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SUPPRESSION OF THE INHIBITING EFFECT OF HARD NUCLEOPHILES ON THE HALOALKYLATION REACTION

Malle SCHMIDT, Koit LAATS. TUGEVATE NUKLEOFIILIDE INHIBEERIVA TOIME ELIMINEERIMINE HALOALKÜLEERIMISREAKTSIOONIDES

Малле ШМИДТ, Коит ЛЭАТС. УСТРАНЕНИЕ ИНГИБИРОВАНИЯ ЖЕСТКИМИ НУКЛЕОФИЛАМИ В РЕАКЦИЯХ ГАЛОАЛКИЛИРОВАНИЯ

Hard nucleophiles such as water, alcohols, and amines prevent haloalkylation of alkenes in the presence of Lewis acids. The presence of alcohols in the reaction medium also decreases the yield and content of monoadducts in the chloroalkoxymethylation products of alkenes [1].

Usually the technical initial haloalkylation agent, alkoxychloromethane, contains a small amount of alcohol which is difficult to remove. Taking this into account, the authors studied the inhibiting effect of isopropanol on the chloroalkoxymethylation of 2-methyl-1,3-butadiene in the presence of $ZnCl_2$. It was established that the inhibiting effect of alcohols on the electrophilic addition of alkoxychloromethanes to alkenes may be suppressed by introducing chloromethoxychloromethane into the reaction mixtures in an amount equimolar to alcohol.

The effect of isopropanol on the yield of monoadducts and the kinetics of haloalkylation of isoprene is demonstrated in Figs. 1 and 2, respectively. The dependence of the yield of monoadduct of chloroisopropoxymethylation of isoprene in the presence of $ZnCl_2$ as catalyst on the ratio of chloromethoxychloromethane (dichloroether) to alcohol is shown in Fig. 3. The results indicate that the growth of the concentration of dichloroether up to the amount equimolar to alcohol in the presence of 0.01—0.03 moles of isopropanol in the reaction medium increases the yields of monoadducts by 75% to reach those obtained in the presence of $ZnCl_2$ without isopropanol. It was established that the composition of monoadducts does not depend on the presence of isopropanol and dichloroether in the reaction medium.

The method enables to use alcohol solutions of catalysts poorly soluble in the reaction medium as well as ingredients not purified from nucleophilic additives in order to initiate the reaction.

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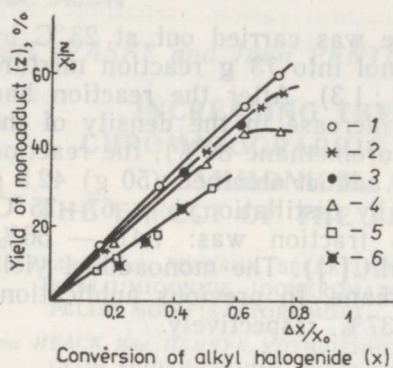


Fig. 1. The effect of isopropanol on the monoadducts yield of haloalkylation of isoprene in the presence of $ZnCl_2$. Concentration of isopropanol (mole/reagent mole): 1 — 0.00; 2 — 0.014; 3 — 0.026; 4 — 0.041; 5 — 0.068; 6 — 0.11.

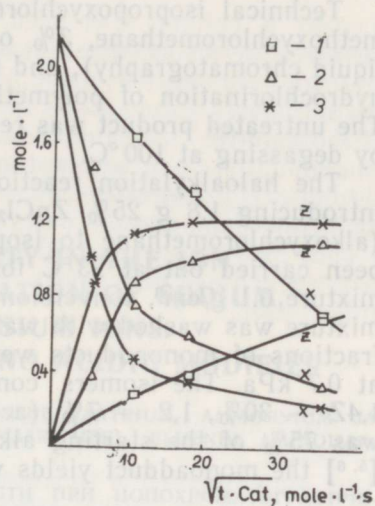


Fig. 2. Reaction time dependence on the concentration of the initial alkyl halogenide (x) and the monoadduct formed (z) in the reaction of chloroisopropoxymethylation of isoprene in the presence of $ZnCl_2$. Concentration of isopropanol 1 — 0.068; 2 — 0.041; 3 — 0.014.

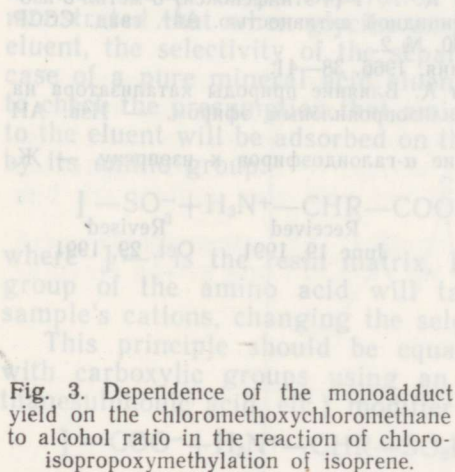


Fig. 3. Dependence of the monoadduct yield on the chloromethoxychloromethane to alcohol ratio in the reaction of chloroisopropoxymethylation of isoprene.

Experimental

The experiment was carried out using an ion chromatographic system equipped with... In determining the kinetic constants of haloalkylation of isoprene with isopropoxychloromethane [2] the halogen derivatives containing 3% dichloroether have been used as starting reaction mixtures. The low deactivation constant values of the catalyst ($r_s=0.01$) calculated in [2] also confirm the suppression of the inhibiting effect of alcohols by chloromethoxychloromethane. The synthesis of an intermediate to obtain juvenoid efoksen (JHA 80 A) — 1-chloro-3-methyl-5-isopropoxy-2-pentene [3] — from technical ingredients in the presence of $ZnCl_2$ solution in isopropanol has been presented.

Technical isopropoxychloromethane (88%) containing 3% of chloromethoxychloromethane, 3% of diisopropoxymethane (according to gas liquid chromatography), and 6% of nondistilled residue was prepared by hydrochlorination of polymethanal and isopropanol [4] (1.1 : 1) at 5°C. The untreated product was released from the dissolved hydrogen chloride by degassing at 100°C.

The haloalkylation reaction of isoprene was carried out at 23°C by introducing 1.8 g 25% ZnCl₂ in isopropanol into 73 g reaction mixture (alkoxychloromethane to isoprene ratio 1 : 1.3). After the reaction had been carried out at 23°C for 150 min (increase in the density of the mixture 0.1 g/cm³, conversion of alkoxychloromethane 80%), the reaction mixture was washed with water. From the adduct obtained (50 g) 42.5 g fractions of monoadducts were separated by distillation, b. p. 67–75°C, at 0.7 kPa. The isomers content in this fraction was: 1,4E — 56%, 1,4Z — 30%, 1,2 — 7% (according to GLC[5]). The monoadduct yield was 75% of the starting alkoxychloromethane. In previous publications [5, 6] the monoadduct yields were 65 and 37%, respectively.

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