Anal. Calcd. for $C_9H_7F_3O$ (188): C, 57.44: H, 3.7. Found: C, 57.48; H, 3.5.

A small sample of the above product was heated with 20% sodium hydroxide until gas evolution ceased and the resulting clear solution was acidified with dilute hydrochloric acid. The resulting white precipitate was recrystallized several times from hot water and dried; m.p. 180°. There was no depression in melting with a sample of pure *p*-toluic acid. The amide melted at 158°. Thus, it was concluded that the product of this Friedel–Crafts reaction was *p*-methyl-ω,ω,ω-trifluoroacetophenone.

Physical Properties

A summary of the physical properties of these compounds is reported in Table I.

The infrared absorption spectra were measured using an automatic recording Perkin–Elmer infrared spectrometer, model 12C. The results are given in Fig. 1 and Fig. 1a.

BOULDER, COLORADO RECEIVED JULY 21, 1950

[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

The Addition Products of Trifluoroethylene[1]

BY J. D. PARK, W. R. LYCAN[2] AND J. R. LACHER

This paper covers the preparation of trifluorinated derivatives of ethane through the use of trifluoroethylene. This latter compound, which has been neglected, is easily made in almost quantitative yields from commercial trifluorochloroethylene by addition of hydrogen bromide to form $CF_2Br-CHClF$ followed by treatment of the adduct with zinc to remove bromine and chlorine from adjacent carbon atoms. Trifluoroethylene reacts with chlorine, bromine or methanol to yield the adducts in almost quantitative fashion. The usual physical properties of these adducts, including their magnetic susceptibilities, are presented along with their ultraviolet and infrared absorption spectra.

In our program of studies involving heats of reactions[3] and magnetic susceptibilities[4a] of aliphatic fluorinated compounds, the conventional methods[4b] of preparing the fluorinated derivatives of ethane and ethylene were found to be too devious and lacking in reasonable organic yields.

This paper presents the preparation of symmetrically trifluorinated derivatives of ethane starting with trifluoroethylene.[5] This compound, previously prepared in poor yields by Swarts[6] from the fluorination of $CHBr_2-CHBr_2$ followed by debromination of $CBrF_2-CHBrF$, is easily made from commercial $CF_2=CFCl$ ("Freon-1113")[7] by addition of HBr to form $CF_2Br-CHClF$, and followed by treatment with zinc to remove chlorine and bromine from adjacent carbon atoms. Trifluoroethylene (I) reacts with chlorine, bromine or methanol to yield, in almost quantitative fashion, $CF_2Cl-CFHCl$ (II), $CF_2Br-CFHBr$ (III) and $CH_3O-CF_2-CFH_2$ (IV), respectively.

TABLE I

THE PHYSICAL PROPERTIES OF THE ADDUCTS OF TRIFLUOROETHYLENE

Compound	B. p. Obsd., °C.	B. p. Press., mm.	B. p. Lit. ref.	Density, $D^{0^\circ}_4$	n^t_D	AR_F	Susceptibility, $-\chi_M \times 10^6$ Exptl.	Susceptibility, Calcd.[a]
$CF_2=CHF$	−56	628	−51[6]	$1.265^{27.4^\circ}$			32.2	+43.9
$CF_2Cl-CHClF$	23.3	632.6						
	28.2	760	28[8]	1.498	1.3371^{15}	1.12	66.2	83.4
$CF_2Br-CHBrF$	69.5	630						
	76	760	76[6]	2.274	1.4191^{24}	1.07	90.9	110.6
$CH_3-O-CF_2CH_2F$	39.5	630						
	45.2	760	45[9]	1.182	1.2997^{25}	1.36	55.9	

[a] Molar magnetic susceptibility calculated from Pascal's modified constants. L. Michaelis, "Technique of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1946, Vol. II, p. 1231.

II and III have been previously obtained in poor yields from the fluorination of C_2HCl_5[8] and $CHBr_2-CHBr_2$,[6] respectively. IV had been prepared by Swarts[9] by the action of $NaOCH_3$ on CF_2BrCH_2F.

Procedure

Preparation of $CF_2=CHF$.—The vapor phase addition of HBr to $CF_2=CFCl$ was carried out at 100°, with an excess of hydrogen bromide according to a previously described method.[10]

The conversion to $CF_2Br-CFClH$ was quantitative; b.p. 46° at 619.5 mm.

The dehalogenation of $CF_2Br-CHClF$ to $CF_2=CHF$ was carried out according to the method of Henne and Zimmerschied.[11] Conversion was 85%.

Chlorination of $CF_2=CHF$ to $CF_2Cl-CHClF$.—The chlorination of the olefin was carried out in an apparatus similar to one previously described.[10] The catalyst was prepared by mixing reduced iron (10% by wt. of the carbon

---

[1] This work was supported in part by contract N6-onr-231, Task Order 6, with the Office of Naval Research, United States Navy.

[2] This paper represents in part a thesis presented by W. R. Lycan to the University of Colorado in partial fulfillment of the requirements for the degree of Master of Arts, June, 1950.

[3] J. R. Lacher, J. D. Park, *et al.*, THIS JOURNAL, **71**, 1330 (1949); **71**, 1334 (1949); **72**, 331 (1950).

[4] (a) J. R. Lacher, R. E. Scruby and J. D. Park, *ibid.*, **72**, 333 (1950); *ibid.*, **71**, 1797 (1949). (b) A. L. Henne, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 50.

[5] U. S. Patent 2,426,172 (A. F. Benning to Kinetic Chemical, Inc.). *Chemical Abstracts* does not disclose $CF_2=CHF$. However, the original patent shows in Ex. III the production of $CF_2=CHF$ as a by-product in the fluorination of $CH\equiv CH$ with SbF_5.

[6] F. Swarts, *Bull. Acad. Roy. Belg.*, **37**, 357 (1899).

[7] Available from the Kinetic Chemicals Division, Orchem. Department, du Pont & Co., Deepwater, New Jersey.

[8] A. L. Henne and E. C. Ladd, THIS JOURNAL, **58**, 402 (1936).

[9] F. Swarts, *Bull. acad. roy. Belgique Cl. sci.*, 563 (1911).

[10] J. D. Park, M. L. Sharrah and J. R. Lacher, THIS JOURNAL, **71**, 2339 (1949).

[11] A. L. Henne and W. J. Zimmerschied, *ibid.*, **69**, 281 (1947).

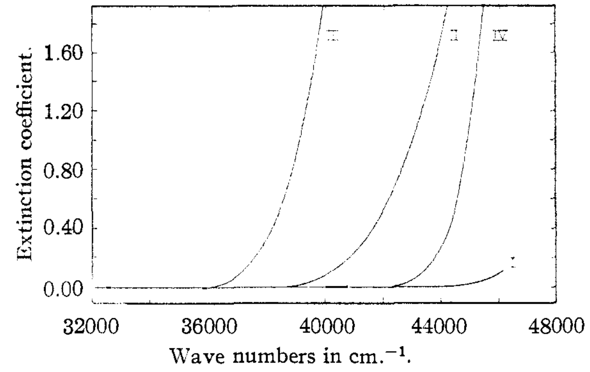

Fig. 1.—The ultraviolet absorption spectra in a 10-cm. gas cell at ind. press.: I, CF_2=CFH at 400 mm.; II, CF_2Cl—CHClF at 64.3 mm.; III, CF_2Br—CFHBr at 100 mm.; IV, CH_3—O—CF_2CFH_2 at 400 mm.

used) with 12-mesh "Columbia" activated carbon, followed by conversion of the iron to ferric chloride. Flow of the reactants, chlorine and CHF=CF_2, was then started and allowed to react in the catalyst chamber maintained at about 100°. Excess of olefin flow was maintained to ensure that no substitution of the hydrogen in the molecule took place. Conversion, after fractionation, was 90%; organic recovery 96%. No CF_2Cl-CCl_2F was detected.

Bromination of CF_2=CHF to CF_2Br—CHBrF.—The olefin was bubbled through a sintered-glass distributor through a head of 40 cm. of liquid bromine in the presence of actinic light. After a lengthy induction period, reaction took place quite rapidly; conversion 82%; organic recovery 100%. No CF_2Br-CBr_2F was isolated.

Physical Properties.—The physical properties are listed in Table I.

The ultraviolet absorption spectra were measured with a Beckman model DU quartz spectrophotometer. All samples were run in the vapor phase in a 10-cm. gas cell. The extinction coefficient, E, defined by $\log I/I_0 = -El$ was measured; l is length of the cell in cm. which is unity in the present case. Readings were made at approximately every 10 Å. in the regions where absorption took place. The results are given in Fig. 1. No peaks or fine structure were found, and absorption started sharply below 280 mμ in every case.

The infrared absorption spectra were measured using an automatic recording Perkin-Elmer Infrared Spectrometer, Model 12C. All of the gas samples were run in a 10-cm. cell. The results obtained are given in Fig. 2. Some qualitative assignments of the various peaks are possible using the data of Barnes, *et al.*[12]

The experimental magnetic susceptibilities were determined by the Quincke tube method previously described[4].

Boulder, Colorado Received July 21, 1950

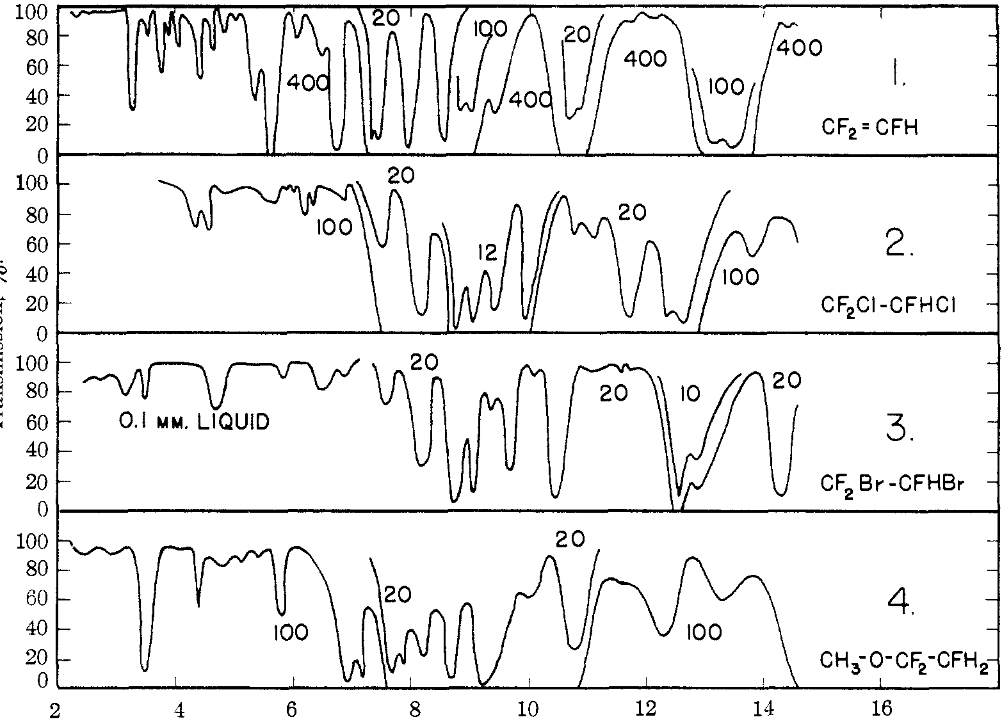

Fig. 2.—The infrared absorption spectrograms at room temperature in a 10 cm. gas cell at ind. press. in mm. and in a 0.1 mm. liquid cell of: (1) CF_2=CFH; (2) CF_2Cl—CFClH; (3) CF_2Br—CFBrH; (4) CH_3—O—CF_2CFH_2.

---

[12] R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).