Preparation of 4-Nitrostyrene

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Abstract—The interaction of D,L-1-(4-nitrophenyl)ethanol with SOCl₂ and P₄O₁₀ has been studied. In the reaction of D,L-1-(4-nitrophenyl)ethanol with SOCl₂ a mixture of 1-(4-nitrophenyl)-1-chloroethane, 1,1'-bis-(4-nitrophenyl)diethyl ether, and 4-nitrostyrene (yield 21%) has been formed. The direction of reaction of D,L-1-(4-nitrophenyl)ethanol with P₄O₁₀ in toluene has been affected significantly by the order of reagents addition and the solution concentration. 4-Nitrostyrene has been obtained in the only case: the addition of P₄O₁₀ to a diluted solution of D,L-1-(4-nitrophenyl)ethanol and subsequent refluxing. Also the procedure of 4-nitrostyrene preparation via the cleavage of 2-(4-nitrophenyl)ethyl nitrate with alkoxy anion in the alcoholic solution has been upgraded.

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Nowadays several methods of 4-nitrostyrene preparation are known, for instance, decarboxylation of 4-nitrocinnamic acid in the presence of quinoline and copper powder at 160–165°C [1, 2] dehydrohalogenation of β-(4-nitrophenyl)ethyl bromide in the presence of triethanolamine [3], and the interaction of 2-(4-nitrophenyl)ethyl nitrate with alkaline reagents [5, 6]. However, the latter method has remained imperfect, being time-, energy-, and materials-consuming and giving only a crude product that requires purification. Other procedures to prepare 4-nitrostyrene have not been described so far. Therefore, development of new synthetic pathways to this compound as well as improvement of the existing procedures is an important task.

This work aimed at a study of D,L-1-(4-nitrophenyl)ethanol interaction with thionyl chloride and phosphorus(V) oxide and at an upgrading of the known method of 4-nitrostyrene preparation via the treatment of 2-(4-nitrophenyl)ethyl nitrate with alkoxy anion.

The starting 4-nitroacetophenone was reduced in ethanol or methanol, avoiding heating above 30°C;
that gave nitroalcohol II in 93.8–100% yield without amine impurities. Further treatment of II with SOCl₂ gave a mixture of products III–V, the corresponding chloro derivative being the major one. After elimination of most part of minor 1,1'-bis-(4-nitrophenyl)-diethyl ether, we obtained a mixture containing about 21% of 4-nitrostyrene (¹H NMR).

In [4] 3-nitrostyrene was obtained with low yield via dehydration of 1-(3-nitrophenyl)ethanol with phosphorus(V) oxide in benzene solution. The amount of consumed P₄O₁₀ and the reaction duration were not reported; the described procedures implied a set of technology cycles. In this work, the dehydration of p-isomer of nitroalcohol II was performed in toluene solution, thus the reaction temperature could be increased, whereas the reaction duration was shortened. In the case of P₄O₁₀ addition to the diluted solution of 1-(4-nitrophenyl)ethanol and subsequent refluxing the dehydration became the major reaction pathway. After isolation of organic part and steam distillation of major part of starting nitroalcohol with admixture of 4-nitrostyrene, a mixture of products was obtained containing 60–70 mol % of 4-nitrostyrene. For the reaction to proceed smoothly, the solvent should be anhydrous.

From the ¹H NMR spectrum (see the Figure), the major component of the products mixture was 4-nitrostyrene. To the CH₂= protons corresponds the doublet of doublets at δ = 5.536–5.564 ppm, the vicinal proton at the double bond appeared as quartet at δ of 6.904–6.948 ppm, whereas the aromatic protons at the 2, 6 and 3, 5 appeared at doublets at 7.79, 7.81 ppm (J = 8.83 Hz) and 8.23, 8.25 ppm (J = 8.73 Hz), respectively.

When the reagents were mixed without solvent, their interaction was faster, in particular, after a short induction period the exothermic decomposition of the reaction products occurred. If a certain amount of solvent with high boiling point was added to the mixture prior to the start of the uncontrolled reaction, it allowed for efficient heat exchange, and the process was fast but safe. Within 15–20 min of such reaction a mixture of products was obtained, however, containing only minor amount of 4-nitrostyrene. Its subsequent treatment with phosphorus(V) oxide under reflux during 5.5 h gave a solid complex compound, decomposition of it with water gave a mixture lacking 4-nitrostyrene.

As was discussed above, the method of 4-nitrostyrene production via nucleophilic cleavage of 2-

![1H NMR spectrum of the residue after volatile compounds after steam distillation.](image-url)