allene, sealed, and rocked for 3 days at room temp. in a hydrogenation bomb. At the end of this period the bomb was cooled in Dry Ice, opened, the glass tube cooled further in liquid nitrogen and opened. The low boiling material, mainly unreacted monomer, was distilled out at room temp. leaving 4.9 g. of a white waxy solid which melted sharply at 118°. Other runs produced polymer having the same infrared spectrum but with melting points of 100–103° and 125–126°.

The polymer was insoluble in all of the common organic solvents and also in such fluorocarbons as perfluoroheptane. It did not dissolve in dimethylformamide, but when a suspension in this solvent was allowed to stand overnight the precipitate was dark red and the solvent a clear orange. The infrared spectrum of the polymer was determined in a potassium bromide disk; strong bands were observed at 1715, 1343, 1196, 1072 and 1020 cm.$^{-1}$.

Dimerization of Tetrafluoroallene.—Tetrafluoroallene (6.7 g., 0.06 mole) to which had been added less than 1% Terpene B[20] as an inhibitor was sealed in a heavy-walled glass tube. The tube was placed in a small hydrogenation bomb and heated for 20 hours at 40°.

At the end of this period the tube was cooled in liquid nitrogen, opened, and the volatile components distilled out by allowing them to vaporize at room temperature. The higher boiling components of the reaction mixture consisted of 0.225 g. of a solid polymer and 5.3 g. (yield 83%) of a liquid, b.p. 64.0°, which was found to have a molecular weight (by vapor density) of 225; calcd. for $(C_3F_4)_2$, 224.

Oxidation of the Dimer from Tetrafluoroallene.—About 2.0 g. (0.009 mole) of the dimer was sealed in a heavy-walled glass tube at Dry Ice temperature with a solution containing 2.76 g. (0.018 mole) of potassium permanganate and 1.95 g. (0.035 mole) of potassium hydroxide. The tube was allowed to warm to room temperature, placed in a shaker, and vigorously agitated. After three days the tube was opened and the theoretical amount of sulfuric acid needed to neutralize the reaction mixture was added. The manganese oxide was reduced with sulfur dioxide and the organic material was isolated by continuous ether extraction. The ether extract was dried with magnesium sulfate and evaporated to give 0.91 g. of an oil which after chromatographing on a 1:1 mixture of Celite and Baker Analyzed silicic acid $(SiO_2.n.H_2O)$ gave 0.39 g. (yield 23%) of a solid white acid believed to be the monohydrate of perfluorosuccinic acid. The infrared spectrum of this acid in acetonitrile was found to be identical with that of an authentic sample[29] in the same solvent with strong absorption bands at 3440, 1765, 1230 and 1150 cm.$^{-1}$. Also a 1:1 mixture of equal molar solutions in water of this acid and of the authentic sample gave a nuclear magnetic resonance spectrum with a single peak which was of the same area as that found for the authentic perfluorosuccinic acid.

Anal. Calcd. for $C_4H_4O_5F_4$ [$HO_2CCF_2CF_2CO_2H \cdot H_2O$]: C, 23.13; H, 1.93; equiv. wt., 104.0. Found: C, 23.18; H, 2.09; equiv. wt., 105.5.

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[29] We wish to thank Dr. Tom Brice of the Minnesota Mining and Manufacturing Co. for sending us a sample of this compound.

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[CONTRIBUTION FROM THE RADIOCARBON LABORATORY, UNIVERSITY OF ILLINOIS]

Reduction of Organic Compounds by Mixed Hydrides. III. 3-Bromopropionic Acid, 3-Bromopropionyl Chloride, Methyl 3-Bromopropionate and Halides

BY ROBERT F. NYSTROM

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By application of the lithium aluminum hydride–aluminum chloride reagent improvements have been made in the conversion of 3-bromopropionic acid, 3-bromopropionyl chloride and methyl 3-bromopropionate to 3-bromo-1-propanol. The halogen is reduced slowly or not at all by use of the acidic hydride.

In two previous publications[1,2] the reduction of nitriles, nitro compounds, bromoacid chlorides, ketones and alcohols by the lithium aluminum hydride–aluminum chloride reagent has been described. The purpose of the present work has been to further investigate the behavior of the mixed hydride toward a representative acid, acid chloride and ester of the β-bromoacid series in order to utilize the knowledge gained to simplify future synthetic work.

The mechanism of halide reductions with lithium aluminum hydride has been reported.[3,4] In one publication,[4] a 62% yield of 1-propanol and a 21% yield of 3-chloro-1-propanol was obtained when 3-chloropropionic acid was reduced by lithium aluminum hydride at 35° for one to two hours.

The results achieved with the lithium aluminum hydride–aluminum chloride reagent indicate that this process offers definite advantages in the preparation of bromohydrins when compared to the lithium aluminum hydride method. First, reduction of halogen is retarded or prevented by use of the acidic hydride. Second, the experimental procedures are simpler because the bromohydrin can be obtained without resorting to reverse order of addition techniques or lowered temperatures. Finally, a decided advantage in yield is realized.

Reduction of 3-bromopropionic acid, 3-bromopropionyl chloride and methyl 3-bromopropionate by both lithium aluminum hydride and the lithium aluminum hydride–aluminum chloride reagent was studied by normal and reverse order of addition and at temperatures of 35, −15 and −75°. In all instances a ratio of one mole of organic compound per mole of hydride was employed.

Treatment of 3-bromopropionyl chloride with the mixed hydride furnished 76-90% yields of 3-bromo-1-propanol regardless of mode of addition and temperature as shown in Table I. The corresponding reaction with lithium aluminum hydride proceeded well under all conditions listed except when it was carried out by normal order of addition at 35°. These results can best be explained by assuming that the acidic hydride is formed *"in situ"* during the reduction of the bromoacid chloride by lithium aluminum hydride. Accordingly, one would expect to obtain higher yields of bromohydrin from the hydride reduction of a bromoacid chloride than from the corresponding ester or acid. This is readily apparent by inspection of Tables I, II and III.

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(1) R. F. Nystrom, THIS JOURNAL, **77**, 2544 (1955).

(2) R. F. Nystrom and C. R. A. Berger, *ibid.*, **80**, 2896 (1958).

(3) E. E. Eliel and T. J. Prosser, *ibid.*, **78**, 4045 (1956).

(4) E. E. Eliel and J. T. Traxler, *ibid.*, **78**, 4049 (1956).

Table I

Reduction of 3-Bromopropionyl Chloride to 3-Bromo-1-propanol

Hydride employed	Conditions		Bromohydrin, %
	Addition	Temp., °C.	
$LiAlH_4$	Normal	35	46
$LiAlH_4$–$AlCl_3$	Normal	35	83
$LiAlH_4$	Reverse	35	76
$LiAlH_4$–$AlCl_3$	Reverse	35	86
$LiAlH_4$	Normal	−15	80
$LiAlH_4$–$AlCl_3$	Normal	−15	77
$LiAlH_4$	Reverse	−15	68
$LiAlH_4$–$AlCl_3$	Reverse	−15	90
$LiAlH_4$	Normal	−75	87
$LiAlH_4$–$AlCl_3$	Normal	−75	90
$LiAlH_4$	Reverse	−75	82
$LiAlH_4$–$AlCl_3$	Reverse	−75	76

Table II

Reduction of Methyl 3-Bromopropionate to 3-Bromo-1-propanol

Hydride employed	Conditions		Bromohydrin, %
	Addition	Temp., °C.	
$LiAlH_4$	Normal	35	18
$LiAlH_4$–$AlCl_3$	Normal	35	78
$LiAlH_4$	Reverse	35	14
$LiAlH_4$–$AlCl_3$	Reverse	35	72
$LiAlH_4$	Normal	−15	4
$LiAlH_4$–$AlCl_3$	Normal	−15	85
$LiAlH_4$	Reverse	−15	52
$LiAlH_4$–$AlCl_3$	Reverse	−15	90
$LiAlH_4$	Normal	−75	47
$LiAlH_4$–$AlCl_3$	Normal	−75	90
$LiAlH_4$	Reverse	−75	30
$LiAlH_4$–$AlCl_3$	Reverse	−75	85

Table III

Reduction of 3-Bromopropionic Acid to 3-Bromo-1-propanol

Hydride employed	Conditions		Bromohydrin, %
	Addition	Temp., °C.	
$LiAlH_4$	Normal	35	15
$LiAlH_4$–$AlCl_3$	Normal	35	50
$LiAlH_4$	Reverse	35	15
$LiAlH_4$–$AlCl_3$	Reverse	35	40
$LiAlH_4$	Normal	−15	10
$LiAlH_4$–$AlCl_3$	Normal	−15	44
$LiAlH_4$	Reverse	−15	26
$LiAlH_4$–$AlCl_3$	Reverse	−15	30
$LiAlH_4$	Normal	−75	7
$LiAlH_4$–$AlCl_3$	Normal	−75	18
$LiAlH_4$	Reverse	−75	2
$LiAlH_4$–$AlCl_3$	Reverse	−75	2

Next, in the conversion of methyl 3-bromopropionate to the bromohydrin it was found that the lithium aluminum hydride–aluminum chloride reagent furnished higher yields than lithium aluminum hydride. Again it is to be noted that the acidic hydride retards or prevents reduction of the halogen whereas the more basic reagent, lithium aluminum hydride, facilitates reduction of the halogen. The highest yield of bromohydrin, secured by adding a solution of lithium aluminum hydride to an ethereal solution of the bromoester cooled at −15°, was 52%. In comparison the acidic hydride gave 72-90% yields of 3-bromo-1-propanol under all the conditions in Table II.

Transformation of 3-bromopropionic acid to the bromohydrin proceeded with difficulty with both the acidic hydride and lithium aluminum hydride. 3-Bromo-1-propanol was obtained in 50% yield by adding an ethereal solution of 3-bromopropionic acid to a solution of lithium aluminum hydride–aluminum chloride at 35°. In contrast to this the highest yield, 26%, attained by lithium aluminum hydride reduction was accomplished by adding a solution of the hydride to a solution of the bromoacid at −15°. One difficulty encountered in these reductions was the limited solubility of the acid and its lithium aluminum salt in ether at lowered temperatures.

Finally a number of miscellaneous reactions involving halides were examined and are reported in Table IV. No evidence of reduction was found when benzyl iodide and 9-bromofluorene were treated separately with the lithium aluminum hydride–aluminum chloride reagent. These results further demonstrate that reduction of halogen is slowed down or prevented by use of the acidic hydride under the conditions listed. In contrast to this, using lithium aluminum hydride, benzyl iodide was converted to toluene in 86% yield and 9-bromofluorene to a mixture of fluorene and dibiphenylene-ethane.[5] Also, Wiberg and Jahn[6] reported a 41% conversion of benzyl iodide to toluene by employing a mixture of AlH_2Cl and $AlHCl_2$.

Table IV

Attempted Reduction of Halogen Compounds by Lithium Aluminum Hydride–Aluminum Chloride

Compound	Product
t-Butyl iodide	No reduction
9-Bromofluorene	No reduction
Benzyl iodide	No reduction

Experimental

Experimental results are summarized in Tables I, II, III, IV. Products were further identified by suitable derivatives. The experimental techniques for the preparation of the hydride solution and for determining the stoichiometry are given in a previous paper.[1]

Following procedures similar to those outlined below, modified only to the extent necessitated by the individual problems of isolating and purifying the products, a number of compounds were reduced using the concentration of organic material and hydride shown below.

In all cases the reduction was performed in a 1-liter, three-necked flask equipped with a reflux condenser, a mechanical mercury-sealed stirrer and a dropping funnel. The gas outlet tube on the condenser was attached to two traps cooled at −75° and then to a wet-test meter. In the experiments carried out at lowered temperatures the excess hydride was destroyed by adding an ethereal solution of methanol because it was found that an ethereal solution containing 5 ml. of ethyl acetate did not completely destroy the hydride at −75°.

Reduction of 3-Bromopropionyl Chloride to 3-Bromo-1-propanol by Lithium Aluminum Hydride–Aluminum Chloride—Reverse Addition at 35°.—The mixed hydride, prepared by introducing a solution of 13.3 g. (0.1 mole) of granular aluminum chloride in 100 ml. of ether to a solution of 0.1 mole of lithium aluminum hydride in 100 ml. of ether, was added to 17.1 g. (0.1 mole) of 3-bromopropionyl chlo-

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(5) L. W. Trevoy and W. G. Brown, This Journal, **71**, 1675 (1949);

(6) E. Wiberg and A. Jahn, *Z. Naturforsch.*, **7b**, 580 (1952).

ride in 150 ml. of ether at a rate such as to produce gentle reflux. Then after 30 minutes an addition of 100 ml. of water and 100 ml. of 6 *N* sulfuric acid was made. The clear solution was transferred to a separatory funnel and, after removing the ether layer, the aqueous layer was continuously extracted with ether for 48 hours. From the combined ether extracts the crude product was obtained, after drying the solution over Drierite and removal of ether. This material was purified by fractional distillation through a Nester–Faust 18″ micro spinning band column under reduced pressure and there was secured an 86% yield of 3-bromo-1-propanol, b.p. 70–72° (10 mm.). The α-naphthylurethan derivative was prepared and melted at 73°.

Reduction of Methyl 3-Bromopropionate to 3-Bromo-1-propanol by Lithium Aluminum Hydride–Aluminum Chloride—Normal Addition at −75°.—The mixed hydride was prepared as described above. Through the dropping funnel, a solution of 16.7 g. (0.1 mole) of methyl 3-bromopropionate in 150 ml. of ether was added to 0.1 mole of the lithium aluminum hydride–aluminum chloride reagent which was cooled at −75°. Thirty minutes after the last addition of ester, a solution containing 20 ml. of methanol and 20 ml. of ether was added dropwise to destroy the excess hydride. After allowing the mixture to warm to room temperature, 100 ml. of water and 100 ml. of 6 *N* sulfuric acid were added. The reaction mixture was treated as described in the previous example. There was obtained a 90% yield of 3-bromo-1-propanol, b.p. 71–72° (10 mm.). The α-naphthylurethan derivative was prepared and melted at 73°.

Reduction of 3-Bromopropionyl Chloride to 3-Bromo-1-propanol by Lithium Aluminum Hydride—Normal Addition at −75°.—A solution of 17.1 g. (0.1 mole) of 3-bromopropionyl chloride in 150 ml. of ether was added dropwise to 0.1 mole of lithium aluminum hydride in 200 ml. of ether at −75°. Thirty minutes after the last addition of acid chloride, the excess hydride was destroyed with methanol and the product isolated as described above. An 87% yield of 3-bromo-1-propanol was obtained, b.p. 71–72° (10 mm.). The α-naphthylurethan derivative was prepared and melted at 73°.

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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY]

The Beckman Rearrangement. VIII. The Influence of Alkyl Groups on the Rates of Rearrangement of Acetophenone Oximes[1]

BY PATRICK J. MCNULTY[2] AND D. E. PEARSON[3]

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Several rather unusual observations were made in comparing rates of rearrangement of alkyl-substituted acetophenone oximes. The most remarkable observation was that *p*-alkyl substituents show less electron-release ability (relative to hydrogen) than they do in nucleophilic reactions, a fact hardly compatible with present-day theory of alkyl group behavior. The second observation was that σ-constants of alkyl groups occupying positions *ortho* to each other were not additive in predicting rate. A third observation was that the rate of rearrangement of propiophenone oxime was much faster than anticipated, suggesting a considerable influence of the non-migrating group on the rate. A fourth observation was that the log rate of rearrangement of acetophenone oxime was correlative with H_0(slope = −0.72). These observations were made possible by the development of a new spectrophotometric method of analysis of ketone concentration.

In our opinion knowledge concerning the electronic behavior of alkyl groups is in an advanced state of confusion. Theoretically, as surmised from the resultant dipole of several carbon–hydrogen bonds, the sequence of electron release for alkyl groups should be in the order: *t*-butyl>isopropyl>ethyl>methyl. This order is found in many nucleophilic reactions for which the Hammett equation[4] has been found applicable. Thus, the σ-constant for the *p*-*t*-butyl group is −0.20 and for the *p*-methyl group is −0.17, the ethyl and isopropyl group constants probably falling in between these values.[5] In other words, alkyl groups have considerable electron-release ability compared with a hydrogen atom, but only small differences compared with each other. In certain reactions, and it is impossible to always predict when, the order of electron release of alkyl groups is methyl>ethyl>isopropyl>*t*-butyl>>hydrogen, often called the hyperconjugative order.[6,7] The question then arises as to what happens to the σ-constants of alkyl groups in the hyperconjugative order. We studied this problem several years ago[8,9] in connection with the observation of the influence of substituents on the rates of the Beckmann rearrangement of substituted acetophenone oximes. One tentative conclusion was that atoms or groups with unshared electrons, such as the amino, hydroxyl, alkoxyl, vinyl, aryl and halogens attached in either the *o*- or *p*-positions of the aromatic ring showed greater electron-release ability in influencing the rates of rearrangement of aromatic oximes than they did in nucleophilic reactions as represented by the Hammett σ-constants. On the basis of this conclusion, more negative σ-constants, called σ_e constants, were proposed for these groups in electrophilic reactions. Another tentative conclusion was that alkyl groups retained the same electrical influence and that the hyperconjugative order of these groups was caused by some type of solvation inhibition in the stabilization of the transition complex,[8,10] the *t*-butyl grouping having the

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[1] Paper VII, Frances Greer and D. E. Pearson, THIS JOURNAL, **77**, 6649 (1955).

[2] National Science Foundation Research Grant Fellow throughout graduate work. Ph.D. thesis to be microfilmed, University Microfilm Service, Ann Arbor, Mich.

[3] To whom correspondence should be sent.

[4] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[5] The σ-value for the *p*-ethyl group is given as −0.15.[4] This value is based on one set of experimental data and therefore is open to question.

[6] J. W. Baker, "Hyperconjugation," Oxford at the Clarendon Press, 1952.

[7] The term hyperconjugation implies the contribution to the hybrid of a canonical form which has double-bonded character between the alkyl group and the aromatic ring. We believe that the term has been used much too loosely to explain simple inductive or inductomeric effects. The inductomeric effect, if existent, would be merely a distortion toward the benzene ring of the sp^3-hybridized orbital of the electrons bewteen the alkyl group and the ring. Nevertheless, until otherwise proved, we will use the word hyperconjugative order whenever this particular sequence is met.

[8] D. E. Pearson, J. F. Baxter and J. C. Martin, *J. Org. Chem.*, **17**, 1511 (1952).

[9] D. E. Pearson and J. D. Bruton, *ibid.*, **19**, 957 (1954).

[10] C. C. Price and D. C. Lincoln, THIS JOURNAL, **73**, 5836 (1951).