Anomalous Lithium Aluminium Hydride Reduction of Aromatic Trifluoromethyl Groups to Methyl Groups

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Summary Benzotrifluorides which are *ortho-* or *para*-substituted by an amino- or a hydroxy-function are easily reduced to the corresponding hydrocarbons by lithium aluminium hydride.

THE lithium aluminium hydride reduction of organic halides to hydrocarbons is well known.[1] The halogen may be chlorine, bromine, or iodine, the last being the most reactive. However, trifluoromethyl groups are unreactive towards lithium aluminium hydride. For example, the reduction of ethyl *p*-trifluoromethylbenzoate leads to *p*-trifluoromethylbenzyl alcohol[2] leaving the trifluoromethyl group intact.

We have observed that aromatic trifluoromethyl groups are reduced to a methyl group with lithium aluminium hydride if an activating *ortho* or *para* amino- or hydroxy-function is present. This is the first example, to our knowledge, of the reduction of a benzotrifluoride with lithium aluminium hydride.

The reductions were carried out by heating the benzotrifluoride with an excess of lithium aluminium hydride in ether solution under reflux. The course of the reaction was followed by g.l.c.; reaction times of 18 h were sufficient for complete reduction to be effected. The products were isolated by decomposing the excess of lithium aluminium hydride with 3N-NaOH, filtering off the inorganic salts, and concentrating the filtrates to yield the crude products, which were distilled if necessary. The reaction products were identified by their spectral properties (appearance of an aromatic methyl group in the n.m.r. spectrum) and/or by comparison with authentic samples. The starting materials and reaction products are shown in the Table. The yields of isolated products ranged from 80—100%.

Starting material		Product
$CF_3{\cdot}C_6H_4X$	$\longrightarrow$	$CH_3{\cdot}C_6H_4X$
X		X
o-$NHCO_2CH_2CH_3$		*o*-$NHCH_3$
o-NH_2		*o*-NH_2
o-OH		*o*-OH
p-NH_2		*p*-NH_2

The necessity of having an *ortho* or *para* activating group present was shown by attempting to reduce *m*-aminobenzotrifluoride and *m*-hydroxybenzotrifluoride. In both cases, only the starting material was isolated (>90%) after 18 h heating with lithium aluminium hydride in ether under reflux.

(*Received, March* 15*th*, 1971; *Com.* 247.)

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[1] N. G. Gaylord, 'Reduction with Complex Metal Hydrides,' Interscience, New York, 1956, pp. 889—924.

[2] H. B. Hass and M. L. Bender, *J. Amer. Chem. Soc.*, 1949, **71**, 1767.