoal) and once from 50% ethanol. It formed fine, colorless needles melting at 220–221°. The reported melting point is 217°. The equivalent weight by titration was 146.9.

Table I gives $K_{A_xB_x}$, the equilibrium constant for the reaction of equation 1. This equilibrium constant is the ratio of the dissociation constant of *p*-cyanobenzoic acid to that of benzoic acid.

TABLE I
RATIO OF THE DISSOCIATION CONSTANT OF *p*-CYANO-BENZOIC ACID TO THAT OF BENZOIC ACID AT 25°

Solvent	Dielectric constant	$K_{A_xB_x}$ (obs.)	$\frac{K_{A_xB_x}}{K_{A_xB_0}}$ (calcd. by equation 2)
Water	78.5	4.48 ^a	4.51
Ethylene glycol	37.7	6.59	6.68
Methyl alcohol	31.5	8.13	7.85
Ethyl alcohol	24.2	9.97	10.2
Dioxane-water	25	9.27	9.80

^a Calculation from the data of Kirschner, Wingfield and Lucas, *THIS JOURNAL*, **52**, 27 (1930), yields 4.64.

The results for the pure solvents may be expressed by the equation

$$\log K_{A_xB_0} = 0.496 + (12.4/D) \quad (2)$$

and the agreement between experiment and equation (2) is shown in Fig. 1 and the last

(4) Preparation by H. J. Schneider under the direction of Dr. M. Carmack of this Laboratory.