Notes

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Shigehiko Sugasawa and Yoji Arata: A Synthesis of 6-Formylbenzodioxane.

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Due to the personal reason of one of us (Y. A.) a projected synthesis using 6-formylbenzodioxane as one of the starting materials had to be postponed and therefore the preparation of this aldehyde only will be placed on record.

This aldehyde was first prepared by Moureau[1] by treating protocatechuic aldehyde with ethylene bromide in the presence of sodium ethoxide with unspecified yield. Later, Gattermann[2] succeeded in introducing formyl group into benzodioxane by his own general method for preparing aromatic hydroxyaldehydes. It was now found that the aldehyde could more conveniently be prepared by applying Gattermann-Adams method[3] to benzodioxane. The commercial zinc cyanide was found quite useful in this reaction and the product obtained formed colorless needles of m.p. 49.5∼50.5° (reported m.p. 50∼51.5°) after one purification from hexane. Its structure was proved beyond doubt by direct comparison with an authentic sample prepared through ethylenation of protocatechuic aldehyde.

Experimental

To a solution of benzodioxane (20.4 g., 0.15 mole) in pure benzene (200 cc.) was added finely powdered dry $Zn(CN)_2$ (152.7 g., 0.45 mole, of commercial product), and dry HCl gas stream was introduced briskly into this solution for ca. 1.5 hrs. with vigorous stirring and cooling, the mixture assuming a pinkish color. Finely powdered $AlCl_3$ (59.9 g., 0.45 mole) was now added in small portions and after the addition, dry HCl gas was again introduced for ca. 4 hrs., during which time the temperature of the mixture was raised to 40∼45°, the color now changing from brown to dark purple. The whole was allowed to stand over night. The condensation product was then decomposed, together with unreacted $Zn(CN)_2$ and $AlCl_3$, by adding an excess of 10% HCl with cooling and stirring, precipitating a dark yellow substance. The mixture was now gently refluxed on a water bath for 0.5 hr., when the precipitate disappeared, separating into two layers. The aqueous layer was extracted with benzene, which solution was combined with the original benzene layer, washed, dried, and the solvent was removed, leaving a faint yellow oil, which soon solidified on standing to a mass of m.p. 48∼50°. Yield, 18 g. or 73%. Purified once from hexane, forming colorless needles of m.p. 49.5∼50.5°. The aldehyde could also be separated from the benzene solution by $NaHSO_3$ with nearly the same result.

On the other hand, protocatechuic aldehyde and ethylene bromide were refluxed in AcOEt in the presence of powdered, ignited K_2CO_3 and a little Cu powder, furnishing the neutral aldehydic portion in a poor yield (less than 10%), which, when purified from hexane, formed colorless needles of m.p. 49∼50.5°, alone or on admixture with the specimen obtained above.

Summary

6-Formylbenzodioxane was prepared by applying Gattermann-Adams method to benzodioxane in 73% yield as a crude product of m.p. 48∼50° (pure substance melts at 49.5∼50.5°) pure enough for most purposes. The position of the formyl group was proved beyond doubt by direct comparison with an authentic sample. The commercial zinc cyanide was found quite useful in this reaction.

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[2] L. Gatterman : Ann., **357**, 373(1907).

[3] R. Adams, Montgomery : J. Am. Chem. Soc., **46**, 1520(1924).