ticularly interesting in view of the fact that the work of Erlenmeyer, Schoenauer and Schwarzenbach[3] indicates that all three hydrogen atoms of hypophosphorus acid exchange rapidly with deuterium oxide. Apparently in the deamination reaction a hydrogen atom was extracted from another aromatic nucleus, since that is the only source of hydrogen which is not equilibrated with deuterium.

(3) Erlenmeyer, Schoenauer and Schwarzenbach, *Helv. Chim. Acta*, **20**, 732 (1937); see also Franke and Mönch, *Ann*, **550**, 1 (1941).

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CAUSE OF EXPLOSIONS OCCASIONALLY OBSERVED DURING EVAPORATION OF SOLUTIONS OF ALUMINUM HYDRIDE AND RELATED COMPOUNDS

Sir:

In experiments involving dimethyl ether solutions of aluminum hydride, as well as of lithium and sodium aluminum hydrides, explosions have occasionally occurred. The details to be described have demonstrated that the explosions were caused by carbon dioxide present as an impurity in some samples of the ether.

Explosions have occurred toward the end of distillations undertaken to remove the solvent from dimethyl ether solutions of lithium aluminum hydride. That the explosions were due to an impurity more volatile than dimethyl ether was indicated by the facts (1) that later samples of the ether taken from a cylinder caused less violent explosions than the first few samples, and (2) ether taken from another cylinder at no time caused these explosions. These facts, as well as chemical tests to prove their absence, excluded aldehydes, alcohols or peroxide as the offending impurity. Considerable carbon dioxide was present in the cylinders whose contents led to explosions; its removal by fractionation *in vacuo* rendered the contents harmless. After carbon dioxide was reintroduced into the purified sample, the explosions recurred. It was then found that diethyl ether solutions of lithium aluminum hydride, which can ordinarily be safely evaporated, may also cause explosions if first treated with carbon dioxide in considerable amount.

Evaporation of dimethyl ether solutions of aluminum hydride and subsequent slow heating of the residue may result in a very rapid reaction in which, at slightly above 40°, relatively large quantities of gaseous material are suddenly released, but which is not accompanied by detonation, unless a large excess of aluminum chloride is present. But carbon dioxide-free ether leads to a residue which begins to decompose *slowly* above 70°, if aluminum chloride is not present in large amount; even in the presence of a large excess of the latter (2.5 moles/l.), the decomposition above 40° is sudden but without detonation. Other experiments have shown that aluminum chloride accelerates the decomposition of aluminum hydride.

On one occasion a violent explosion occurred when the residue resulting from evaporation of a dimethylcellosolve solution of aluminum hydride was warmed. The aluminum hydride was contaminated with aluminum chloride, which is known to decrease the stability of the former, and the dimethylcellosolve was impure. No explosion resulted when the experiment was repeated with purified materials.

Lithium aluminum hydride is considerably more stable than aluminum hydride. Approximately two hundred different reactions using the former reagent have been carried out in this Laboratory without untoward results although no precautions were taken to exclude carbon dioxide. We are, therefore, convinced that it may be used with perfect safety if the precautions suggested by the facts herein reported are followed. In other words, we recommend that in the reduction of organic compounds the normal procedure of hydrolyzing the initial reaction product before evaporation of the solvent be employed. If, as would rarely be the case, it is desired to evaporate the solvent before hydrolysis of the initially produced organic salts, the safety of the procedure should first be tested by use of a small sample.

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CRYSTALLINITY OF HYDRO-CELLULOSES

Sir:

Hydrolytic methods are being used at present for evaluating the intramolecular structure of cellulose. It has been suggested in a paper to be published in THIS JOURNAL that such methods might possibly cause additional crystallization in the initial stages of hydrolysis. We have succeeded in obtaining data which indicate that such changes do occur. Consequently, it would seem necessary to reinterpret accessibility measurements based on hydrolysis rates in terms of two competing processes: hydrolysis and further crystallization.

The data in Table I were obtained on a beechwood pulp that had been digested in boiling 2.5 *N* hydrochloric acid–0.6 *M* ferric chloride solution constantly saturated with air.

TABLE I

Time treated, minutes	Percentage of samples destroyed	Specific vol. of bone-dry hydrocellulose, ml./g.	Percentage increase in crystallinity from Sp *V*. change, %
0	0	0.652	
10	4.8	.647	15
19	6.0	.646	18
28	39.0	.645	19