Summary

Monomethyldiethylmercaptoglucose has been isolated as a by-product from the preparation of pentamethyldiethylglucose.

New York City

NOTE

The Use of Aryl Esters for the Preparation of Amides and Derivatives of Urea.—During my investigations with Professor W. A. Noyes concerning optically active diazo compounds, the preparation of N-substituted acid amides was frequently necessary in order to separate certain stereoisomeric amines. They were also required as intermediate products in obtaining the diazo compounds. These preparations have been accomplished, usually, by condensation of the ethyl esters of the organic acids concerned with the amine by means of refluxing for several hours. In this condensation it has been observed that in general the esters of phenol or substituted phenols react more rapidly and at lower temperatures than the corresponding ethyl esters. Occasionally a considerable development of heat was noticed. Isolated examples of this behavior may be found in the literature. Diphenyl carbonate has been recommended as especially adapted for the preparation of urea, since it reacts very readily with ammonia even at water-bath temperature.[1] The corresponding ethyl ester reacts only by heating at 180° for a long time in a sealed tube.[2]

It has been recorded in the literature that guaiacol carbonate behaves with ammonia and amines in the same manner as diphenyl carbonate, forming urea or its N-substituted derivatives, instantly.[3] Dr. Noller, in this Laboratory, has recently prepared diphenylcarbazide $(C_6H_5NH\text{-}NH)_2\text{-}CO$, from phenylhydrazine and guaiacol carbonate.[4]

It has now been found that diphenyl carbonate reacts as readily with aniline, bornylamine and other amines as it does with ammonia. A mixture of bornylamine and diphenyl carbonate melts with an evolution of heat. By warming on the water-bath the reaction will be finished after five to ten minutes, with solidification. In the use of diethyl carbonate no action could be obtained even by heating to 180° in a sealed tube for four hours.

It has also been found that diphenyl oxalate shows a behavior very similar to the diphenyl and guaiacol carbonates, being much more reactive than the diethyl ester. Bornylamine and diphenyl oxalate react at 80° within a few minutes, forming dibornyloxamide, while the reaction with diethyloxalate requires refluxing for three to four hours. Also, the formation of

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[1] Hentschel, *Ber.*, **17**, 1286 (1884).

[2] Natanson, *Ann.*, **98**, 289 (1856).

[3] Cazeneuve, *Bull. soc. chim.*, [3] **15**, 714 (1896).

[4] Private communication.

oxanilide and other derivatives proceeds more rapidly when using the phenyl ester.

By the use of the aryl esters a method of obtaining N-substituted amides is available which is much more suitable than the one employing ethyl esters, ordinarily used. The phenol formed by the reaction can be removed easily by the addition of aqueous sodium hydroxide and filtering off the amide from the soluble phenolate. In some cases steam distillation of the phenol is possible. Aryl esters are easily obtained by treating a mixture of the phenolic compound and the free acid with phosphorus oxychloride. Of course, for preparation of the carbonate, phosphene is used.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

ULRICH HEUBAUM

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COMMUNICATIONS TO THE EDITOR

PHOTOSENSITIZATION BY AMMONIA

Sir:

A research by Farkas, Haber and Harteck[1] on the photosensitization of the oxidation of hydrogen and carbon monoxide by means of ammonia is so similar in concept to work at present in progress in this Laboratory that it seems desirable to record immediately our data already obtained.

The illumination of mixtures of ammonia and ethylene at room temperatures and 100° by a mercury arc produces a rapid reduction in pressure which does not obtain with ethylene alone or with ethylene–hydrogen mixtures. It is not, therefore, a mercury resonance-radiation effect but is determined by the ammonia. During the reaction an oil separates which, as it accumulates, slows down the reaction rate.

By analogy with our earlier work[2] with excited mercury one might attribute the pressure change to a polymerization of ethylene under the influence of atomic hydrogen liberated in the photodecomposition of ammonia. We have shown, however, that in the presence of ethylene the normal decomposition of ammonia is much retarded. In the presence of 15 cm. of ethylene the photodecomposition of 5 cm. of ammonia is reduced to 5% of the normal rate. A further distinction from the work with excited mercury is found when hydrogen is present in the reaction system. With hydrogen, ethylene and ammonia an equally rapid pressure decrease occurs on illumination but no hydrogen disappears. Hence, even in presence of hydrogen, the reaction is one of polymerization.

[1] Farkas, Haber and Harteck, *Naturwissenschaften*, **18**, 266 (1930).

[2] Taylor and Hill, THIS JOURNAL, **51**, 2922 (1929).