Letters to the Editor

Lithium-sodium synergism in alkylation of toluene and naphthalene with ethene under the action of the ArH/alkali metal systems in THF

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Recent studies demonstrated an unexpectedly high efficiency of naphthalene/alkali metal systems in THF toward activation of C—H bonds in hydrocarbons.[1—3] It was found, in particular, that systems of this type, which are formed on treatment of naphthalene with metallic lithium, sodium, or potassium, are able to perform alkylation of toluene and naphthalene with ethene under mild conditions.[3] In these reactions, which occur at room temperature, toluene is converted into higher monoalkylbenzenes and naphthalene is transformed into alkylnaphthalenes. The efficiency of alkylation depends substantially on the nature of the alkali metal and the hydrocarbon used and on other factors. Study of sodium-containing systems showed that the yield of alkylation products considerably increases when the Na : naphthalene molar ratio increases from 1 : 1 to 2 : 1 and diminishes almost to zero when the reaction is carried out in the presence of 15-crown-5.

In this study, we report on an unusual synergistic effect of lithium and sodium on the course of the above-mentioned alkylation reactions. The discovery of this synergistic effect not only makes it possible to increase substantially the efficiency of alkylation but is also of great importance for elucidation of the mechanism of activation of C—H bonds in hydrocarbons by such systems.

The experiments were carried out by a standard procedure with thorough exclusion of oxygen and air moisture. The starting solid and liquid components were placed in a Schlenk tube under Ar, and the mixture was stirred at room temperature in an ethene atmosphere for 24 h. The amount of naphthalene was 3 mmol, and its initial concentration was 2 mol L^{-1}. The relative amounts of Li and Na were varied but an (Li + Na) : $C_{10}H_8$ molar ratio equal to 2 : 1 was maintained. The experiments with toluene were carried out at an equimolar PhMe : naphthalene ratio. The products were analyzed by GLC and GC/MS. In addition to the naphthalene-containing systems, similar systems containing phenanthrene were also studied ((Li + Na) : phenanthrene = 3 : 1).

The greatest synergistic effects were observed in the alkylation of toluene. It was found that naphthalene-based systems exhibit the highest activity when Li : Na = 1 : 3. When this particular Li : Na ratio is used, the reaction of toluene with ethene affords *n*-propylbenzene

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(47%), 3-phenylpentane (44%), and 3-phenylheptane (3%) in a total yield of 94% based on toluene. In the absence of sodium, the degree of conversion of toluene into alkylation products does not exceed 48% (*n*-propylbenzene, 30%; 3-phenylpentane, 8%, 3-phenylheptane, 5%; and *n*-pentylbenzene, 5%), and in the absence of lithium, the degree of conversion is only 18% (*n*-propylbenzene, 15%, and 3-phenylpentane, 3%).

Alkylation of naphthalene with ethene in the presence of toluene is also accelerated when both alkali metals are present in the mixture; however, in this case, the dependence of the system activity on the proportions of lithium and sodium does not pass through a clear-cut maximum. For a Li : Na ratio ranging from (1 : 5) to (4.5 : 1.5), the total yield of naphthalene alkylation products (1-ethyl-, butyl-, hexyl-, and octylnaphthalenes and their dihydro derivatives) varies in the 72—78% range. If the reaction is carried out without sodium, the yield of these products decreases to 55%, while in the absence of lithium, it diminishes to 38%. The system with Li : Na = 2 : 1 is the most active toward alkylation of naphthalene without toluene. The reaction of ethene with this system affords the above-listed alkylnaphthalenes and their dihydro derivatives in a total yield of 81%. When either lithium or sodium alone (instead of a mixture of Li and Na) is used, the degree of conversion of naphthalene into alkylation products again substantially decreases (to 60 and 32%, respectively).

Similar synergistic effects are observed in systems based on phenanthrene. For example, when the Li : Na ratio in the phenanthrene-containing system is 1 : 2, the yield of products of toluene alkylation with ethene reaches 91% of the theoretical value with respect to toluene (*n*-propylbenzene, 43%; 3-phenylpentane, 45%; and 3-phenylheptane, 3%). An increase and a decrease in this ratio both diminish the alkylation efficiency. In the absence of sodium, the degree of conversion of toluene into alkylation products is only 36% (*n*-propylbenzene, 27%; 3-phenylpentane, 3%; 3-phenylheptane, 2%; and *n*-pentylbenzene, 4%), and that without lithium is 11% (*n*-propylbenzene, 10%; and 3-phenylpentane, 1%).

Thus, the use of synergistic mixtures of lithium and sodium opens up the way to almost quantitative transformation of toluene into higher monoalkylbenzenes and to a substantial increase in the degree of conversion of naphthalene into alkylation products. The synergistic effects of alkali metals in olefin oligomerization have been described in a review.[4] In these reactions, occurring at elevated temperatures, alkali metals were used as dispersions and were not activated by addition of aromatic promoters.

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Simple synthesis of 1,4,8-triazabicyclo[5.3.0]dec-4-ene derivatives from β-amino-β-polyfluoroalkylvinyl ketones and diethylenetriamine

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It is known[1] that heating of β-amino-β-polyfluoroalkylvinyl ketones **1a,b** with diethylenetriamine to 90 °C over 36 h afforded a mixture of 1,5-di(polyfluoroacyl)amino-3-azapentanes and *N,N'*-(3-azapentamethylene)-bis(3-amino-3-polyfluoroalkyl-1-phenylprop-2-en-1-ones) in a ratio of 1 : 2. We found that the reactions of aminoenones **1a—d** with diethylenetriamine without a solvent at room temperature over 4—7 days afforded compounds **2a—d**, which are derivatives of the new fused triazabicyclo[5.3.0]dec-4-ene system containing a bridgehead nitrogen atom, in 64—74% and 25—33% yields in the case of the trifluoromethyl and tetrafluoroethyl substituents, respectively. In this case, diethylenetriamine acted as a trinucleophile and its reactions with aminoenones **1a—d** involved the double nucleophilic addition at the β-carbon atom with elimination of am-

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