[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Perfluoroalkyl Aluminum Complexes[1a]

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A detailed study of the unconventional behavior of perfluoro-*n*-propyl iodide with lithium aluminum hydride has been made. The perfluoropropyl iodide acts as an active hydrogen compound and perfluoropropyl aluminum complexes are formed. Trifluoromethyl iodide also behaves as an active hydrogen compound. On decomposition with water, the formation of the complete reduction product methane (in addition to trifluoromethane) was an unexpected result.

The reaction of alkyl halides with lithium aluminum hydride,[2,3] is known to proceed essentially by the equation

$$4\ RX + LiAlH_4 \longrightarrow 4\ RH + LiAlX_4$$

where R is a hydrocarbon radical.

We have found that the fluorocarbon halide, perfluoro-*n*-propyl iodide reacts with lithium aluminum hydride initially to liberate hydrogen.[4] A detailed study of this reaction has been made and the stoichiometry has been established as

$$C_3F_7I + LiAlH_4 \longrightarrow LiAl(C_3F_7)H_2I + H_2 \quad (1)$$

$$C_3F_7I + LiAl(C_3F_7)H_2I \longrightarrow LiAl(C_3F_7)HI_2 + C_3F_7H \quad (2)$$

$$C_3F_7I + LiAl(C_3F_7)HI_2 \longrightarrow LiAl(C_3F_7)_2I_2 + HI \quad (3)$$

or as the sum of the above three essentially consecutive reactions

$$3C_3F_7I + LiAlH_4 \longrightarrow LiAl(C_3F_7)_2I_2 + C_3F_7H + HI + H_2 \quad (4)$$

The complexes $LiAl(C_3F_7)H_2I$, $LiAl(C_3F_7)HI_2$ and $LiAl(C_3F_7)_2I_2$ may be considered as average composites of $LiAl(C_3F_7)_2H_2 + LiAlH_2I_2$, $LiAl(C_3F_7)_2H_2 + LiAlI_4$ and $LiAl(C_3F_7)_4 + LiAlI_4$, respectively.

When perfluoropropyl iodide is added to an ethereal solution of lithium aluminum hydride under dilute conditions at temperatures as low as −78°, a vigorous evolution of hydrogen gas ensues. Hydrogen liberation ceases abruptly as soon as one mole of the iodide has been added to one mole of the hydride. One mole of hydrogen is formed in the process. When the complex is then decomposed with water at 0° a reaction occurs which is represented by the equation

$$LiAl(C_3F_7)H_2I + 3H_2O \longrightarrow C_3F_7H + LiI + Al(OH)_3 + 2H_2 \quad (5)$$

Stoichiometric quantities of hydrogen and lithium iodide were collected, while the conversion to C_3F_7H was 85%. The slight deficiency in the latter is not attributed entirely to handling losses, but may be due to some interaction of complex with ether during the exothermal reaction with water.

The stability of the complex in ether was investigated by allowing the solution to reflux (35–40°) for a few hours. After the addition of water only 41 and 54% of the theoretical hydrogen and C_3F_7H, respectively, were obtained. There was isolated a dense liquid, b.p. 70–80°, $n^{20}D$ 1.3722, containing much fluorine and iodine. Thus some interaction of the first complex with ether to yield an "organic" product other than C_3F_7H must have taken place.

An attempt to isolate the complex in (1) by evaporation of the ether resulted in a vigorous spontaneous decomposition. Aluminum, lithium iodide, hydrogen and probably C_3F_7H were formed. The residue contained no fluorinated material. The complex $LiAl(C_3F_7)H_2I$ takes on the character of $Al(C_3F_7)H_2 + LiI$ rather than $LiC_3F_7 + AlH_2I$. Support is furnished by the following facts: (a) LiI can be separated from the complex in benzene solution; (b) LiC_3F_7 is known to be decomposed into perfluoropropene under conditions similar to those used in many of our experiments[5]; actually, no traces of perfluoropropene were detected at any time; (c) LiC_3F_7 does not react with excess C_3F_7I; thus equation (2) could not take place.

It was of interest to find that after one mole of perfluoropropyl iodide had been added to exactly one mole of lithium aluminum hydride, the further addition of iodide caused the liberation of C_3F_7H, but no additional hydrogen. It was demonstrated that an additional mole of C_3F_7I reacted rapidly to yield 100% of C_3F_7H in accordance with equation 2. Finally, it was shown that a third mole of C_3F_7I reacted more slowly with the complex formed by equation 2 in accordance with equation 3. Only after the addition of three moles of C_3F_7I to the original one mole of lithium aluminum hydride, did the resulting solution fail to liberate hydrogen upon addition of water.

Although, as stated previously, stoichiometric amounts of hydrogen for equation 1 were produced under dilute conditions, it was found that when undiluted perfluoropropyl iodide was added to one molar lithium aluminum hydride solution (in *ca.* equimolar quantities) only 80–90% of the theoretical amount of hydrogen was liberated. This may be accounted for by the fact that as the reaction proceeds subsequent iodide additions (under the concentrated environment) commence to react *to a small extent* according to equation 2 producing C_3F_7H directly. As should be expected, however, reactions carried out with an appreciable excess of

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[1] (a) The work herein reported was carried out on Project NR 055-354 between the Office of Naval Research and the Research Institute of Temple University. Reproduction in whole or in part is permitted for any purpose of the United States Government. Part of a thesis to be submitted to the Temple University Graduate Council in partial fulfillment of the requirements for the Ph.D. degree. (b) Pennsylvania Salt Mfg. Co., Whitemarsh Research Laboratories, Chestnut Hill, P. O. Box 4388, Philadelphia 18, Penna.

[2] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3738 (1948).

[3] J. E. Johnson, R. H. Blizzard and H. W. Carhart, *ibid.*, **70**, 3664 (1948).

[4] J. C. Tatlow and co-workers, *J. Chem. Soc.*, 1251, 4695 (1952); 1177, 4426 (1954), reported that cycloperfluoroalkyl chlorides, bromides and dichlorides were reduced with lithium aluminum hydride to the corresponding hydrides. No mention was made as to whether hydrogen gas or an organometallic intermediate was formed.

[5] O. R. Pierce, E. T. McBee and G. F. Judd, THIS JOURNAL, **76**, 474 (1954).

TABLE I

REACTION OF PERFLUOROPROPYL IODIDE WITH LITHIUM ALUMINUM HYDRIDE[a,b]

Undiluted				Dilution[e] or excess iodide				Dilution and excess iodide			
C_3F_7I	LAH	H_2[c]	H_2,[d] %	C_3F_7I	LAH	H_2	H_2, %	C_3F_7I	LAH	H_2	H_2, %
0.0311	0.0277	0.0248	89.5	0.0566	0.0558	0.0554	99.3	0.0774	0.0666	0.0678	101.8
.0283	.0277	.0239	86.3	.0686	.0672	.0668	99.4	.117	.0392	.0378	96.4
.0566	.0558	.0460	82.4	.0476	.0111	.0110	99.1	.225	.112	.111	99.1
.0566	.0555	.0502	90.5	.117	.0392	.0378	96.4	.495	.169	.168	99.4
.0566	.0555	.0475	85.6	.336	.111	.107	96.4	.693	.226	.226	100.0

[a] Reactions were carried out at −78° with approximately 1 *M* $LiAlH_4$ solution. [b] All quantities are expressed in moles. [c] Solvent correction applied to the hydrogen liberated. [d] Initial hydrogen is based on equation 1. [e] The volume of anhydrous ether employed to dilute the iodide was 2/3 to 5 times the volume of $LiAlH_4$ solution used.

C_3F_7I gave stoichiometric amounts of hydrogen, since reaction 1 could easily be completed in spite of the small amount of concurrent side reaction 2 (see Table I).

The reaction of CF_3I with lithium aluminum hydride has been carried out in a manner similar to the much more thoroughly studied C_3F_7I reaction. Evidence is presented which supports equations 6 and 7.

$$CF_3I + LiAlH_4 \longrightarrow LiAl(CF_3)H_2I + H_2 \qquad (6)$$

$$2LiAl(CF_3)H_2I + 3H_2O \longrightarrow$$
$$CH_4 + CHF_3 + H_2 + Al(OH)_3 + AlF_3 + 2LiI \qquad (7)$$

The formation of methane, which represents complete reduction of all the fluorine atoms in addition to the iodine atom in CF_3I, is of particular interest. The CF_3– group is normally a very stable entity and it is reported[6] that the CF_3– group in iodotrifluoromethylarsine is not affected by lithium aluminum hydride.

Currently, the possible usefulness of perfluoroalkyl aluminum complexes in the synthesis of fluorocarbon derivatives is under investigation.

Experimental

Materials.—Perfluoropropyl iodide was prepared from silver perfluorobutyrate[7] and carefully fractionated samples were used in the reactions. Trifluoromethyl iodide was similarly prepared. Mallinckrodt anhydrous ethyl ether was employed in the dilutions. The lithium aluminum hydride ethereal solution was prepared by the standard procedure, filtered through a sintered glass tube, and standardized by the amount of hydrogen evolved upon the addition of water.

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2 \qquad (8)$$

The solution was stored in a pre-dried vessel under dry pre-purified nitrogen and periodically restandardized. All the manipulations and procedures herein described were performed in scrupulously dried systems and in atmospheres of dried pre-purified nitrogen.

Reaction of Perfluoropropyl Iodide with Lithium Aluminum Hydride in a 1:1 Molar Ratio.—The following is representative of the experimental procedure employed in this work. Fifty milliliters (0.0555 mole) of standardized lithium aluminum hydride ethereal solution was pipetted under nitrogen into a rigorously dried flask repeatedly flushed with nitrogen. Perfluoropropyl iodide (16.75 g., 0.0566 mole) was placed in a pressure-equalized dropping funnel attached to the reaction flask containing a high speed mechanical stirrer and a water condenser. To this system was connected a manometer, sulfuric acid scrubber, and two traps (the latter one containing glass beads) cooled in a Dry Ice–acetone mixture. The iodide was added drop by drop to the lithium aluminum hydride solution at −78°. The addition of iodide produced 0.0475 mole (85.6%, cor.) of hydrogen collected at 21° by the displacement of water. Table I summarizes the results of typical runs under the above conditions and under varying conditions of dilution and using excess perfluoropropyl iodide. Hydrogen as high as 90% of theory required by equation 1 can be obtained in the undiluted reactions by slow addition of small amounts of C_3F_7I with efficient stirring.

The reaction solution was brought to 0° upon the cessation of hydrogen evolution and slowly decomposed with dilute sulfuric acid to give 0.113 mole (95.8%) of hydrogen. Further evidence confirming the stoichiometry of equation 1 is summarized in Table II.

TABLE II

AQUEOUS DECOMPOSITION OF $LiAl(C_3F_7)H_2I$[a]

			Theory final H_2[d]				
C_3F_7I[b]	LAH	Initial H_2[c]	Excess $LiAlH_4$	Complexes	Total	Final H_2	Final H_2, %
0.0566	0.0558	0.0460	0.0392	0.0814	0.1206	0.124	102.8
.0566	.0555	.0502	.0212	.0940	.1152	.112	97.5
.0566	0558	.0554	.0032	.1096	.1128	.114	101.1
.0566	.0555	.0475	.0320	.0859	.1179	.113	95.8

[a] Temperature of decomposition was 0°. [b] All quantities in moles. [c] Solvent correction applied to the hydrogen collected. [d] Sample calculation: 0.0558 − 0.0460 = 0.0098 mole excess $LiAlH_4$ which gives 0.0098 × 4 or 0.0392 mole of hydrogen by equation 8. Iodide reacting according to equation (2) is 0.0566 − 0.0460 or 0.0106 mole. Upon addition of water, theory for the remaining complex of equation 1 (0.0460 − 0.0106 or 0.0354 mole) is 0.0354 × 2 or 0.0708 mole of hydrogen by equation 5. For the complex formed by equation 2 (0.0106 mole) theory is 0.0106 mole of hydrogen. Total theory of hydrogen from both complexes is 0.0708 + 0.0106 or 0.0814 mole. It should be noted that for each hydrogen atom in a complex, a hydrogen molecule is formed in the decomposition with water.

Upon refluxing the decomposed solution for several hours there was isolated, after a sulfuric acid scrubbing, 8.15 g. (0.048 mole, 85%) of C_3F_7H; mol. wt. calcd. 170, found 170 (gas density balance); b.p. (lit.[8]) −15°, found −16°. No traces of perfluoropropene were detected. A yield of 98% silver iodide was obtained based on the total amount of perfluoropropyl iodide added.

In another experiment when C_3F_7I (0.0450 mole) was treated with an excess of lithium aluminum hydride (0.0669 mole) there was obtained 0.0418 mole (93.0%) of hydrogen in accordance with equation 1. Addition of water liberated the theoretical amount of hydrogen (0.181 mole) in accordance with equations 1 and 5.

Decomposition Studies on $LiAl(C_3F_7)H_2I$.—The addition of 8.8 g. (0.0311 mole) of perfluoropropyl iodide to 25 ml. (0.0277 mole) of lithium aluminum hydride solution under conditions described previously liberated 0.0248 mole (89.5%) of hydrogen. Traces of C_3F_7H were collected in the Dry Ice cooled trap. As usual, in the reaction solution at −78°, a white solid was evident which redissolved on heating to 0°. After remaining at room temperature and at 40° for two hours the solution became a colorless ice-like slush. Essentially all of the ether was tied up since refluxing stopped. The amount of C_3F_7H collected was only 0.0069 mole (0.0063 mole is theory for side reaction 2) indicating that the decomposition of the complex into C_3F_7H under the above conditions is insignificant.

To the reaction at 0° was added wet ether followed by dilute sulfuric acid with the evolution of 0.0228 mole

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[6] H. J. Emeleus, R. N. Haszeldine and E. G. Walaschewski, *J. Chem. Soc.*, 1552 (1953).

[7] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951).

[8] R. N. Haszeldine, *J. Chem. Soc.*, 1748 (1953).

(41.5%) of hydrogen and the formation of a white precipitate which was soluble in excess acid solution. The clear colorless mixture was refluxed and yielded 2.84 g. (0.0167 mole, 53.7%) of C_3F_7H. The presence of a small amount of hydrogen sulfide was apparent. Distillation of the dried ether layer produced a fraction, b.p. 70–80°, $n^{20}D$ 1.3722, containing fluorine and iodine. Qualitative tests for fluoride ion on the aqueous layer were negative.

In an attempt to isolate and further characterize the complex $LiAl(C_3F_7)H_2I$, about half of the ether was removed by distillation at atmospheric pressure when a violent decomposition occurred. Addition of water to the remaining solid produced no evolution of gas. Aluminum powder, lithium iodide, hydrogen and probably C_3F_7H were formed. An alternate method of isolation was attempted by evaporating most of the solvent *in vacuo* to a slush, adding benzene and removing by filtration through a sintered glass funnel the remaining undissolved solid. The filtered white solid was lithium iodide only. The benzene filtrate on standing for 0.5 hour under nitrogen decomposed spontaneously. An aliquot previously taken produced C_3F_7H on the addition of water.

Reaction of Perfluoropropyl Iodide with Lithium Aluminum Hydride in a 3:1 Molar Ratio.—To 35 ml. (0.0392 mole) of lithium aluminum hydride solution at −78° was slowly added 34.72 g. (0.1170 mole) of perfluoropropyl iodide in 150 ml. of anhydrous ether with the evolution of 0.0378 mole (96.4%) of hydrogen. The reaction solution was allowed to remain at −80° to −20° for two hours and at 0° for one hour and then the solution gently refluxed for three hours and flushed intermittently with nitrogen. The original clear colorless solution became red, a crystalline substance was deposited and the sulfuric acid trap in the system also became markedly red. The colorless material collected in the trap was passed through distilled water, redried and condensed to yield 6.6 g. (0.0388 mole) of C_3F_7H, 99% of theory in accordance with equation 2. Several additional runs also produced stoichiometric amounts of C_3F_7H according to equation 2 before the addition of water. The distilled water above was acidic, liberated CO_2 from a bicarbonate solution and gave a strong silver iodide precipitate. This conforms with the fact that a product of equation 3 is hydrogen iodide.

The reaction solution was then cooled to −10° and a 1% sulfuric acid solution added slowly under nitrogen. Hydrogen gas was evolved in the small amount corresponding to the slight deficiency (<3:1) of iodide used. The mixture was then refluxed for two hours and an additional 3.3 g. (0.020 mole) of C_3F_7H was obtained. The aqueous acid layer contained no fluoride ion. The ether layer was dried over magnesium sulfate, decolorized with silver powder and distilled to yield 1 g. of a fraction, b.p. 70–80°, $n^{21}D$ 1.3714, and 4 g. of a product b.p. 50–51° (20 mm.), $n^{23}D$ 1.4970. Both fractions liberated iodine on standing.

In a reaction of 0.0476 mole of perfluoropropyl iodide with 0.0111 mole of lithium aluminum hydride, the C_3F_7H produced by equation 2 was collected after decomposition with water and amounted to 0.022 mole (66.7%). C_3F_7I in excess of the 3:1 ratio was recovered. The C_3F_7H obtained above represents 100% from equation 2 and therefore 50% from equation 3 after the addition of water.

Reaction of Trifluoromethyl Iodide with Lithium Aluminum Hydride.—To 50 ml. (0.0550 mole) of lithium aluminum hydride solution at −78° was added 8.4 g. (0.0429 mole) of trifluoromethyl iodide in a system similar to the above, with liquid nitrogen used as the refrigerant. The hydrogen collected was 0.0393 mole (91.5% of theory for equation 6). The reaction solution contained a white solid which dissolved when the temperature was raised to 0°. The reaction mixture was allowed to stand at 0° for two hours. A trace of material (CHF_3) was present in the liquid nitrogen-cooled trap.

The solution was then decomposed with 5% sulfuric acid and 0.0460 mole of hydrogen was evolved. A white precipitate formed which dissolved in the excess acid solution. Upon refluxing the mixture there was obtained methane, mol. wt. calcd. 16, found 16 (gas density balance), and CF_3H, mol. wt. calcd. 70, found 70 ± 1 (gas density balance); b.p. (lit.[9]) −84°, found *ca.* −80°. There were some losses in handling these low boiling gases. However, the methane and CF_3H were obtained in approximately equimolar quantities which amounted to about 50% of theory for equation 7. Qualitative tests for fluoride ion on the decomposed solution were positive.

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[9] O. Ruff, O. Bretschneider, W. Luchsinger and G. Miltshitzky, *Ber.*, **69**, 299 (1936).

PHILADEPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

Factors Influencing the Resonance Contribution of an Expanded Valence Shell. A Comparison of the Electrical Effects of the Triphenylsilyl and Triphenylgermanyl Groups on an Aromatic Ring

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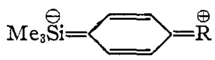
Hammett sigma values for the *meta* and *para* triphenylsilyl and triphenylgermanyl groups have been determined from a series of reaction rates. These values indicate that both groups function principally through a −I effect, and when conjugated to a strong electron supplying group *both* central atoms are capable of valence shell expansion to ten electrons. The contribution of this expanded valence structure is approximately the same in both the aforementioned groups, indicating that the atomic radius of the central element does not influence such structures appreciably. It is demonstrated further that the expanded valence structure is affected little by the nature of the R group attached to the central element, but that these substituents do play a role in determining the over-all electrical effect of the R_3M- group.

The electrical effects of the trimethylsilyl group on an aromatic nucleus and side chains attached to it have been reported.[1] These studies indicated that this group exerts its influence mainly as an electron-supplying group (+I effect). When it is substituted *para* to strongly electron-releasing groups such as hydroxyl, amino and dimethylamino, however, the trimethylsilyl group functions as an electron-withdrawing group. This latter effect has been interpreted as involving a resonance interaction between the electron-releasing group and the trimethylsilyl group in which the silicon atom has expanded its valence shell to accommodate ten electrons.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The above results prompted a study of the electrical effects of the triphenylsilyl group. The purpose of the study was threefold: (1) to determine

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[1] R. A. Benkeser and H. R. Krysiak, THIS JOURNAL, **75**, 2421 (1951), and references reported therein.