ON THE CONVERSION OF LEVOGLUCOSAN INTO AROMATIC COMPOUNDS

[Reaction scheme shown on the page.]

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Abstract

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ON THE CONVERSION OF LEVOGLUCOSAN INTO AROMATIC COMPOUNDS

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The transition from carbohydrates to carbocyclic compounds was first carried out in the laboratory by Micheel (1), who obtained dimethylenetetraoxycyclohexane by the action of silver on 1,6-diiododimethylmannitol upon heating at 165—170° for 8 hours. The first successful attempt to convert carbohydrates into aromatic compounds was carried out by P. P. Shorygin and N. N. Shorygina (2): by the action of metallic sodium in liquid ammonia on trimethyllevoglucosan, phenol was obtained in a yield of 34%. The authors proposed a scheme for this transformation based on the cleavage of simple ether bonds by metallic sodium.

[Reaction scheme shown on the page.]

The present communication is a continuation of the indicated investigation, the aim of which is a more detailed study of this interesting reaction.

Levoglucosan was obtained by dry distillation of starch in vacuo with a yield of 14%; its trimethyl ether was obtained by methylation with dimethyl sulfate. An experiment carried out under conditions analogous to those described (2) gave the same result—phenol was obtained in a yield of 31%.

Certain changes in carrying out the reaction and in isolating the reaction products made it possible to obtain phenol in a yield of 50–56% of theory (according to the scheme given above).

The experiments were carried out as follows: a weighed portion of trimethyllevoglucosan was placed in a 300-ml ampoule, dissolved in dry liquid ammonia, and then metallic sodium was gradually added to the solution over the course of 30 min. The ampoule was left overnight (18 hours) in a Dewar vessel with dry ice; on the following day the ampoule was sealed and left at room temperature. The end of the reaction was determined by complete decolorization of the dark-blue solution of sodium in ammonia. Before opening, the ampoule was cooled, the ammonia was removed, and the contents were treated first with moist ether and then with water acidified with H_2SO_4. The ethereal extract from the acidic (to Congo) aqueous solution was dried over anhydrous Na_2SO_4. After removal of the ether, a dark-brown syrup remained, from which phenol was distilled with steam. The amount of phenol in the distillate was determined by the Koppeschaar method. The ethereal extract from the aqueous distillate, after drying and removal of the ether, gave pure phenol, crystalliz-

separating out on cooling and giving a characteristic benzoate with m.p. 68-69°, by the Schotten–Baumann reaction.

The results of the experiments (see Table 1) showed that phenol is the main product of the reaction.

Periodic shaking of the reaction mixture after sealing the ampoule, as expected, accelerated the reaction almost 5-fold (see Table 1; expts. 4, 5). It also seemed of interest to determine the effect of the amount of sodium on the yield of phenol. The formation of bright-red products of the interaction of trimethyllevoglucosan with metallic sodium, which disappear with time, makes it possible to suppose that sodium-organic compounds are intermediates in this reaction.

Table 1

No.	Trimethyllevoglucosan (mol.)	Sodium (mol. per mol. of trimethyllevoglucosan)	Liquid ammonia (ml)	Reaction time (days)	Phenol yield (%)	Notes
1	0.005	6	15	16	50	
2	0.019	6	45	16	56	
3	0.02	6	50	16	54	
4	0.01	6	25	3	51	Shaking of the ampoule on a rocking apparatus
5	0.005	6	15	3	55	Same

As is evident from the experiments given in Table 2, the yield of phenol is directly proportional to the amount of sodium up to a maximum corresponding to 6 atoms per molecule of trimethyllevoglucosan, required for cleavage of 3 ether groups.

In experiments with a smaller amount of sodium, unreacted trimethyllevoglucosan was isolated; an excess of sodium does not increase the yield of phenol.

This fact is of substantial importance, since it indirectly confirms the reaction scheme proposed by P. P. Shorygin and N. N. Shorygina,

Table 2

No.	Trimethyllevoglucosan (mol.)	Sodium (mol. per mol. of trimethyllevoglucosan)	Liquid ammonia (ml)	Reaction time (days)	Phenol yield (%)
1	0.01	3	25	3	24.5
2	0.01	4.5	25	4	41.8
3	0.01	6	25	4	51
4	0.01	9	25	8	52

As was shown further by the experiments summarized in Table 3, the course of the reaction is affected by temperature: the formation of phenol depends on the time of preliminary holding of the reaction mixture at the temperature of dry ice. The shorter the holding period, the faster the reaction proceeded, but the yield of phenol decreased. The minimum cooling time necessary for obtaining the maximum yield of phenol was established. In addition to monohydric phenol, the formation of dihydric phenols, pyrocatechol and resorcinol, was detected.

From the aqueous solution, after distillation of the phenol, an ether extract was taken. After drying and removal of the ether, a dark syrup remained, which was chromatographed. Chromatograms were obtained on crab paper by the

Table 3

No.	Trimethyllevoglucosan (mol)	Sodium (mol per mol of trimethyllevoglucosan)	Liquid ammonia (ml)	Ampoule cooling time (h)	Time before discoloration of the reaction mixture at room temperature (h)	Phenol yield (%)
1	0.005	6	15	2	3	40.6
2	0.005	6	15	5	3	44
3	0.005	6	15	8	50	48
4	0.005	6	15	10	50	55
5	0.005	6	15	19	50	53
6	0.005	6	15	25	50	51

descending method. A solvent mixture of benzene—petroleum ether—water (1 : 1 : 1) was used; diazotized sulfanilamide served as the developer.

Work on the study of the carboxylation reaction of 1,6-anhydrohexoses is continuing.

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Note: Figure translations are in progress. See original paper for figures.