

SYNTHESIS OF BENZO-1,4-DIOXANE IN THE PRESENCE OF
INTERPHASE CATALYSTS

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Quaternary ammonium salts markedly accelerate the formation of benzo-1,4-dioxane from 1,2-dibromoethane and pyrocatechol under the influence of aqueous alkali and increase its yield.

Of the various methods for the preparation of benzo-1,4-dioxane [1], the most widely used procedure is the reaction of pyrocatechol with 1,2-dihaloethanes in the presence of aqueous solutions of alkali. At the same time, its realization is hindered by the mutual insolubility of the reagents. This problem is usually solved by using solvents that have simultaneously hydrophilic and lipophilic properties (glycerol, dioxane, and acetone) or dipolar aprotic solvents (hexametapol, dimethyl sulfoxide, and dimethylformamide), which solvate the cation of the nucleophile and make its anion relatively free and, consequently, more reactive [2, 3]. However, the use of such solvents is restricted by their high cost and the difficulties encountered in their purification, drying, and regeneration. It therefore seemed of interest to study the possibility of the use of interphase catalysts [4] in the synthesis of benzo-1,4-dioxane.

Kinetic experiments show that this reaction, both in the absence and presence of interphase catalysts, is satisfactorily described by a second-order equation. The addition of $[(C_2H_5)_4N^+I^-]$ and $[(CH_3)_2C_{16}H_{33}N^+(CH_2)_2NC_{16}H_{33}(CH_3)_2]2Br^-$ in concentrations of 0.005 mole/liter increases the reaction rate by factors of two and 25, respectively. A study of the dependence of the yield of benzo-1,4-dioxane on the nature of the additive (Table 1) shows that the use of ammonium salts leads to doubling of the yield; compounds with two quaternary nitrogen atoms in their molecules give the best results. Thus the results of our study indicate the promising character of interphase catalysts in the synthesis of benzo-1,4-dioxane.

EXPERIMENTAL

Pyrocatechol, dibromoethane, K_2CO_3 , NaOH, decane, o-dichlorobenzene (chemically pure-grade), dibenzo-18-crown-6, PEG-3000, sodium stearate, and $[(C_2H_5)_4N^+I^-]$ were used as the

TABLE 1. Dependence of the Yields of Benzo-1,4-dioxane on the Type of Catalyst

Catalyst	Yield, %
PEG-3000	43
Dibenzo-18-crown-6	40
$[C_{16}H_{33}N^+(CH_3)_3]CH_3SO_4^-$	71
$[C_{16}H_{33}N^+(CH_3)_2(CH_2)_4(CH_3)_2NC_{16}H_{33}]2Br^-$	77
$[C_{16}H_{33}N^+(CH_3)_2CH_2CH=CHCH_2(CH_3)_2NC_{16}H_{33}]2Br^-$	84
$[C_{15}H_{31}CH(OH)CH_2CH_2N^+(CH_3)_3]Cl^-$	76
$[C_{16}H_{33}(CH_3)_2N^+CH_2CH_2N^+(CH_3)_2C_{16}H_{33}]2Br^-$	89
$C_{17}H_{35}COONa$	48
Without a catalyst	44

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reagents. The quaternary ammonium salts were synthesized by refluxing trialkylamines with the corresponding halo derivatives in benzene or alcohol.

The kinetic experiments were carried out at $60 \pm 0.5^\circ\text{C}$ in an inert gas atmosphere. A 1.88-g (10 mmole) sample of 1,2-dibromoethane, 2.75 g (25 mmole) of pyrocatechol, 1 g of decane (the internal standard), and the catalyst were dissolved in 50 ml of o-dichlorobenzene, after which 50 ml of 2 N aqueous NaOH solution was added, and 0.5-ml samples (in 1 ml of 3 N HCl) were withdrawn at definite time intervals. After separation of the layers, the organic layer was analyzed by gas-liquid chromatography (GLC) [with an LKhM-8MD chromatograph with a 3×0.003 m steel column packed with 10% Apiezon L on Chromaton N AW (0.2 mm); the column temperature was 180°C , the detector was a catharometer, the carrier gas was hydrogen, and the flow rate was 35 ml/min]. The reaction rate was estimated from the magnitude of the effective rate constant.

To study the effect of additives on the yield of benzo-1,4-dioxane a mixture of 56.4 g (0.3 mole) of 1,2-dibromoethane, 40 ml of water, and 0.001 mole of the appropriate catalyst was heated to the boiling point, a solution of 22 g (0.2 mole) of pyrocatechol and 20 g (0.5 mole) of NaOH in 100 ml of water was added dropwise in the course of 2 h, and the mixture was stirred for another hour. It was then extracted twice with 40-ml portions of benzene, and the extract was dried with K_2CO_3 . The benzene was removed by distillation, and the benzo-1,4-dioxane was distilled at 100°C [20 mm (mercury column)].

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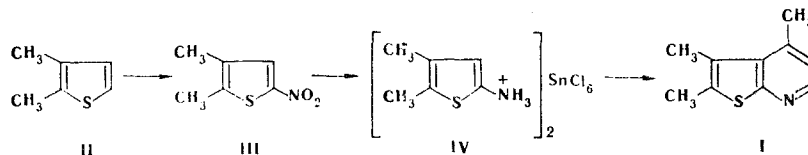
SYNTHESIS OF 2,3,4-TRIMETHYLTHIENO[2,3-b]PYRIDINE

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2,3,4-Trimethylthieno[2,3-b]pyridine was obtained by the reaction of 2,3-dimethyl-5-ammoniothiophene hexachlorostannate with methyl vinyl ketone in the presence of ferric chloride and zinc chloride.

4-Methylthieno[2,3-b]pyridine, which serves as the starting compound for the synthesis of various polymethine dyes, was described in [1]. It was subsequently established that the photographic effectiveness of sensitizing dyes that are derivatives of heterocyclic compounds that contain a condensed thiophene ring is increased significantly if there are methyl groups in the 2 and 3 positions of the thiophene ring [2]. In this connection, we accomplished the synthesis of the previously undescribed 2,3,4-trimethylthieno[2,3-b]pyridine (I) on the basis of 2,3-dimethylthiophene (II) via the scheme



Compound II was synthesized by known methods on the basis of disodium methylsuccinate; the characteristics of all of the intermediates were in agreement with the literature data [3-5].

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