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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[1] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 41–60.

[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).

[3] P. Karrer and O. Rutter, *Helv. Chim. Acta*, **33**, 812 (1950); V. L. Tweede and M. Cuscurida, THIS JOURNAL, **79**, 5463 (1957).

[4] R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948); F. Bohlmann, *Chem. Ber.*, **85**, 390 (1952); G. A. Olah, paper presented at the Organic Chemistry Symposium of the Chemical Institute of Canada, December 8, 1958, Ottawa (Ontario).

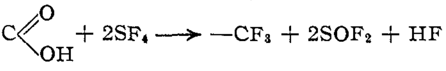
[5] H. Gilman and T. N. Goreau, THIS JOURNAL, **73**, 2939 (1951).

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

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



$$-C\begin{matrix}\diagup O \\ \diagdown OH\end{matrix} + 2SF_4 \longrightarrow -CF_3 + 2SOF_2 + HF$$

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.

method known for the synthesis of trifluoromethyl compounds. For example, SF_4 reacts with dodecanoic acid at 130° under autogenous pressure to give 1,1,1-trifluorododecane, b.p. 92° (12 mm.), $n^{25}D$ 1.3896, in 88% yield (*anal.* calcd. for $C_{12}H_{23}F_3$: C, 64.25; H, 10.34; F, 25.41. Found: C, 64.01; H, 10.27; F, 25.81). The reaction works well with aliphatic, aromatic and polycarboxylic acids. The unusual specificity of the reaction is shown by the excellent conversion of unsaturated acids to the corresponding trifluoromethyl derivatives, *e.g.*, trifluoropropene and trifluoropropyne are now easily accessible from acrylic and propiolic acids, respectively.

Fluorination of aldehydes and ketones by SF_4 is typified by the high yield preparation of α,α-difluorotoluene from benzaldehyde and of 2,2-difluoropropane from acetone. Some quinones react like ketones, but in other cases subsequent reactions result in fluorination and aromatization of the ring. For example, chloranil in the presence of hydrogen fluoride at 270° gave 1,2,4,5-tetrachloro-3,3,6,6-tetrafluoro-1,4-cyclohexadiene, m.p. 46°, in 75% yield (*anal.* calcd. for C_6Cl_4: C, 24.86; Cl, 48.92; F, 26.22. Found: C, 25.02; Cl, 48.94; F, 26.24). However, the product from quinone was 1,2,4-trifluorobenzene in 30% yield. Such carbonyl compounds as carbon monoxide and carbon dioxide are converted to CF_4 by SF_4.[2]

Another example of the versatility of SF_4 as a fluorinating agent is the excellent conversion of benzenearsonic acid to $C_6H_5AsF_4$, b.p. 52–53° (2 mm.) (*anal.* calcd. for $C_6H_5AsF_4$: C, 31.60; H, 2.21; F, 33.33; As, 32.85. Found: C, 31.72; H, 2.48; F, 33.38; As, 32.41).

A new class of compounds, the organoiminosulfur difluorides, has been obtained from the reaction of SF_4 with compounds containing carbon-nitrogen multiple bonds. The only previously known iminosulfur difluoride was $F—N{=}SF_2$.[3] Examples of organoiminosulfur difluorides are the products from phenyl isocyanate and benzonitrile.[4]

$$C_6H_5N{=}C{=}O + SF_4 \longrightarrow C_6H_5N{=}SF_2 + F_2C{=}O$$

$$C_6H_5C{\equiv}N + SF_4 \longrightarrow C_6H_5CF_2N{=}SF_2$$

Phenyliminosulfur difluoride, b.p. 36° (2 mm.), was obtained in 88% yield from phenyl isocyanate at 200° (*anal.* calcd. for $C_6H_5F_2NS$: C, 44.71; H, 3.13; F, 23.58; N, 8.69; S, 19.90. Found: C, 44.12; H, 3.40; F, 24.00; N, 8.27; S, 19.76). The assigned structure is in accord with the infrared and n.m.r. spectra. Benzonitrile was converted to α,α-difluorobenzyliminosulfur difluoride, b.p. 55° (11 mm.) (*anal.* calcd. for $C_7H_4F_4NS$: F, 35.99; S, 15.18. Found: F, 35.81; S, 15.11).

Sulfur tetrafluoride has been made readily available by the discovery of a high-yield synthesis based on the reaction of SCl_2 with NaF suspended in acetonitrile at 70–80°. One distillation gives SF_4 of greater than 90% purity with thionyl fluoride as the main impurity. Sulfur tetrafluoride should be used with extreme caution because it has an inhalation toxicity comparable to that of phosgene and releases hydrogen fluoride on contact with moisture.

A large number of reactions of SF_4 and its derivatives are under investigation, and detailed reports on this research are being prepared.

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RECEIVED MAY 12, 1959

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[2] W. C. Smith, U. S. Patent 2,859,245 (1958).

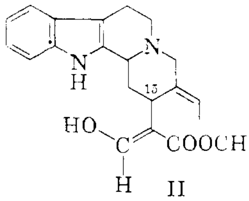
[3] O. Glemser and H. Schröder, *Z. anorg. allgem. Chem.*, **284**, 97 (1956).

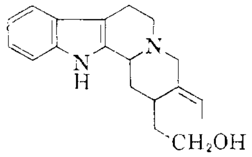
[4] W. C. Smith, U. S. Patent 2,862,029 (1958).

THE STRUCTURE OF GEISSOSCHIZINE

Sir:

Recently[1] we reported that treatment of geissospermine ($C_{40}H_{48}N_4O_3$, I) with concd. hydrochloric acid gave three products, *viz.*, geissoschizine ($C_{21}H_{24}N_2O_3$), apogeissoschizine ($C_{21}H_{22}N_2O_2$), and geissoschizoline ($C_{19}H_{26}N_2O$).[2] We now wish to report that geissoschizine possesses structure II.


II


III

Both the acidic character of II and the profound, reversible ultraviolet spectral changes observed on adding acid and alkali[3] suggest the presence of a readily enolizable carbonyl. To confirm this II was treated with one mole of aniline to give the expected anilinoacrylic ester ($C_{27}H_{29}N_3O_2$, m.p. 170–172°) with a carbonyl absorption at 6.11 μ as compared to 5.96 μ for II. The ethylidene side chain was shown by ozonolysis, which gave acetaldehyde, and by the observation that Kuhn–Roth oxidation of II gave one mole of acetic acid whereas oxidation after catalytic reduction gave one mole of mixed acetic–propionic acids.[4]

On boiling II with 1 *N* hydrochloric acid, an amorphous aldehyde was formed by loss of methanol and carbon dioxide, and this aldehyde with sodium borohydride gave a crystalline carbinol (III, $C_{19}H_{24}N_2O$, m.p. 210–215° dec.). Wolff–Kishner reduction of the aldehyde gave an oxygen-free compound (IV, $C_{19}H_{24}N_2$). Although III still shows the presence of only one $C–CH_3$, two are present in IV. Heating IV with palladized charcoal at 220° gave one mole of hydrogen and alstyrine,[5] from which *o*-aminopropiophenone and 4,5-diethylpicolinic acid were obtained on further degradation.

Additional evidence for the structure II resulted from selenium dehydrogenation studies on geis-

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[1] H. Rapoport, T. P. Onak, N. A. Hughes and M. G. Reinecke, THIS JOURNAL, **80**, 1601 (1958).

[2] Satisfactory analyses have been obtained for all compounds for which molecular formulae are given. The identity of known compounds has been established by comparison with authentic samples.

[3] The ultraviolet spectrum of II in 0.1 *N* alkali could be very closely reproduced by combining the spectra of alloyohimbine and of ethyl acetoacetate in 0.1 *N* alkali.

[4] H. Bickel, H. Schmid and P. Karrer, *Helv. Chim. Acta*, **38**, 649 (1955).

[5] T. B. Lee and G. A. Swan, *J. Chem. Soc.*, 771 (1956).