[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

Directed Halogenation in Fluorinated Aromatic Compounds[1]

BY J. D. PARK, H. A. BROWN AND J. R. LACHER

A method for chlorinating the two compounds α,α-dichloro-β,β,β-trifluoroethylbenzene and *m*-chloro-α,α-dichloro-β,β,β-trifluoroethylbenzene in sealed Pyrex tubes is discussed. From these studies it is found that the $-COCF_3$, and the $-CCl_2CF_3$ groups like the $-CF_3$ group are meta directors in electrophilic aromatic substitution reactions. The physical properties, including infrared absorption spectra, of several aromatic compounds containing the trifluoromethyl group are reported.

It is well known that the trifluoromethyl and trichloromethyl groups are strong meta directors in electrophilic aromatic substitution reactions.[2] The object of the present work was to determine the directive influence of the trifluoro-alkyl and -acyl groups in the chlorination of the aromatic nucleus.

Attempts to chlorinate ω,ω,ω-trifluoroacetophenone (I)[3] with sulfuryl chloride[4] and by passing chlorine through an illuminated, heated solution were unsuccessful. However, (I) was readily chlorinated in 85.3% yield in a sealed tube employing ferric chloride as a catalyst. The chlorinated product was identified as *m*-chloro-ω,ω,ω-trifluoroacetophenone (II).

The chlorination of α,α-dichloro-β,β,β-trifluoroethylbenzene[4] (III) by a similar method resulted in a mixture of *m*-chloro-α,α-dichloro-β,β,β-trifluoroethylbenzene (IV) and 3,4-dichloro-α,α-dichloro-β,β,β-trifluoroethylbenzene (V) in 66.9 and 23.8% yields, respectively. The chlorination of (IV) gave a 62% yield of (V). Compound (IV) was also prepared in 64.8% yield by refluxing (II) with PCl_5 for about 40 hours following the method of Cohen.[3]

p-Methyl-ω,ω,ω-trifluoroacetophenone (VI) was prepared by a Friedel–Crafts reaction[5] but was not chlorinated.

It is concluded that the trifluoroacetyl group is a stronger meta director than the α,α-dichloro-β,β,β-trifluoromethyl group. Also, chlorine which directs ortho and para in the aromatic nucleus, overshadows the meta directional effects of the dichlorotrifluoroethyl group.

Experimental[6]

***m*-Chloro-ω,ω,ω-trifluoroacetophenone.**—Twenty-five grams (0.14 mole) of ω,ω,ω-trifluoroacetophenone and 0.1 g. of anhydrous ferric chloride were placed in a Pyrex tube (25 mm. o.d., 18 mm. i.d., 65 cm. in length). The end of the tube was cooled in a Dry Ice–acetone mixture, and about 10 g. (6.5 cc., 0.14 mole) of chlorine was condensed in the tube. Next, the sealed tube was heated in an oven for 24 hours at 100–110°. After cooling to room temperature, the tube was again cooled in a Dry Ice–acetone mixture, opened, and then warmed to expel dissolved hydrogen chloride and excess chlorine. Fractionation of the chlorinated material gave 21.74 g. of material having a boiling point of 93° at 36.5 mm. along with 3.7 g. of unreacted starting material; yield 85.3%.

Anal. Calcd. for $C_8H_4OClF_3$ (208.56): Cl, 17.00. Found: Cl, 17.05, 17.01.

ω,ω,ω-Trifluoroacetophenone when treated with sodium hydroxide solution, undergoes a haloform-type reaction resulting in the formation of the sodium salt of benzoic acid and fluoroform. Hence, the position of the chlorine substituent in the chlorinated product is easily determined.

A sample of the chlorinated material was heated with 20% sodium hydroxide until gas evolution ceased, and then was acidified with dilute hydrochloric acid. Recrystallization from hot water gave a white crystalline material, m.p. 154°. No depression in m.p. was observed with pure *m*-chlorobenzoic acid (m.p. 154–155°).

Chlorination of α,α-Dichloro-β,β,β-trifluoroethylbenzene.—The α,α-dichloro-β,β,β-trifluoroethylbenzene was made using the procedure of Jones.[3] The chlorination of 32.4 g. (0.14 mole) of α,α-dichloro-β,β,β-trifluoroethylbenzene, prepared in 85.3% yield by the method of Cohen[3] in a sealed tube, resulted in a mixture of 24.7 g. (66.9%) of *m*-chloro-α,α-dichloro-β,β,β-trifluoroethylbenzene, b.p. 114° at 37 mm., and 8.8 g. (23.8%) of 3,4-dichloro-α,α-dichloro-β,β,β-trifluoroethylbenzene, b.p. 144.5° at 37 mm.

Anal. Calcd. for $C_8H_4Cl_3F_3$ (263.48): Cl, 40.37. Found: Cl, 40.36, 40.28, 40.44. Calcd. for $C_8H_3Cl_4F_3$ (297.93): Cl, 47.60. Found: Cl, 47.53. 47.67.

In attempting to determine the position of the chlorine on the benzene nucleus, it was found that both of these compounds were stable to alkaline permanganate, concentrated sulfuric acid, and strong sodium hydroxide solution. Hence, the following procedure was employed: Five grams of the chlorinated product was treated with 0.35 g. of lithium aluminum hydride in 100 ml. of dry ether. After refluxing for 1 hour the mixture was hydrolyzed with ice-water. The ether layer was separated and washed with cold water and the ether removed with a water aspirator. The remaining oily residue was then treated with 5.8 g. of potassium permanganate and 2.0 g. of potassium hydroxide in 50 ml. of water and refluxed for 12 hours. Upon filtration and acidi-

TABLE I

SUMMARY OF PHYSICAL PROPERTIES OF SOME AROMATIC COMPOUNDS CONTAINING THE TRIFLUOROMETHYL GROUP

Compound	B.p. °C.	B.p. Mm.	Density, d^t_4 g./cc.	t	Refractive index, n^t_D	t
m-Cl—$C_6H_4CF_3$[a]	138	760	1.3345	30	1.4432	30
	100	235				
	50	31				
$C_6H_5COCF_3$	152	730	1.2752	25	1.4576	20
	106.5	177				
	69.5	38				
m-Cl—$C_6H_4COCF_3$	131.5	170	1.4211	25	1.4800	20
	105	61				
	93	36.5				
$C_6H_5CCl_2CF_3$	173	631	1.4150	25	1.4767	20
	133	174				
	92	38				
m-Cl—$C_6H_4CCl_2CF_3$	201	632	1.5173	25	1.4970	20
	159	169				
	114	37				
3,4-di-Cl—$C_6H_3CCl_2CF_3$	187.5	172	1.6244	25	1.5221	20
	166	85.5				
	144.5	37				
p-CH_3—$C_6H_4COCF_3$	131	172.5	1.2304	25	1.4693	20
	111	84				
	92	37.5				

[a] This compound was obtained from Hooker Electrochemical Company and was redistilled using a 20-plate helix-packed column.

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[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] Roberts, Webb and McElhill, THIS JOURNAL, **72**, 408 (1950).

[3] This substance was prepared in 62% yield by the addition of diphenylcadmium to trifluoroacetyl chloride according to the method of Jones, THIS JOURNAL, **70**, 143 (1948). See also Cohen, Wolosinki and Scheuer, *ibid.*, **71**, 3439 (1949).

[4] Kharasch and Brown, *ibid.*, **61**, 2142 (1939).

[5] Simons and Ramler, *ibid.*, **65**, 389 (1943).

[6] All m.p.'s and b.p.'s are uncorrected.

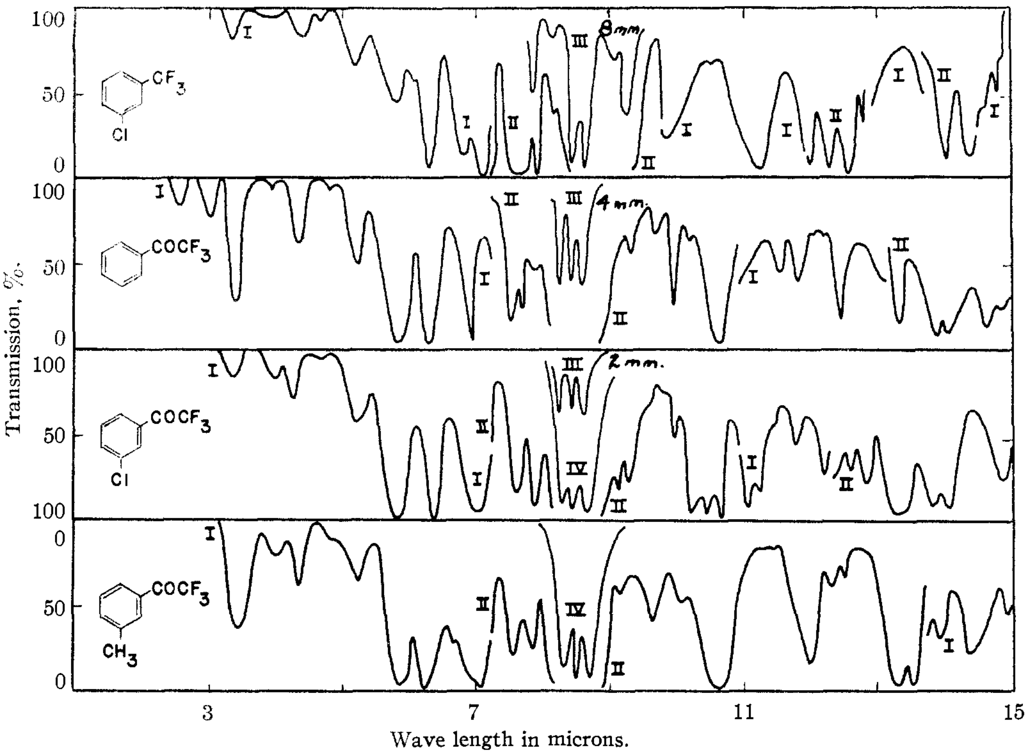

Fig. 1.—The infrared absorption spectrograms at room temperature: I in a 0.1 mm. liquid cell; II in a 0.025 mm. liquid cell; III in a 10 cm. gas cell at ind. press. and IV film thickness of the sample.

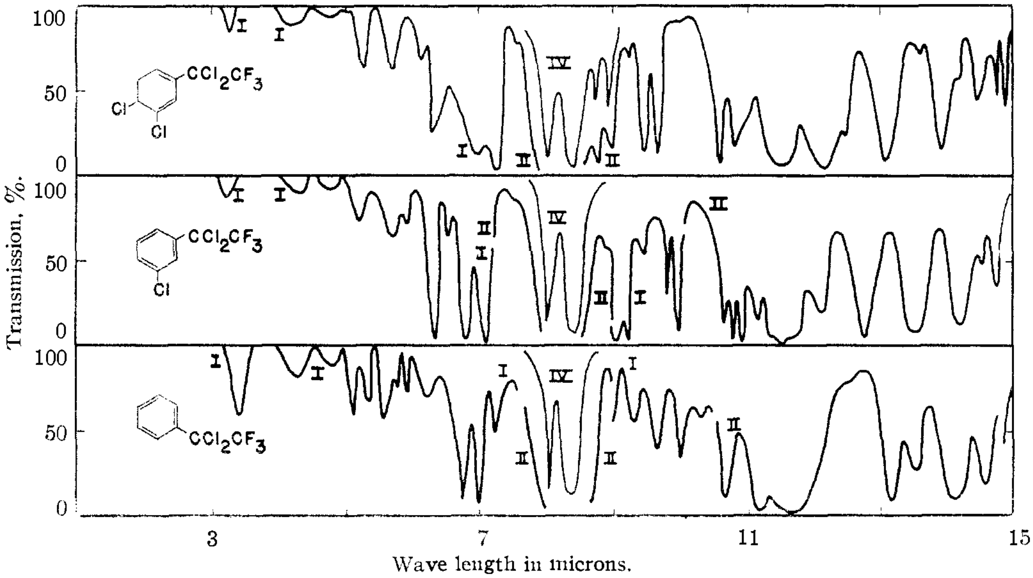

Fig. 1a.—The infrared absorption spectrograms at room temperature: I in a 0.1 mm. liquid cell; II in a 0.025 mm. liquid cell and IV film thickness of the sample.

fication of the solution, a white precipitate was obtained. This procedure was used for both fractions and no depression in m.p. was observed with pure *m*-chlorobenzoic acid and pure 3,4-dichlorobenzoic acid, respectively.

Chlorination of *m*-Chloro-α,α-dichloro-β,β,β-trifluoroethylbenzene.—Twenty-four and eight-tenths grams of *m*-chloro-α,α-dichloro-β,β,β-trifluoroethylbenzene was heated in a sealed tube for 18 hours at 100–110° with 6.5 g. (4.15 ml., 0.09 mole) of chlorine and 0.1 g. of ferric chloride. Fractionation gave 17.39 g. (62% yield) of 3,4-dichloro-α,α-dichloro-β,β,β-trifluoroethylbenzene.

***m*-Chloro-α,α-dichloro-β,β,β-trifluoroethylbenzene.**—Following the method described by Cohen,[3] 29.2 g. (0.14 mole) of *m*-chloro-ω,ω,ω-trifluoroacetophenone and 44 g. (0.21 mole) of phosphorus pentachloride was heated under reflux and 64.8% yield of pure product b.p. 114° at 37 mm. was obtained on fractionation. This product was identical with the *m*-chloro-α,α-dichloro-β,β,β-trifluoroethyl benzene obtained in the chlorination of α,α-dichloro-β,β,β-trifluoroethylbenzene.

***p*-Methyl-ω,ω,ω-trifluoroacetophenone.**—This compound was prepared by the method described by Cohen[3] with slight modifications. After hydrolysis, the reaction mixture was steam distilled. The carbon disulfide and excess toluene were removed from the oily layer of the steam distillate with a water aspirator and the remaining liquid fractionated to give 21.8 g. of product; b.p. 92° at 37.5 mm.; 53% yield.

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]

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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

	B. p.						Susceptibility, $-\chi_M \times 10^6$	
Compound	Obsd., °C.	Press., mm.	Lit. ref.	Density, $D^{0°}_{4}$	n^{t}_{D}	AR_F	Exptl.	Calcd.[a]
$CF_2{=}CHF$	−56	628	−51[6]	$1.265^{27.4°}$			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

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[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).