prevent optimum interaction with the adjacent hydroxyl group. The same objections hold for the results with β-haloethanols (Table I).

Completely unambiguous data confirming the same order, I > Br > Cl > F, is provided by intermolecular studies (Table II). Data for analogous oxygen and nitrogen compounds have been included for comparison. Clearly, electronegativity does not play a dominant role. In addition, results for similar derivatives of the second and third row elements, sulfur, phosphorus and arsenic, have been added to the tables where available. It is particularly noteworthy that, as proton acceptors, they rival their first row congeners despite their larger covalent radii.

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CATALYTIC EFFECT OF METAL HALIDES AND OXIDES ON THE LITHIUM ALUMINUM HYDRIDE REDUCTION OF AZOBENZENES AND NITROBENZENES TO HYDRAZOBENZENES

Sir:

The interaction of metal halides and oxides with lithium aluminum hydride (LAH) is known.[1] A reduction method based on the use of mixed hydrides prepared from equimolar quantities of LAH and aluminum halides also was developed.[2] Different metal halides were used as additives in ether cleavage reactions with LAH.[3]

LAH alone can reduce azobenzenes to hydrazobenzenes only with considerable difficulty.[4] Large excess of the hydride, higher temperatures and prolonged reaction times (some days) are needed. Nitrobenzenes were known to be reduced by LAH only to the corresponding azobenzenes, a reaction which also is used for the qualitative analytical determination of nitro groups.[5]

It has now been observed that the addition of catalytic amounts of certain metal halides such as $MoCl_5$, $TiCl_4$, $TiCl_3$, $TiCl_2$, VCl_3, WCl_6, $CrCl_3$, $FeCl_3$, Cu_2Cl_2, $CoBr_2$, $SnCl_4$, CdI_2, $CbCl_5$, $BiCl_3$, $SbCl_5$ $PbCl_2$ has a very marked effect on the reduction of azobenzenes with LAH to hydrazobenzenes. In ethereal solution and at room temperature 0.1 mole of azobenzene was reduced quantitatively in the presence of less than 0.001 mole of the above mentioned metal halide catalysts to hydrazobenzene by LAH. The reductions are very fast and generally are completed in less than ten minutes. Some less active metal halide catalysts are $ZrCl_4$, $TaCl_5$ and $PtCl_2$. With them the completion of the reduction of azobenzene to hydrazobenzene takes thirty minutes at room temperature. Similar to azobenzene itself, substituted derivatives such as 4-fluoroazobenzene, 4,4′-difluoroazobenzene, 4,4′-dichloroazobenzene, 3-trifluoromethylazobenzene and 4-fluoro-3′-trifluoromethylazobenzene were reduced by the catalytic LAH reduction to the corresponding hydrazobenzenes with 90% yields or better.

It is possible to use instead of the metal halides other metal salts (such as nitrates, carbonates, sulfates, acetates) or metal oxides.

However, metal oxides as MoO_3, V_2O_5, WO_3, TiO_2, CrO_3, CuO and NiO are considerably less active catalysts than the corresponding metal halides and the completion of the reduction of 0.1 mole of azobenzene in ethereal solution at room temperature takes from 2–6 hr.

Nitrobenzenes are reduced by the catalytic LAH reduction in ether solution directly and with 90% yield or better to hydrazobenzenes. As the reduction of nitrobenzenes by LAH to the corresponding azobenzenes in itself is quite vigorous, it is advantageous to add the ethereal solution of the azobenzene first to the ethereal LAH solution and then the catalyst.

On addition of an ethereal solution or suspension of the catalytic halide to the ethereal LAH solution generally a dark colour and some precipitate is formed. The color of the solution is due to the formed intermediate, unstable but highly active mixed metal hydride. The precipitate is finely dispersed metal from the decomposition of the metal hydride. Similarly using metal oxides as catalyst a marked change of color is observed. The presence of metal-hydrogen bonds in the intermediate metal compounds has been proved.

It is interesting to note that aluminum halides are quite inactive as catalysts in the above mentioned reduction.

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(2) R. F. Nystrom, THIS JOURNAL, **77**, 2544 (1955); R. F. Nystrom and C. R. Berger, *ibid.*, **80**, 2896 (1958); R. F. Nystrom, *ibid.*, **81**, 610 (1959).

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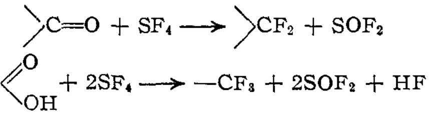
FLUORINATION REACTIONS OF SULFUR TETRAFLUORIDE

Sir:

In an investigation of the little-known chemistry of sulfur tetrafluoride (SF_4),[1] we have found this compound to be an unusual fluorinating agent, especially for the unique replacement of carbonyl oxygen with fluorine. The reaction is effective



$$>C{=}O + SF_4 \longrightarrow >CF_2 + SOF_2$$

$$-C(=O)OH + 2SF_4 \longrightarrow -CF_3 + 2SOF_2 + HF$$

with a variety of carboxylic acids and carbonyl compounds including aldehydes, ketones, and quinones, and makes available many new or relatively inaccessible fluorine compounds.

The reaction of SF_4 with a carboxylic acid group has proved to be the most direct and general

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(1) R. N. Haszeldine, "Chemical Society Symposia—Bristol 1958," The Chemical Society, Burlington House, W.I, London, 1958, p. 319.