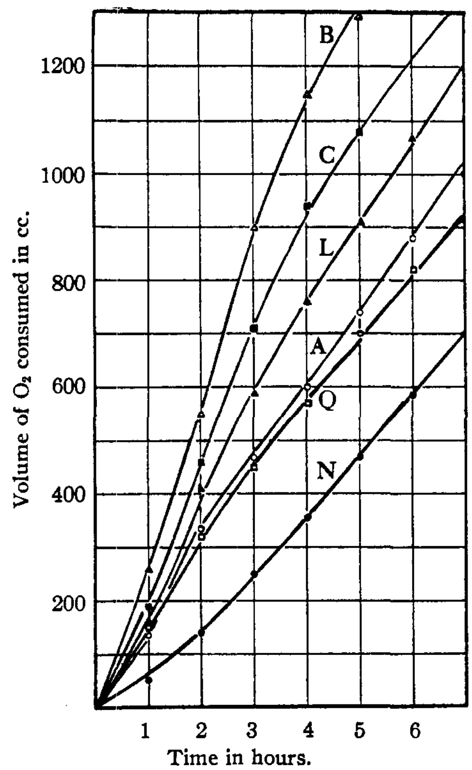

Fig. 1.—Effect of the addition of 0.001 *M* quantities of oxidation catalysts on the oxygen uptake in the oxidative condensation of 2-methoxy-4-nitrotoluene: ●, no catalyst, N; □, anthraquinone, Q; ○, acetone, A; ▲, cyclohexanol, L; ■, cyclohexanone, C; △, benzoquinone, B.

hexanol may be oxidized first to cyclohexanone which then acts as a catalyst. The total oxygen consumption was well above the expected theoretical amount. Therefore, oxygen was also used up in some side reaction.

Atmospheric oxygen as in the original method[1] was then tried in the presence of a catalyst and it proved to be effective. When benzoquinone was used and air bubbled through the reaction mixture for seven hours a 55% yield of the bibenzyl was obtained. When acetone was used and air bubbled through for twenty-two hours, 60% yield of a mixture of two parts of the bibenzyl and one part of the stilbene was obtained.

Experimental

Preparation of 2,2′-Dimethoxy-4,4′-dinitrobibenzyl.—Air is bubbled through a suspension of 10 g. of pure 2-methoxy-4-nitrotoluene in 200 ml. of 33% solution of methanolic potassium hydroxide containing one gram of benzoquinone for seven hours. The product is filtered, washed with dilute hydrochloric acid then with hot methanol and recrystallized from ethyl acetate, m. p. 179°; yield 5.5 g. On bromination it gives α,α'-dibromo-2,2′-dimethoxy-4,4′-dinitrobibenzyl, m. p. 247–249°.

Preparation of 2,2′-Dimethoxy-4,4′-dinitrobibenzyl and 2,2′-Dimethoxy-4,4′-dinitrostilbene.—Forty grams of 2-methoxy-4-nitrotoluene is placed in 800 ml. of 33% methanolic potassium hydroxide and 20 ml. of acetone. The mixture is well stirred and air is bubbled through at room temperature. After twenty-two hours the precipitate is filtered off. The mixture is then taken up in boiling ethyl acetate which dissolves the bibenzyl. The stilbene is filtered off and weighs 7.5 g. On cooling 16 g. of bibenzyl is collected from the ethyl acetate. The stilbene on bromination gives the same α,α'-dibromo-2,2′-dimethoxy-4,4′-dinitrobibenzyl as was obtained by brominating the bibenzyl.

Procedure Followed to Determine the Rate of Oxygen Consumption (see Fig. 1).—Ten grams of 2-methoxy-4-nitrotoluene and 0.001 *M* quantities of the different oxidation catalysts were placed in 200 ml. of 33% methanolic potassium hydroxide and shaken for twenty-two hours in the Adams shaker in the presence of oxygen at atmospheric pressure. The yield of mixture of the bibenzyl and the stilbene for all the catalysts tried varied between 30% and 38%. The mixture contained about equal quantities of the two substances.

RESEARCH LABORATORIES
SCHIEFFELIN & CO.
NEW YORK 3, N. Y.

RECEIVED SEPTEMBER 5, 1947

COMMUNICATIONS TO THE EDITOR

STUDIES ON THE MECHANISM OF THE DEAMINATION OF DIAZONIUM SALTS WITH HYPOPHOSPHOROUS ACID

Sir:

In an attempt to introduce a deuterium atom into the *meta* position of nitrobenzene, a deamination reaction with hypophosphorous acid[1] was carried out. Thus, to a solution of diazotized *m*-nitroaniline containing 30% deuterium oxide was added a solution of hypophosphorous acid in water which contained 50% of deuterium oxide. Before use the hypophosphorous acid solution was allowed to stand at room temperature for twenty-four hours. Much to our surprise *the nitrobenzene which was obtained was found to contain no deuterium.* This was determined for us by Mrs. James L. Johnson and Dr. Foil A. Miller with an infrared spectrometer.[2] Similarly, aniline hydrochloride prepared from this sample of nitrobenzene was found to show no absorption in the region of the C–D stretching frequencies (2270 cm.$^{-1}$).

We are not yet in a position to comment on the mechanism of the reaction, but this result is par-

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(1) See Kornblum, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 277.

(2) The lower limit of the sensitivity of this method for the detection of deuterium in an aromatic ring has not yet been completely determined. From dilution experiments conducted with deuterobenzene in benzene, however, it appears that if 1–2% of the nitrobenzene molecules contained deuterium, it could be detected.

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).

DEPARTMENT OF CHEMISTRY
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RECEIVED DECEMBER 22, 1947

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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RECEIVED DECEMBER 15, 1947

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