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Synthesis of 2,3,6-Trimethylbenzyl Alcohol

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Synopsis. 2,3,6-Trimethylbenzyl alcohol was prepared by the Cannizzaro reaction of 2,3,6-trimethylbenzaldehyde; mp 83—85 °C. It was found that the substance regarded by Golivets *et al.* as 2,3,6-trimethylbenzyl alcohol is an eutectic mixture of 2,3,6- and 2,4,5-trimethylbenzyl alcohol.

In the condensation of 1,2,4-trimethylbenzene(1,2,4-TMB) with formaldehyde, bis(2,4,5-trimethylphenyl)-methane was formed as the main product, and a few asymmetric hexamethyldiphenylmethanes(HeMDPM) such as 2,3,6,2′,4′,5′-HeMDPM were formed as by-products.[1] As the routes for the formation of 2,3,6,-2′,4′,5′-HeMDPM, the reaction of 1,2,4-TMB with 2,3,6-trimethylbenzyl alcohol(2,3,6-TMBA) and/or the reaction of 1,2,4-TMB with 2,4,5-TMBA are considered. These TMBA's are formed a sprimary products in the condensation of 1,2,4-TMB with formaldehyde.

In order to obtain the starting materials for an investigation of this reaction scheme we attempted the synthesis of alcohols.

In the preparation of 2,4,5-TMBA(mp 83—84 °C) by the hydrolysis of monoacetoxymethyl-1,2,4-trimethylbenzenes obtained by the chloromethylation of 1,2,4-TMB and subsequent acetoxylation, Golivets *et al.*[2] isolated a substance (A) melting at 55—56 °C, which they regarded as 2,3,6-TMBA.

We also obtained a small amount of the substance (mp 54—55 °C) by the above reactions. However, from its IR and NMR spectra measurements, and mixed melting point test, it was suggested that the substance is not pure and that it might be an eutectic mixture of 2,3,6- and 2,4,5-TMBA.

We have applied the Cannizzaro reaction of 2,3,6-trimethylbenzaldehyde to the synthesis of 2,3,6-TMBA.

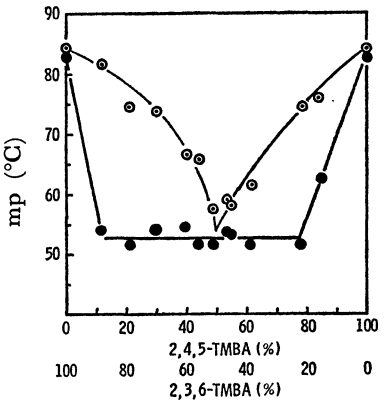

Fig. 1. Melting-point curve of 2,3,6-TMBA and 2,4,5-TMBA.

This was prepared by Lowe *et al.*[4] We obtained 2,3,6-TMBA as colorless needles, melting at 83—85 °C. For an estimation of its purity we attempted its hydrogenolysis[3] with a CoO–MoO_3–Al_2O_3 catalyst. The products obtained were tetramethylbenzenes(TeMB) and 1,2,4-TMB. The former consists of 1,2,3,4-: 98%, 1,2,4,5-: 1.1%, and 1,2,3,6-TeMB: 0.9%. The latter was formed by the dehydroxymethylation of the TMBA. Thus it was found that the purity of 2,3,6-TMBA obtained was 98%.

The IR spectrum of 2,3,6-TMBA showed a characteristic band assigned to two adjacent hydrogen systems at 805 cm^{-1}, and that of 2,4,5-TMBA three bands due to one adjacent hydrogen system in the 900—875 cm^{-1} regions. The IR spectrum of (A) showed two absorption bands in both regions. The NMR spectrum of (A) showed two absorptions at δ 4.52 and 4.39, assigned to the methylene hydrogens of 2,3,6- and 2,4,5-TMBA, respectively. The results suggest that (A) is a mixture of these alcohols.

We have made the melting-point curve of binary system of these alcohols. The eutectic mixture of the system consists of 2,3,6- (50%) and 2,4,5-TMBA (50%), melting at 53—54.5 °C. The melting point of the eutectic mixture agrees with that of (A).

Experimental

Hydrolysis of Monoacetoxymethyl-1,2,4-trimethylbenzenes: Monoacetoxymethyl-1,2,4-trimethylbenzenes (145 g, bp 105—108 °C/1 mmHg), prepared by acetoxylation of chloromethylated 1,2,4-TMB, KOH (46.9 g) and absolute methanol (295 ml) were refluxed with stirring for 2 hr. After cooling the separated crystal was collectd. White precipitate was formed by the dilution of the filtrate with twice its volume of water. By recrystallization of these solids from 30% methanol aqueous solution, white needles, 2,4,5-TMBA (mp 83—84 °C, 85 g, 63% yields) were obtained. White needles (substance (A)) (mp 54—55 °C, 1 g) were separated from the mother liquid.

A mixture of (A) and 2,4,5-TMBA showed no depression in melting point.

2,3,6-Trimethylbenzaldehyde: This was prepared by the method of Lowe *et al.* bp; 87—88 °C/1 mmHg (lit,[4] bp 111—114 °C/5 mmHg).

2,3,6-Trimethylbenzyl Alcohol: To a methanolic solution (75 ml) of KOH (50 g) was added a mixture of 2,3,6-trimethylbenzaldehyde (44 g) and formalin (37% concn., 29 ml) in methanol (30 ml) with stirring at 60 °C. After being kept at 60—70 °C for 3 hr, 90 ml of ice water was added. The yellowish solid was separated and recrystallized from 25% methanol aqueous solution. Colorless needles, 2,3,6-TMBA (mp 83—85 °C, 12 g), were obtained.

Found: C, 79.71; H, 9.41; O, 10.88%. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39; O, 10.65%.

References

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