methods.[2] However, it served as a basis for study of a series of compounds having the conjugated diene structure plus one hetero atom. The basic structure is

I

The compounds reported here all contain phenyl R_1, R_2, R_3, R_4. The nature of R_5 and R_6 substituents may vary with the possibility of one or both being absent, e.g., with As, $R_5 = C_6H_5$ and R_6 is not present. Also, R_5 and R_6 may represent a second ring as in a spiro compound. Preparation of spiro compounds imposes several limitations on the general reaction, i.e., the need for (1) a hetero atom with a valence of four or greater and (2) use of 1 mole of a tetrahalide of the hetero atom plus 2 moles of LTPBD.

Referring to structure I, compounds have been prepared with M = S, P, Sn, As, Sb and Ge (also spiro compounds with M = Sn and Ge). These are all high melting (>160°) crystalline solids. Molecular weight determinations and elemental analysis verified the ring structure. A typical member of the series is pentaphenylphosphole (M = P, $R_5 = C_6H_5$) m.p. 261–262°; mol. wt. calcd. 464, found 463 (mass spec.); calcd: C, 88.1; H, 5.4; P, 6.65; found: C, 88.2; H, 5.5; P, 6.55.

Work is in progress to prepare heterocycles of this type with R groups I–IV other than phenyl. Other synthetic routes to these compounds and the preparation of other type compounds having this basic unit are being investigated. Concurrent with the synthetic studies, we are attempting to determine the chemical nature of these new ring systems with regard to the possible aromaticity of the five-membered ring, ability to form π electron complexes with metals and the normal diene reactions.

(2) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, New York, N. Y., 1952, pp. 473 f.

THE DOW CHEMICAL COMPANY F. C. LEAVITT
EASTERN RESEARCH LABORATORY T. A. MANUEL
FRAMINGHAM, MASSACHUSETTS F. JOHNSON

COMPARISON OF COVALENTLY BONDED ELECTRONEGATIVE ATOMS AS PROTON ACCEPTOR GROUPS IN HYDROGEN BONDING

Sir:

Generalization,[1,2] widely held and widely quoted, concerning the requirements for hydrogen bonding, has emphasized the necessity of having as the

(1) These references may serve as illustrations: M. Davies, Ann. Repts. on Prog. Chem. (Chem. Soc. London), 43, 5 (1946); L. Hunter, ibid., p. 141; L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Second Edition, 1948, pp. 286 f.; C. A. Coulson, "Valence," Oxford University Press, London, 1952, pp. 298 f.; T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, pp. 188–189; G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1955, pp. 49 f.; E. Cartmell and G. W. A. Fowles, "Valency and Molecular Structure," Butterworths Scientific Publications, London, 1956, p. 138; G. M. Badger, Revs. Pure Appl. Chem. (Australia), 7,

proton acceptor group an element of small atomic radius and strong electronegativity (i.e., N, O, F). Although these conclusions may be valid when very strong hydrogen bonding to anions is involved (e.g., HF_2^-), their extension to covalently bonded negative atoms is not possible. On the contrary, we wish to present spectroscopic evidence which demonstrates that the relative electron donor abilities of the alkyl halides decreases in the order I > Br > Cl > F. Furthermore, the hydrogen bonds formed by compounds of these elements with suitable proton donors are weak relative to those of the other electronegative elements.

The order given above has long been known to hold for the intramolecular hydrogen bonding exhibited by the o-halophenols.[3] The criteria for strength, or more precisely the enthalpy, of the hydrogen bond is taken to be related to $\Delta\nu$, the spectral shift in cm.$^{-1}$ from the "free" to the "bonded" peaks.[4] However, the interpretation of the o-halophenol data is ambiguous because, in the rigidly held aromatic systems, the small covalent radii of the lower atomic weight halogen atoms may

TABLE I[5]

$\Delta\nu$ VALUES OF β-SUBSTITUTED ETHANOLS

Substituent	F	Cl	Br	I	EtO	EtS	Et_2N
$\Delta\nu$, cm.$^{-1}$	12	32	38	46	30	92	166

TABLE II[5]

FREQUENCY SHIFTS DUE TO INTERMOLECULAR HYDROGEN BONDING (cm.$^{-1}$)

Compound	$\Delta\nu$ CH_3OH[b]	$\Delta\nu$ Phenol[b]
n-Butyl fluoride	19	40
Cyclohexyl fluoride	..	53
n-Butyl chloride	37	59
Cyclohexyl chloride	..	66
n-Butyl bromide	41	69
Cyclohexyl bromide	..	82
n-Butyl iodide	47	77
Isopropyl iodide	..	85
Di-n-butyl ether	155	281
Di-n-butyl sulfide	155	258
Tri-n-butylamine[a]	396	..
Tri-n-butylphosphine[a]	267	..
Tri-ethylarsine[a]	310	..

[a] Solution in C_2Cl_4. [b] Positions of the free peaks: 3610 cm.$^{-1}$ for phenol; 3643 cm.$^{-1}$ for methanol in both CCl_4 and C_2Cl_4.

55 (1957); J. A. A. Ketalaar, "Chemical Constitution," Elsevier, Publ. Co., New York, N. Y., Second Edition, 1958, p. 408.

(2) For recent reviews on hydrogen bonding not referred to above: L. Kellner, Repts. Progr. in Phys., 15, 1 (1952); L. Hunter in W. Klyne, Ed., "Progress in Stereochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1954, pp. 223 f.; C. A. Coulson, Research, 10, 149 (1957); C. G. Cannon, Spectrochimica Acta, 10, 341 (1958).

(3) O. R. Wulf, U. Liddel and S. B. Hendricks, THIS JOURNAL, 58, 2287 (1936); O. R. Wulf and E. J. Jones, J. Chem. Phys., 8, 745 (1940); G. Rossmy, W. Lüttke and R. Mecke, ibid., 21, 1606 (1953); and especially A. W. Baker and A. T. Shulgin, THIS JOURNAL, 80, 5358 (1958); A. W. Baker, ibid., 80, 3598 (1958).

(4) R. M. Badger and S. H. Bauer, J. Chem. Phys., 5, 839 (1937); R. M. Badger, ibid., 8, 288 (1940); R. C. Lord and R. E. Merrifield, ibid., 21, 166 (1953); K. Nakamoto, M. Margoshes and R. E. Rundle, THIS JOURNAL, 77, 6480 (1955); G. C. Pimentel and C. H. Sederholm, J. Chem. Phys., 24, 639 (1956).

(5) Perkin–Elmer Model 21 and Model 112 Spectrophotometers, LiF prisms, CCl_4 solutions except where noted. Intramolecular concentrations were about 0.005 M. Intermolecular concentrations were about 1 M for the proton acceptor and 0.01 M for the donor.

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.

FRICK LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY   PAUL VON R. SCHLEYER
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN   ROBERT WEST
MADISON, WISCONSIN
RECEIVED MAY 1, 1959

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 com-

(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).

pletion 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.

CONTRIBUTION NO. 18
EXPLORATORY RESEARCH LABORATORY
DOW CHEMICAL OF CANADA, LIMITED   G. A. OLAH
SARNIA, ONTARIO, CANADA
RECEIVED APRIL 3, 1959

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

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

$$\ce{-C(=O)OH + 2SF_4 -> -CF_3 + 2SOF_2 + HF}$$
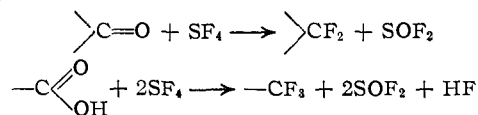
with a variety of carboxylic acids and carbonyl compounds including aldehydes, ketones, and quinones, and makes available many new or relatively inaccessible fluorine compounds.

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

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