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ON THE INTERACTION OF ORGANOLITHIUM COMPOUNDS WITH SODIUM AND POTASSIUM ALKOXIDES.
A NEW METHOD FOR THE SYNTHESIS OF ORGANOSODIUM AND ORGANOPOTASSIUM COMPOUNDS

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In the investigation of the mechanism of anionic methyl methacrylate polymerization we also attempted to find some relationships between the initiation and the structure of organic derivatives of alkali metals. In this connection we have studied up to now in some detail the interaction between organolithium compounds and lithium alkoxides. These compounds form in some cases stable association compounds[1]. The investigation of these systems has now been extended to sodium and potassium alkoxides. Between organolithium and the latter compounds a reaction takes place which may be expressed schematically by the equation

$$\text{t-BuOMe} + \text{RLi} \longrightarrow \text{RMe} + \text{t-BuOLi}$$

(where Me = Na, K). It probably proceeds via an intermediate of the starting alkoxide with the organolithium compound. In case of some organopotassium compounds this reaction takes a more complicated course and is accompanied by the formation of additional association products.

Organolithium compounds containing normal alkyl groups react with sodium tert-butoxide to give a good yield of the organosodium compound in a high degree of purity. The procedure is very simple. Thus n-butylsodium may be prepared as follows: to a suspension of 0.0643 mole of sodium tert-butoxide (purified by double sublimation, 23.87% Na) in 10 ml of dry heptane (free of unsaturated compounds) 90 ml of 0.930 M n-butyllithium in heptane (i.e. 0.0837 mole) at 0°C. in about 15 min. is added under stirring. After the addition of n-butyllithium is started the alkoxide first partly dissolves (the formation of the intermediate association product) at normal temperature a complete solution may be observed. By the addition of more n-butyllithium the separation of n-butylsodium in the form of a white powder occurs. To complete the reaction the mixture is stirred 1 hr at 0°C. and 1 hr at 30-40°C. The precipitate is sucked off, washed with heptane and dried for 5 hours at 50°C./1 mm Hg; yield 91.3%. Analysis: Na calculated 28.70%, found (acidimetric titration) 28.73%, 28.90%; lithium found 0.070%, 0.074% (flame spectrophotometer Unicam). The n-butylsodium was carbonised with solid CO_2; from the reaction mixture valeric acid was isolated, b.p. 184.5-185.5°C., n_D^{20} = 1.4085. The acid was also identified by gas chromatography with an authentic sample of valeric acid. The infrared spectrum of the filtrate of the reaction mixture proved to contain only the bands of the system lithium tert-butoxide - n-butyllithium. n-Butylsodium prepared in this way reacted lively with ether; this was probably due to the fact that the content of the lithium compounds in the system was too low for the organosodium compound to be stabilized as described by Wittig[2].

By similar procedure the following organosodium compounds were prepared: (a) from sodium tert-butoxide and n-octyllithium in heptane n-octylsodium in the form of a yellowish powder resulted (analysis: Na found 16.80%, 16.80%; calculated 16.89%. Li found 0.074%, 0.076%) and (b) from n-dodecyllithium in heptane pink-white n-dodecylsodium was obtained (analysis: Na found 11.86%, 11.89%; calculated 11.95%. Li found 0.10%, 0.11%). The yields of the two organosodium compounds exceeded 85%.

Organolithium compounds with the lithium bound on a secondary or tertiary carbon (e.g. sec. butyllithium, tert. butyllithium) react with sodium tert-butoxides at room temperature to give products with high contents of sodium (60 to 90%). One of their components is probably sodium hydride. The composition depends on the experimental conditions and the type of the compound. With secondary alkyllithium compounds the formation of these products takes several hours, while in case of tert-butyllithium it is faster. This finding can be explained by the decomposition of the organosodium compounds formed by primary reaction and, possibly, by subsequent reactions of the decomposition products.

If an organolithium compound is treated with sodium tert-butoxide in the presence of an organic compound capable of metallation with alkylsodium compounds, the sodium derivative of the corresponding organic compound results; thus triphenylmethane gives triphenylmethylsodium. In some cases, depending on experimental conditions and the nature of the metallated compound, the reaction mixture may contain both the metallated compound and the alkylsodium compound.

The products formed by treating a heptane solution of n-butyllithium with potassium tert-butoxide have a different composition, which depends on the ratio of the reactants. If close to the equimolar a pink-white compound is formed, turning brown at room temperature in a short time; gas chromatography of its hydrolysate detected the presence of tert-butyl alcohol. The total alkalinity (determined by acidimetric titration) and the contents of K and Li (determined by spectrophotometry) roughly correspond to an adduct composed of 1 mole of the alkoxide and 1 mole of the organometallic compound. The total amount of potassium in the precipitate corresponds to more than

70% of the amount used. The presence of an organopotassium compound in the product is proved by metallation of organic compounds in systems alkyllithium - potassium tert-butoxide, which proceeds even faster than in case of sodium alkoxide. Thus a good yield of benzylpotassium is obtained by adding dropwise, at room temperature a solution of n-butyllithium to a vigorously stirred toluene suspension of potassium tert-butoxide. Carbonisation with solid CO_2 gave phenylacetic acid as the main product; m.p. 71.5-75° (Kofler).

If potassium tert-butoxide is treated with an excess of n-butyllithium in heptane a white-yellowish compound is formed which changes its colour at room temperature much slower than the product from the equimolar mixture. Its hydrolysate contains only traces of tert-butylalcohol (determined by gas chromatography), which mean that the product obtained is practically free of alkoxide. The ratio of Li to K in the product depends on the ratio of the starting compounds; thus the use of a 4-molar excess of n-butyllithium results in the product which contains 14.9% K and 6.7% Li, which corresponds to a molar ratio Li:K = 2.52. The excess of n-butyllithium in the reaction mixture is probably the reason for the formation of the n-butylpotassium - n-butyllithium adduct. This type of addition compound has been assumed to exist by Bryce-Smith[3], who reacted metallic potassium with n-butyllithium in benzene.

The procedure described allows the preparation of some organic compounds of sodium with much better purity than possible by the usual methods. In case of organopotassium compounds the tendency to form addition products is so strong that by the conversion described simple organometallic compounds cannot be isolated. Nevertheless, the products can be used for metallation reactions or as polymerization catalysts.

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