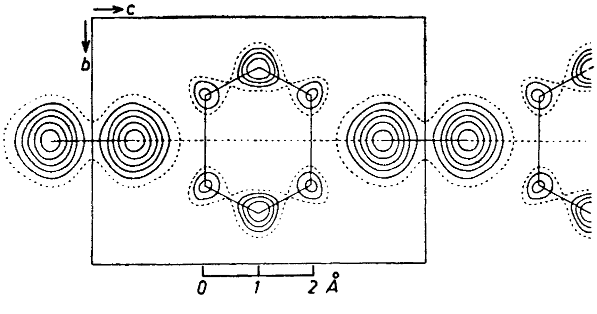

Fig. 1. (a).

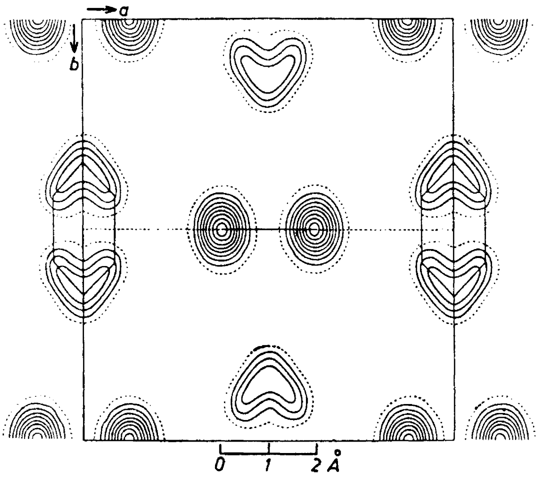

Fig 1. (c).

Preparation of Deuterated Vinyl Fluorides

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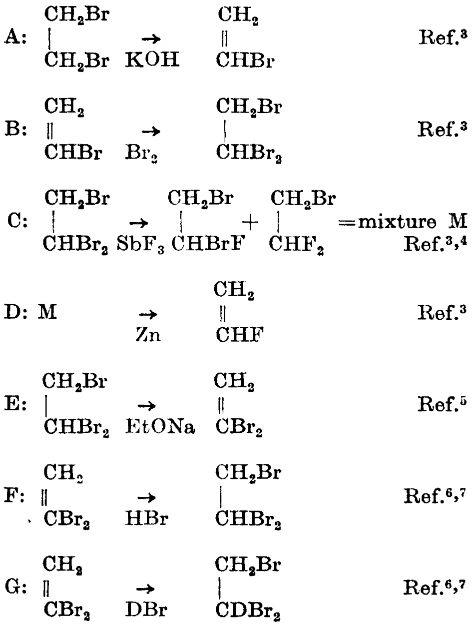
Recent attempts to analyze the infrared spectrum of *vinyl fluoride*[1] and to determine the structure of the molecule by microwave measurements[2] necessitated the preparation of all the deuterated derivatives. Since the combination of processes used and the yields obtained may be of value for future work on vinyl fluoride in the above-mentioned or quite different directions (such as reaction kinetics) it seemed justified to give a brief account of our results. Vinyl fluoride (I) and its seven deuterated derivatives have been prepared, three as pure compounds, CH_2CDF (II), CD_2CHF (V), and CD_2CDF (VI), and four as *cis-trans* mixtures, *cis-trans* CHDCHF (III), and *cis-trans* CHDCDF (IV).

Experimental. All the preparations described here are combinations of 4 or 6 of the following 7 processes (A—G), for sake of brevity illustrated below with 'light' ethylene bromide, vinyl bromide *etc.*



A: $\begin{matrix}CH_2Br\\|\\CH_2Br\end{matrix} \xrightarrow[KOH]{} \begin{matrix}CH_2\\\|\\CHBr\end{matrix}$ Ref.[3]

B: $\begin{matrix}CH_2\\\|\\CHBr\end{matrix} \xrightarrow[Br_2]{} \begin{matrix}CH_2Br\\|\\CHBr_2\end{matrix}$ Ref.[3]

C: $\begin{matrix}CH_2Br\\|\\CHBr_2\end{matrix} \xrightarrow[SbF_3]{} \begin{matrix}CH_2Br\\|\\CHBrF\end{matrix} + \begin{matrix}CH_2Br\\|\\CHF_2\end{matrix}$ =mixture M Ref.[3,4]

D: $M \xrightarrow[Zn]{} \begin{matrix}CH_2\\\|\\CHF\end{matrix}$ Ref.[3]

E: $\begin{matrix}CH_2Br\\|\\CHBr_2\end{matrix} \xrightarrow[EtONa]{} \begin{matrix}CH_2\\\|\\CBr_2\end{matrix}$ Ref.[5]

F: $\begin{matrix}CH_2\\\|\\CBr_2\end{matrix} \xrightarrow[HBr]{} \begin{matrix}CH_2Br\\|\\CHBr_2\end{matrix}$ Ref.[6,7]

G: $\begin{matrix}CH_2\\\|\\CBr_2\end{matrix} \xrightarrow[DBr]{} \begin{matrix}CH_2Br\\|\\CDBr_2\end{matrix}$ Ref.[6,7]

The directions given in the literature [3-6] were modified with respect to the fact that much smaller quantities than usual were prepared. For example, procedure *C* was carried out in a sealed-off glass tube (24 h at 100°C) instead of in the platinum apparatus prescribed by Swarts, without serious decrease in the yield. In the *E* process, 2.5 ml $CH_2BrCHBr_2$ (or $CD_2BrCDBr_2$ a.s.o.) were converted to CH_2CBr_2 in a nitrogen atmosphere. Vinylidene bromide was removed from the small reaction container by a syringe and rapidly transferred to a nitrogen-filled test tube, from which it was distilled *in vacuo* at 20°C ($p \sim 60$ mm) after drying over $CaCl_2$ for a couple of hours. — SbF_3 and DBr were prepared according to prescriptions in Ref.[8] resp. Ref.[7]

The purity of all intermediates was controlled by infrared spectra. In all cases except one, the intermediates were 95—100 % pure. The reaction product from *C* is a mixture ('M') which was not separated into its components, since both yield the product desired. The addition of HBr, resp. DBr to the double bond (processes *F* and *G*) occurred very smoothly at room temperature under irradiation by mercury light in containers of ordinary Pyrex glass. Addition of a trace of pure oxygen had a pronounced catalytical effect. No exchange reactions took place.

The isotopic vinyl fluorides were liberated as gases (b.p. —51°C) from the mixture of 'M', Zn-dust, and ethyl alcohol. They were condensed in a trap cooled by liquid air and afterwards distilled, the trap being immersed in a —80°C bath. Only fractions of approximately correct pressure were taken. The final purification occurred on dry silica-gel in a gas chromatograph at 43°C (inside diameter of tube $\sim$ 10 mm, length of column 11 cm). In this way, the last non-isotopic impurities were removed as demonstrated by the infrared spectra taken. Also, since a complete collection of deuterated species was prepared, a useful check on the *isotopic* purity of the samples was obtained from the spectra.

Prior to the present investigation we thought that the *stability* of vinyl fluoride, kept in glass containers at room temperature and in daylight would be a problem. Infrared spectra of samples kept for months under the conditions mentioned showed the samples to be stable.

Our results are given in condensed form in Tables 1 and 2.

Table 1. Procedures applied (A—G), per cent yields obtained, and amount of final product (in ml at t°C = 25, p = 760 mm) at the preparation of vinyl fluoride (I), CH_2CDF (II), CD_2CHF (V), CD_2CDF (VI), the *cis-trans* mixture CHDCHF (III), and *cis-trans* mixture CHDCDF (IV). The general formula of the starting material is taken as CXYBrCXYBr, Z grams of this material being applied.

Table 1 continued.

X	Y	Z	Processes						Respective yields						Final product
H	H	16.5	A	B			C	D	72	80			$\sim$40	$\sim$50	CH_2CHF (240 ml)
H	H	19.5	A	B	E	G	C	D	65	90	77	73	$\sim$47	$\sim$23	CH_2CDF (90 —)
D	D	13.7	A	B			C	D	69	97			$\sim$44	$\sim$35	CD_2CDF (180 —)
D	D	9.9	A	B	E	F	C	D	69	97	74	75	$\sim$52	$\sim$42	CD_2CHF (102 —)
H	D	29.5	A	B	E	F	C	D	65	82	76	75	$\sim$38	$\sim$30	CHDCHF* (175 —)
H	D	19.0	A	B	E	G	C	D	69	89	72	72	$\sim$50	$\sim$9	CHDCDF* (35 —)
			Average yields						68	89	75	74	45	23	

* *cis-trans* mixture

CHDBrCHDBr was prepared from acetylene and DBr [7].

Table 2. Per cent isotopic contaminations in the deuterated vinyl fluoride samples prepared. Amounts estimated from infrared gas spectra.

Sample **	Per cent contaminant (I—VI)					
	I	II	III	IV	V	VI
I	—	0	0	0	0	0
II	0	—	0	0	0	0
III*	5—10	0	—	0	0	0
IV*	0	0	3—5	—	0	0
V	0	0	3—5	0	—	0
VI	0	0	0	3—5	3—5	—

* *cis-trans* mixture.

V and VI were prepared from CD_2BrCD_2Br with an indicated isotopic purity of 95 %. The sample was kindly given to us by dr. Leitch, N.R.C., Ottawa.

** Designation as in Table 1, consistent with Ref.[1].

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Determination of Barbituric Acid Derivatives as Mercury Complexes

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Barbituric acid derivatives give precipitates with mercuric ions and this characteristic has since long been used for their detection and determination [1-3]. The precipitates are, however, soluble in certain organic solvents and this fact has been the base for the present method, the principles of which are as follows.

To a solution of 50—250 μg of a barbituric acid in 10 ml of water add 1 ml of 0.3 % mercuric nitrate solution and buffer solution to pH 8.0. Extract with 3 or 4 × 10 ml of a suitable organic solvent. Filter the organic phase through glass-wool moistened with the solvent, carefully avoiding any entrainment. To the combined extracts add an exactly measured volume of a 0.0015 % dithizone solution in chloroform and dilute to 100 ml with chloroform. Make a blank by mixing an equal amount of the dithizone solution with the same volume of the extraction solvent as above and making up to 100 ml with chloroform. Measure the extinction difference at 605 mμ. Calculate the amount of the barbituric acid from a standard curve prepared by applying the method to known quantities of barbiturate. It is, however, more convenient to use mercuric chloride when constructing a standard curve which can be used for all barbituric acids. 1 mole of mercury corresponds to 2 moles of the N-substituted barbiturates and to 1 mole of all the others.

Smaller amounts of barbituric acid can easily be determined by reducing the volumes. Thus, 2 μg of amylobarbitone (amytal) in a final volume of 5 ml gives an extinction difference of 0.130 in 1 cm cuvette, which corresponds to a sensitivity 5 times greater than that obtained by the ultraviolet methods now in use [4].