12-(2'-Ethoxyethyl)-9-amino-1,2,3,4,9,10,11,12-octahydrophenanthrene, V.—In the best of several attempts, 9.08 g. of oxime, purified by extraction from petroleum ether solution with Claisen alkali and precipitation with acid, in 200 cc. of pure anhydrous butyl alcohol at 80° was treated with 14 g. of sodium. The mixture rapidly heated up enough to melt the sodium and was shaken occasionally to break up the molten globules of sodium. At the end additional heat was required to complete the reaction. The crude amine thus obtained was purified by dissolving in dry petroleum ether to which dry hydrogen chloride was added. The precipitated hydrochloride was collected, washed, and treated with alkali. There was thus obtained 5.5 g. (64%) of faintly yellow viscous amine, $n^{25}D$ 1.5518, which distilled at 0.5 mm. when the bath temperature was about 190°. More of a similar product was obtained in 21% yield from the non-crystalline material remaining after the separation of the crystalline oxime acetate described above.

Anal.[a] Calcd. for $C_{18}H_{27}ON$: C, 79.1; H, 10.0; N, 5.1. Found: C, 78.1, 78.4; H, 9.8, 9.9; N, 4.9, 4.9.

The neutral fraction remaining after removal of the amine hydrochloride yielded a small amount of an oily liquid which distilled at 0.5 mm. when the bath temperature was about 190°. This fraction was larger when oxime not purified by the Claisen alkali treatment was used. Treatment with methylmagnesium iodide showed that this substance contained an active hydrogen, and on analysis, figures consistent with the formulation as 12-(2'-ethoxyethyl) - 9 - hydroxy - 1,2,3,4,9,10,11,12 - octahydrophenanthrene were obtained.

Anal.[c] Calcd. for $C_{18}H_{26}O_2$: C, 78.8; H, 9.6. Found: C, 79.1, 78.7; H, 9.1, 8.9.

1,3,4,9,10,10a-Hexahydro-9,4a(2)-iminoethanophenanthrene, VII.—On refluxing a solution of 3.35 g. of the above amine in 60 cc. of 48% hydrobromic acid, an insoluble compound separated. On extraction, washing, and removal of solvent, 3.25 g. of a brittle resin-like substance was obtained. Since this product could not be distilled or crystallized readily, it was immediately subjected to cyclization attempts. An analysis of the crude material is given.

Anal.[a] Calcd. for $C_{16}H_{22}NBr$: C, 62.3; H, 7.2; N, 4.5; Br, 25.9. Found: C, 56.2; H, 6.7; N, 3.8; Br, 26.2.

In the best of several attempts at cyclization, 1.88 g. of bromoamine in 50 cc. of 95% ethyl alcohol was added to 500 cc. of 10% sodium hydroxide containing 200 cc. of ethyl alcohol.[14] After keeping at 60° for three days, the alcohol was largely removed and the organic material extracted to yield 1.63 g. of a substance which was much more fluid than the starting material. On triturating with Skellysolve B 0.37 g. remained undissolved. Analysis showed it to contain 6% of bromine so it was not further studied. On treatment of the Skellysolve B soluble fraction with dry hydrogen chloride, a crude hydrochloride fraction was obtained which was only partially soluble in water. The water insoluble fraction was discarded after preliminary examination and the soluble fraction was made alkaline. The amine thus obtained was vacuum distilled (bath temperature, 180°, pressure 0.5 mm.) to yield 25 mg. of almost colorless, rather fluid product.

Anal.[a] Calcd. for $C_{16}H_{21}N$: C, 84.5; H, 9.3; N, 6.2. Found: C, 84.0; H, 9.4; N, 5.8.

A small amount of solid chloroplatinate was made and analyzed for platinum.

Anal. Calcd. for $C_{32}H_{44}N_2PtCl_6$: Pt, 22.6. Found: Pt, 22.2.

A Van Slyke amino-nitrogen determination[5] showed that 56.2% of this product was primary (undesired) amine, probably 9-amino-12-vinyl-1,2,3,4,9,10,11,12-octahydrophenanthrene. The remainder was probably the desired secondary amine, VII, but further work must be done before this synthesis is firmly established.

12-(2'-Ethoxyethyl)-9-keto-10-oximino-1,2,3,4,9,10,11,-12-octahydrophenanthrene, VIII.—The ketone, IV, was nitrosated with *i*-amyl nitrite and potassium ethoxide[15] to yield 62% of a yellow-orange oil soluble in Claisen alkali. This material could not be vacuum distilled or crystallized but gave the expected analytical figures for VIII after partial purification by chromatographic adsorption over a mixture of 5 parts calcium silicate (Silene, Pittsburgh Plate Glass Co.) and 1 part celite No. 535 (Johns Manville Co.) had removed a dark colored impurity.

Anal.[a] Calcd. for $C_{18}H_{23}O_3N$: C, 71.7; H, 7.7; N, 4.6. Found: C, 71.7; H, 7.9; N, 4.7.

Summary

Steps in the attempted synthesis of 1,3,4,9,10,-10a-hexahydro-9,4a(2)-iminoethanophenanthrene are described.

(14) Compare J. von Braun, W. Haensel and F. Zobel, *Ann.*, **462**, 283 (1928); J. von Braun and K. Schwarz, *ibid.*, **481**, 56 (1930) V. Prelog, *ibid.*, **545**, 229 (1940).

(15) A. Pictet and A. Gams, *Ber.*, **42**, 2943 (1909); L. Claisen *ibid.*, **20**, 655 (1887).

Columbus 10, Ohio Received December 16, 1946

[Contribution from the Department of Chemistry and the Purdue Research Foundation, Purdue University]

Fluorinated Derivatives of Propane[1]

By E. T. McBee, H. B. Hass, R. M. Thomas,[2] W. G. Toland, Jr.,[3] and A. Truchan

This work is an extension of the research undertaken for the purpose of synthesizing fluorine-containing compounds for pharmacological tests. The synthesis of certain fluoro derivatives of propane has been described in a previous paper.[4] The investigation has now been extended to include additional derivatives of propane.

The fluorination of $CCl_3CH_2CH_3$ with antimony fluoride gives a 5–10% yield of $CF_3CH_2CH_3$.[5] Three new syntheses for the preparation of 1,1,1-trifluoropropane have been developed, namely, fluorination of $CCl_3CH_2CH_3$, $CCl_2{=}CHCH_3$ and 1,1-dichloro-cyclopropane with hydrogen fluoride. These reactions also yielded $CClF_2CH_2CH_3$ and $CCl_2FCH_2CH_3$. This same fluorination procedure

(1) The major portion of this paper is taken from the Ph. D. Thesis submitted to the faculty of Purdue University by R. M. Thomas in 1942.

(2) Present address: Firestone Tire and Rubber Co., Akron, Ohio.

(3) Present address: California Research Corporation, Richmond, California.

(4) E. T. McBee, A. L. Henne, H. B. Hass and N. Elmore, This Journal, **62**, 3340 (1940).

(5) A. L. Henne and A. M. Whaley, *ibid.*, **64**, 1157–1159 (1942).

was used to prepare bromofluoropropanes. Fluorination of $CH_2BrCBr_2CH_2Br$ yielded $CH_2BrCF_2CH_2Br$ and fluorination of $CBrCl_2CHBrCH_3$ gave $CF_3CHBrCH_3$ as the principal product with a small amount of $CClF_2CHBrCH_3$. Treatment of $CHBrClCHBrCH_3$ in the same manner produced three new compounds, $CHClFCHBrCH_3$, $CHF_2CHBrCH_3$, and $CHClFCHFCH_3$, which were identified by boiling point analogies and halogen analyses.

Thermal and photochemical chlorination of the above chlorofluoropropanes yielded new chlorinated derivatives of interest as anesthetics. One dichlorodifluoropropane obtained by chlorination of $CClF_2CH_2CH_3$ was identified as $CClF_2CHClCH_3$ by agreement of its physical properties with those of the $CClF_2CHClCH_3$ obtained from reaction between $CCl_3CHClCH_3$, mercury(II) oxide, and hydrogen fluoride. The other dichlorodifluoropropane was assigned the formula $CClF_2CH_2CH_2Cl$, since only two isomeric dichlorodifluoropropanes are possible from the chlorination of $CClF_2CH_2CH_3$ and since the boiling point was in agreement with the value predicted from known compounds.

Three isomeric trichlorodifluoropropanes are possible from chlorination of $CClF_2CH_2CH_3$, namely, $CClF_2CCl_2CH_3$, $CClF_2CHClCH_2Cl$, and $CClF_2CH_2CHCl_2$. Only the last was isolated from the chlorination of $CClF_2CH_2CH_3$, but the others may have been present in traces. Identification of $CClF_2CH_2CHCl_2$ was established by further chlorination to $CClF_2CH_2CCl_3$ and conversion of the latter compound to $CF_3CH_2CF_3$,[6] a known substance.

Two trichlorodifluoropropanes were formed by the vapor phase photochemical chlorination of $CClF_2CHClCH_3$ at 84–88°. One of these compounds boiled at 114.3° and the other at 90.2°. The compound boiling at 114.3° was found to be identical with $CClF_2CHClCH_2Cl$ prepared by addition of chlorine to $CClF_2CH{=}CH_2$ resulting from dehydrochlorination of $CClF_2CH_2CH_2Cl$. The other trichlorodifluoro compound was assigned the formula $CClF_2CCl_2CH_3$, since this is the only other theoretically possible isomer and since there is close agreement in the melting points of $CClF_2CCl_2CH_3$ and $CClF_2CCl_3$. The boiling point is also in agreement with the predicted value.

Physical constants of all new compounds are summarized in Table I. Most compounds reported have been found to produce anesthesia.[7,8]

Experimental

Fluorinations

Equipment and Technique.—Two autoclaves were used in this work; (1) a Monel autoclave of 1.5-liter capacity which was cold tested at 750 atm. (11,000 lb./sq. in.) by hydrostatic pressure, and (2) a nickel-lined autoclave of 750 ml. capacity which was tested at 340 atm. (5000 lb./sq. in.). These autoclaves, equipped with removable heads, were mounted within a shelter of 1/2-inch iron plate. Only valve handles, gages, and exhaust lines were exposed in the operation.

When hydrogen fluoride alone was the fluorinating agent, starting material was poured into the autoclave and the head fastened in place. Hydrogen fluoride was introduced into the autoclave from a 600-ml. iron container, fitted with a brass needle valve and connected with the fluorination equipment, the transfer being facilitated by heating the cylinder. After addition of hydrogen fluoride, the autoclave was heated; when reaction was complete, gaseous products were discharged into 6 *N* sodium hydroxide equivalent in quantity to the hydrogen fluoride charged. Organic material which did not condense in the scrubber passed through a drying tower into a receiver at Dry-Ice temperature.

When mercury(II) fluoride was used as fluorinating agent, it was prepared *in situ* by reaction of hydrogen fluoride with red mercury(II) oxide.[9] Due to the highly exothermic nature of the reaction, the autoclave was first cooled to −70° with a Dry-Ice and trichloroethylene bath, material to be fluorinated then added. Hydrogen fluoride was added directly from a small cylinder. Mercury (II) oxide was then added portionwise with stirring. After addition of reagents was complete, the autoclave was assembled and heating begun. Reaction products were discharged as before.

Residues in the alkali wash bottle were steam-distilled; all products were combined, dried, and rectified in a suitable column, a low-temperature column being used for separation of compounds boiling below room temperature and a Lecky–Ewell column (24 inches long × 1/2-inch diameter) for separation of higher-boiling liquids.

Fluorination of $CCl_3CH_2CH_3$.—Three moles of $CCl_3CH_2CH_3$, prepared by the method of Levine and Cass,[10] and 16 moles of anhydrous hydrogen fluoride were heated in the Monel autoclave at 100–119° for fourteen hours. Maximum pressure of about 82 atm. (1200 lb./sq. in.) was observed. Rectification of the reaction product gave 0.38 mole of $CCl_2FCH_2CH_3$, 2.0 moles of $CClF_2CH_2CH_3$, and 0.34 mole of $CF_3CH_2CH_3$. Yields were, respectively, 12.7, 67.5 and 11.3%.

Fluorination of $CCl_2{=}CHCH_3$.—The Monel autoclave was charged with 2 moles of $CCl_2{=}CHCH_3$ and 15 moles of hydrogen fluoride. After charging, the autoclave and contents were heated to 90–100° for seventy-two hours. The product was rectified in a low-temperature Podbielniak column and found to contain 1.77 moles of $CF_3CH_2CH_3$ and 0.04 mole of $CClF_2CH_2CH_3$. Yields were 88.5 and 2.2%, respectively. There was no evidence of $CCl_2FCH_2CH_3$ in any reaction products.

Fluorination of 1,1-Dichlorocyclopropane.—A mixture of 1.5 moles of 1,1-dichlorocyclopropane and 14.7 moles of hydrogen fluoride was heated in the Monel autoclave at 130° for twenty-five hours. Maximum pressure was about 56 atm. (820 lb./sq. in.). 1,1,1-Trifluoropropane and $CClF_2CH_2CH_3$ were isolated from the reaction product in yields of 47 and 25%, respectively.

Fluorination of $CCl_3CHClCH_3$.—The Monel autoclave was charged with 1.5 moles of $CCl_3CHClCH_3$ prepared by the addition of chlorine to $CH_3CH{=}CCl_2$, 13.7 moles of anhydrous hydrogen fluoride and 2.1 moles of mercury(II) oxide. The reaction mixture was heated at 98–100° for fourteen hours; products were discharged and collected in the usual manner. Rectification of the product yielded 0.48 mole of $CF_3CHClCH_3$ and 0.12 mole of $CCl_2FCHClCH_3$. The yield of fluorinated product was 72%. The dichlorodifluoropropane and the monochlorotrifluoropropane obtained in this reaction are identical with $CClF_2CHClCH_3$ and $CF_3CHClCH_3$ obtained by the chlorination of $CClF_2CH_2CH_3$ and $CF_3CH_2CH_3$, respectively.

Fluorination of $CF_3CCl_2CH_3$.—The nickel-lined autoclave was charged with 0.36 mole of $CF_3CCl_2CH_3$, 4.5

(6) A. L. Henne and P. T. Waalkes, THIS JOURNAL, **68**, 496 (1946).
(7) B. H. Robbins, *J. Pharmacol.*, **86**, 197–204 (1946).
(8) E. T. McBee, unpublished paper.
(9) A. L. Henne, THIS JOURNAL, **60**, 1569–1571 (1938).
(10) A. A. Levine and O. W. Cass, U. S. Patent 2,179,218 (1939).

Table I

New Fluorinated Derivatives of Propane

Cpd.	B. p., °C.	d^{25}_4	$n^{25}D$	Per cent. fluorine Calcd.	Per cent. fluorine Found	Per cent. chlorine Calcd.	Per cent. chlorine Found	Per cent. bromine Calcd.	Per cent. bromine Found
$CCl_2FCHClCH_3$	113.5	1.381	1.4435	..	..	..	..	..	..
$CClF_2CHClCH_3$	69.3	1.304	1.3708	25.5	25.7	47.6	47.7	..	..
$CClF_2CH_2CH_2Cl$	80.8	1.339	1.3775	25.5	25.7	47.6	47.7	..	..
$CClF_2CH_2CHCl_2$	107.8	1.465	1.4079	20.7	20.8	58.0	58.1	..	..
$CClF_2CCl_2CH_3$[a]	90.2	...	....	20.7	20.8	58.0	58.1	..	..
$CClF_2CHClCH_2Cl$	114.3	1.499	1.4116	20.7	20.7	58.0	57.8	..	..
$CClF_2CH_2CCl_3$	132	1.576	1.4290	17.4	18.6	65.1	66.0	..	..
$CHF_2CHClCH_3$	52	1.183	1.3495	33.1	33.9	31.0	30.5	..	..
$CHClFCHClCH_3$	93	1.251	1.4055	14.5	14.3	54.1	55.1	..	..
$CHClFCHFCH_3$	52.9	1.191	1.3487	33.2	34.4	31.0	30.5	..	..
$CHClFCHBrCH_3$	112.5	1.626	1.4460	10.8	11.2	20.2	19.9	43.6	44.8
$CHF_2CHBrCH_3$	72.6	1.601	1.3890	23.9	23.3	..	..	50.3	50.8
$CH_2BrCF_2CH_2Br$	136.0	2.132	1.4586	16.0	16.5	..	..	67.3	67.4
$CF_3CHBrCH_2Br$	115.8	2.121	1.4281	22.2	21.8	..	..	62.3	62.5
$CClF_2CHBrCH_3$	90	1.662	1.4045	19.6	19.6	18.3	18.3	41.2	41.2

[a] M. p. 37–38°.

moles of hydrogen fluoride, and 0.37 mole of mercury (II) oxide, sealed and heated to 110–120° for forty hours. Products were discharged while the autoclave was still hot. Rectification in a low-temperature column gave a yield of 32% $CF_3CClFCH_3$.

Fluorination of $CHCl_2CHClCH_3$.—Two moles of $CHCl_2CHClCH_3$,[11] 10 moles of hydrogen fluoride, and 2 moles of mercury(II) oxide were heated to 100° for twenty-four hours in the 750-ml. nickel-lined autoclave. Reaction products were discharged, dried and rectified to give $CHF_2CHClCH_3$ and $CHClFCHClCH_3$ in yields of 13.6 and 6.2%, respectively. A small quantity of CHF_2CHFCH_3 was also obtained.

Preparation of $CF_3CHBrCH_2Br$.—One-fourth mole of $CF_3CH_2CH_2Cl$ was dehydrochlorinated by treatment with 0.25 mole of alcoholic potassium hydroxide. The evolved $CF_3CH{=}CH_2$ was led directly into liquid bromine at 0°. Excess bromine was destroyed by washing with aqueous sodium hydroxide. The water-insoluble organic layer was washed, dried and rectified to give a 25% yield of $CF_3CHBrCH_2Br$.

Synthesis of $CClF_2CHBrCH_3$.—A 750-ml. nickel-lined autoclave was charged with 0.83 mole of $CBrCl_2CHBrCH_3$, 7.5 moles of hydrogen fluoride, and 1.5 moles of mercury (II) oxide. The autoclave was sealed and heated at 88° for seventy-two hours. Rectification of products gave a 9.6% yield of $CClF_2CHBrCH_3$ and a small amount of $CF_3CHBrCH_3$.

Preparation of $CH_2BrCF_2CH_2Br$.—The following series of reactions was used: $CH_2BrCHBrCH_2Br \rightarrow CH_2{=}CBrCH_2Br$[12] $\rightarrow CH_2BrCBr_2CH_2Br$[13] $\rightarrow CH_2BrCF_2CH_2Br$. Three moles of $CH_2BrCBr_2CH_2Br$, 3 moles of bromine and 4 moles of antimony(III) fluoride were placed in a five-liter, three-necked flask fitted with stirrer and condenser. The reaction mixture was heated at 150° and $CH_2BrCF_2CH_2Br$ distilled therefrom as rapidly as formed. The yield and conversion were 45.3%.

Fluorination of $CHBrClCHBrCH_3$.—Starting material was prepared by dehydrochlorination of $CH_2ClCHClCH_3$ according to the method of Reboul,[14] followed by addition of bromine to the resulting olefin.

A mixture of 2.1 moles of $CHBrClCHBrCH_3$, 7 moles of hydrogen fluoride and 2.1 moles of mercury(II) oxide was placed in the autoclave and heated at 44° for sixteen hours. The product consisted of $CHClFCHBrCH_3$ (12.9% yield), $CHF_2CHBrCH_3$ (10.0% yield) and $CHClFCHFCH_3$ (5.5% yield).

Chlorinations

Apparatus and Technique.—Thermal chlorination was conducted in a glass reactor immersed in an electrically-heated salt-bath, temperature being controlled by a variable resistance. The reactor was in the form of a helix 15 cm. in diameter made from 6.1 m. of 8-mm. Pyrex tubing. Reactants were introduced through a Y-tube at measured rates. Reaction products passed into a Davis rectifying column, maintained at a temperature sufficient to condense any chlorinated materials, and collected in a receiver at the bottom thereof. Unreacted starting material passed into a scrubbing tower, through a drying tower, and into a receiver cooled by a trichloroethylene-Dry Ice mixture.

Chlorination of $CF_3CH_2CH_3$.—The $CF_3CH_2CH_3$ (3.72 moles) was chlorinated thermally at 374–390° in the presence of light from a 200-watt bulb. Chlorine and $CF_3CH_2CH_3$ were passed into the reactor at 10.5 and 13.2 liters per hour, respectively. The contact time was 2.7 seconds at 380°. Rectification of the product gave 0.17 mole of $CF_3CHClCH_3$, 0.60 mole of $CF_3CH_2CH_2Cl$, and 0.15 mole of $CF_3CH_2CHCl_2$. Some unreacted $CF_3CH_2CH_3$ (2.34 moles) also was collected. The results are in general agreement with those reported previously.[15] However, in this work $CF_3CHClCH_3$ was obtained in larger amounts.

Chlorination of $CClF_2CH_2CH_3$.—The $CClF_2CH_2CH_3$ (4.49 moles) was chlorinated at 70–80° in a modified Muskat[16] chlorination apparatus with a three-liter chlorination bulb. Light was furnished by three 200-watt bulbs placed one inch from the reactor. The rate of chlorine flow was regulated to maintain the ratio of $CClF_2CH_2CH_3$ to chlorine greater than 3:1. Rectification of the product gave 1.18 moles of $CClF_2CHClCH_3$, 2.03 moles of $CClF_2CH_2CH_2Cl$, and 0.32 mole of $CClF_2CH_2CHCl_2$. The total yield was 91.1%.

Chlorination of $CClF_2CH_2CH_3$ at −50 to −70° was also conducted in a one-liter, three-necked flask which was partially immersed in a Dry Ice and trichloroethylene mixture. Light was focused through the top of the flask by a projector. Chlorine was added intermittently at the disappearance of yellow color. Rectification of the product gave a 13% yield of $CClF_2CHClCH_3$ and a 68% yield of $CClF_2CH_2CH_2Cl$.

Chlorination of $CF_3CHClCH_3$.—The chlorination of $CF_3CHClCH_3$ (0.65 mole) was conducted in the modified

(11) A. A. Levine and O. W. Cass, U. S. Patent 2,119,484 (May 31, 1938).

(12) "Organic Syntheses," Coll. Vol. I, 209–211 (1941).

(13) C. D. Hurd, R. N. Meinert and L. U. Spence, This Journal, **52**, 1138–1146 (1930).

(14) H. Reboul, *Ann. chim. phys.*, [8] **14**, 464 (1907).

(15) A. L. Henne and A. M. Whaley, This Journal, **64**, 1157–1159 (1942).

(16) I. E. Muskat and H. E. Northrup, *ibid.*, **52**, 4043–4055 (1930).

Muskat apparatus at a reaction temperature of 84–88°. Rates of flow were adjusted so that the ratio of CF_3CHCl-CH_3 to chlorine was always greater than 3:1. The product contained 72% $CF_3CCl_2CH_3$ and 28% CF_3-$CHClCH_2Cl$.

Acknowledgment.—The authors wish to acknowledge the financial assistance of Mallinckrodt Chemical works which made this research possible.

Summary

1. The preparation of $CF_3CH_2CH_3$ and $CClF_2$-CH_2CH_3 has been accomplished in excellent yields.

2. Both photochemical and thermal chlorination of $CClF_2CH_2CH_3$ have yielded several new chlorofluoropropanes.

3. Several new fluorine-containing propanes have been prepared by the fluorination of certain chloro- and chlorofluoropropenes with mercury(II) oxide and hydrogen fluoride. Some bromofluoropropanes also were synthesized by fluorination of the corresponding bromides.

LAFAYETTE, INDIANA RECEIVED[17] JANUARY 2, 1947

(17) Original manuscript received February 25, 1946.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

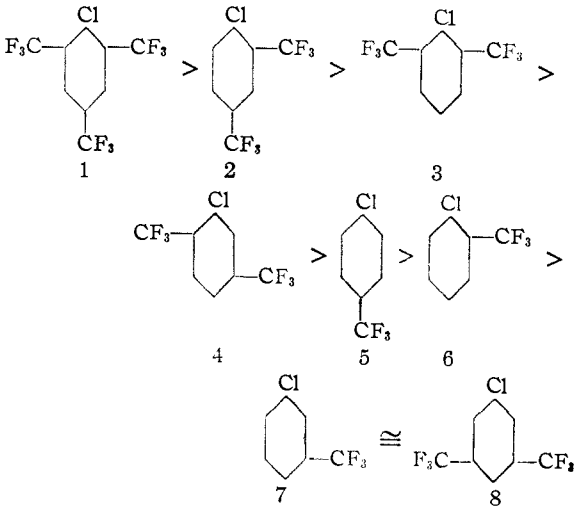
The Preparation of Certain Ethers of Trifluoromethyl-substituted Phenols[1,2]

BY EARL T. MCBEE, ROBERT O. BOLT,[3] PETER J. GRAHAM AND ROBERT F. TEBBE[4]

Certain alkoxy-(trifluoromethyl)-benzenes and alkoxy- and aryloxy-bis-(trifluoromethyl)-benzenes have been synthesized. The preparation of these compounds involves the action of a sodium or potassium alkoxide on a trifluoromethyl-substituted chloro- or bromobenzene. Such ethers are of interest as possible heat-transfer fluids since they exhibit a tendency toward non-flammability, a wide liquid range, and an enhanced stability to heat and the action of metals. Further, it would seem desirable for a heat transfer agent to possess an electron donor center, such as an oxygen atom, in the molecular structure. Dative bond formation between this electron donor and the metallic atoms of a heat transfer wall should effect more efficient transfer of heat. Other interesting possibilities for these ethers might include use as dielectric media, and as materials to improve the lubricating properties of oils.

The new compounds prepared, together with their physical properties, are listed in Table I. Of the compounds synthesized, only 3-methoxy-(trifluoromethyl)-benzene has been mentioned previously in the literature.[5] However, the method of preparation of this compound was not disclosed.

During the present study it was observed that, in the preparation of methyl ethers from trifluoromethyl-substituted chlorobenzenes, the temperature required for a particular synthesis was dependent upon the relative reactivity of the chlorine atom in the benzene derivative. Analogous to the behavior of the nitro-substituted chlorobenzenes, this reactivity appears to be a function of the position of the chlorine atom relative to the meta-directing group or groups. For the compounds investigated the order of reactivity was found to be



Experimental

Preparation of Starting Materials

2- and 4-Chloro-(trifluoromethyl)-benzenes.—These compounds were prepared by the fluorination of commercially available 2- and 4-chloro-(trichloromethyl)-benzenes. The fluorination was carried out at room temperature in iron equipment using anhydrous hydrogen fluoride in the presence of a small quantity of antimony(V) chloride as the fluorinating agent. 2-Chloro-(trifluoromethyl)-benzene (b. p. 148–150° (745)) was obtained in 85% yield; 4-chloro-(trifluoromethyl)-benzene (b. p. 135–136° (745)) was obtained in 91% yield.

3-Chloro-(trifluoromethyl)-benzene.—This compound (b. p. 135–136° (745)) was prepared according to the method of Holt and Daudt[6] by the chlorination, in glass

(1) Presented as a part of the Meeting-in-Miniature, Purdue University, November 17, 1945. Abstracted in part from a thesis submitted (October, 1945) by R. F. Tebbe and a thesis to be submitted (1947) by P. J. Graham to the faculty of Purdue University in partial fulfilment of the requirements for the degree of doctor of philosophy.

(2) Acknowledgment is gratefully made to the Ethyl Corporation for sponsoring the research fellowship on which this work was accomplished.

(3) Present address: California Research Corporation, a subsidiary of the Standard Oil Company for California, Richmond, California.

(4) Present address: University of Maine, Orono, Maine.

(5) Zitscher and Kehlen (to General Aniline), U. S. Patent 2,141,893, Dec. 27, 1938.

(6) Holt and Daudt (to du Pont), U. S. Patent 2,174,513, Oct. 3, 1939.