adenylate. This formulation is supported by the recent O^{18} exchange studies of Boyer[12] and by Jencks[13] who obtained a coA-independent activation of octanoic and similar fatty acids by pyrophosphate split of ATP. Definitive proof of this general mechanism must await experiments demonstrating the enzymatic synthesis of adenyl acetate from ATP and acetate (reaction 2), and the formation of adenyl acetate from acetyl-coA and A5P (reaction 3).

During the course of the above work a methionine requiring PP–ATP exchange system was also purified from yeast.[14] It is possible that this and the previously reported pantoic[15] and amino acid activated PP-ATP exchanges[5] may occur by the formation of the corresponding adenyl-acyl group derivatives. Thus, the pantothenate peptide bond formation may represent a variation of the acetate activation with the amino group of β-alanine serving as the acyl group acceptor in place of the sulfhydryl group of coA.

[12] P. D. Boyer, O. J. Koeppe, W. W. Luchsinger, and A. B. Falcone, *Fed. Proc.*, **14**, 185 (1955).

[13] W. P. Jencks, *ibid.*, **12**, 703 (1953).

[14] P. Berg, unpublished.

[15] W. K. Maas, quoted by F. Lipmann, *Science*, **120**, 855 (1954).

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REDUCTION OF ESTER AND OTHER DIFFICULTLY REDUCIBLE GROUPS BY SODIUM BOROHYDRIDE

Sir:

Since its original discovery[1] sodium borohydride has proven a very useful reagent for the selective reduction of aldehyde and ketone groups.[2] It has not been applicable to the reduction of ester and similar functional groups which are relatively difficult to reduce. Recently Kollonitsch, Fuchs and Gabor[3] reported that they had succeeded in reducing esters by the use of calcium borohydride[3a] and magnesium borohydride.[3b] We wish to report the rapid reduction at room temperatures of esters, carboxylic acids and nitriles by sodium borohydride in the presence of aluminum chloride. 1-Olefins are reduced at 75°; unconjugated 2-olefins are not affected by these conditions. Nitro and amide groups are not reduced by the reagent. Consequently the method offers a convenient procedure for the selective reduction of nitro esters.

The addition of aluminum chloride to a solution of sodium borohydride in diethylene glycol dimethyl ether ("diglyme") results in a clear solution of the reagent. Sodium chloride does not precipitate. Therefore it is improbable that aluminum borohydride is present in other than minor amounts. (We plan to investigate this point.) The reagent has been exposed to dry air with only minor loses in activity. It can be poured in air without difficulty.

Other polyvalent metal halides, such as gallium trichloride and titanium tetrachloride also bring about the reduction of esters. However, aluminum chloride possesses obvious advantages for general laboratory use so that our studies have been concentrated on the applicability of this reagent.

In a typical preparative procedure ethyl *p*-chlorobenzoate was reduced to *p*-chlorobenzylalcohol in 89% yield as follows. A stirred solution of 0.25 mole of sodium borohydride (99% purity) in 250 ml. of diglyme and 0.4 mole of ethyl *p*-chlorobenzoate was treated slowly with a total of 0.084 mole of anhydrous aluminum chloride (42.0 ml. of a freshly prepared 2 *M* solution of $AlCl_3$ in the same solvent). The reaction was vigorous in the initial stages and the rate of addition was controlled to maintain the temperature below 50°. The flask was then heated for a few minutes on the steam-bath to complete the reaction. The reaction mixture was poured onto crushed ice and dilute acid. The solid product (50.9 g., 89%) was recrystallized from hot water to give pure *p*-chlorobenzyl alcohol, m.p. 75°, in a yield of 84%.

We have examined the utilization of hydride from the reagent by various compounds usually at 25°. The first figure gives the time of reaction in hours and the second gives the moles of hydride per mole of compound (one mole of hydride utilized to form hydrogen in the case of carboxylic acids and amides is not included in the figure): ethyl acetate (0.5, 2.0); ethyl stearate (0.5, 2.0); ethyl *p*-chlorobenzoate (0.5, 2.0); ethyl oleate (0.5, 2.2); ethyl cinnamate (0.5, 3.0); ethyl *p*-nitrobenzoate (0.5, 2.0); benzoic acid (0.5, 2.0); benzamide (3.0, 0.0); benzoyl chloride (3.0, 2.0); benzonitrile (3.0, 2.0); acetonitrile (3.0, 2.0); nitrobenzene (3.0, 0.0); 1-nitropropane (3.0, 0.0); pyridine-N-oxide (3.0, 1.0); benzaldehyde (0.5, 1.0); benzophenone (0.5, 1.0); styrene (1.0, 1.0); 1-hexene (25°, 3.0, 0.8; 75°, 1.0, 1.0); cyclohexene (75°, 1.0, 0.0).

These results suggest that the reducing properties of sodium borohydride can be profoundly modified by addition of various polyvalent metal halides. We are continuing to explore the potentialities of these reducing systems.

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[1] H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, THIS JOURNAL, **75**, 199 (1953).

[2] S. W. Chaikin and W. G. Brown, *ibid.*, **71**, 122 (1949).

[3] (a) J. Kollonitsch, O. Fuchs, V Gabor, *Nature*, **175**, 346 (1955); (b) **173**, 125 (1954).

NON-SOLVATED ALUMINUM HYDRIDE[1]

Sir:

Previous preparations of aluminum hydride have resulted either in a very low yield of impure product[2] or in a solid solvated polymer from which it has been impossible to remove all the solvent without decomposition.[3]

We have now succeeded in preparing non-

[1] The work reported herein was carried out under the auspices of the Office of Naval Research under Contract ONR-494(04).

[2] O. Stecher and E. Wiberg, *Ber.*, **75**, 2003 (1942).

[3] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, THIS JOURNAL, **69**, 1199 (1947).