[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Reactions of Organometallic Compounds. IV. The Reactions of Phenylsodium with α- and γ-Methylallyl Chlorides[1]

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α- and γ-methylallyl chlorides reacted with phenylsodium in pentane to give substantially identical mixtures comprising 90–95% of crotylbenzene and 5–10% of α-methylallylbenzene. The results are interpreted in terms of a carbonium-ion process, and it is thus suggested that this type of process is available for the second step of the Wurtz or Wurtz–Fittig reaction.

The mechanisms of reactions of organosodium compounds with alkyl halides are of interest as the second step of the Wurtz or Wurtz-Fittig reaction appears to involve such reactions.[2,3,4]

$$RNa + R'X \longrightarrow R\text{-}R' + NaX$$

In previous work it has been shown that a carbonium-ion process is apparently available for the reactions of alkyl halides with Grignard reagents[5,6] and for organolithium compounds,[7] but at the initiation of this work, no such process had been considered likely with organosodium compounds.[8] We undertook the present work in order to determine whether similar evidence could be obtained for organosodium compounds.

Our results for the reaction of phenylsodium with crotyl and α-methylallyl chlorides are comparable to those with Grignard reagents[5,6,13] and with phenyllithium and *n*-butyllithium.[7] Thus, when either chloride was treated with phenylsodium in pentane, and the resulting product was analyzed in a column rated at 60 theoretical plates, a 25% yield of butenylbenzene was obtained of which 90–95% was crotylbenzene and 5–10% was α-methylallylbenzene. Determination of the relative reactivities of the chlorides was attempted by adding one mole of an equal mixture of the chlorides to 0.6 mole of phenylsodium. A faster rate of reaction for the secondary chloride was indicated, but the determination was complicated by the rearrangement of the chloride. Sixty to seventy per cent. of the unreacted chloride was recovered, of which 90% was crotyl chloride and 10% was α-methylallyl chloride. In order to determine whether the butenyl chlorides were isomerized under the conditions used, one mole of α-methylallyl chloride was added to 0.6 mole of phenylsodium. Eighty-five per cent. of the unreacted chloride was recovered of which 65% was primary chloride and 35% was secondary chloride.

Our results suggest a carbonium-ion intermediate as postulated for the Grignard system by Wilson, Roberts and Young,[6] by us[7] for the organolithium reactions and by Lane and co-workers[10,11,12] for organosodium compounds. The electrophilic sodium atom of the organometallic is assumed to coördinate with the halogen atom of the halide, weakening the carbon–halogen bond, and resulting in an allylic carbonium ion. This ion may then coördinate with a phenyl group available at the surface of the solid phenylsodium–sodium chloride mixture to give the butenylbenzene product mixture or with a chloride ion available at the surface to give a mixture of butenyl chlorides.[14,15] The data suggest that reactions of the ion with chloride ion or with the phenyl group proceed at comparable rates. It is clear from the two sets of results that the secondary chloride is more reactive than the primary, similar to the relative reactivities with phenyllithium.[7] The electrophilic nature of organometallic compounds seems predominant over their nucleophilic character in these reactions and has been discussed by Morton.[16]

The significance of these results and of others in the literature involving the reactions of optically active systems with sodium and sodium alkides in affording at least dual mechanisms (direct displacement and carbonium ion) for the second step of the Wurtz reaction has already been discussed.[7]

It is apparent that our results, comparable to the S_N1 mechanism, are in contradistinction to those of Levy and Cope,[17] whose results with sodio-allylbenzene in liquid ammonia with the butenyl chlorides (coupling *without* rearrangement) indicated a direct-displacement mechanism. This may be due to differences in the character of the sodium–carbon bond in the two solvents—pentane, a solvent of low dielectric constant and poor solvating power for ions, and ammonia, a solvent of high dielectric constant and good solvating power for ions, or may be due to inherent differences in electrophilic and nucleophilic character of the two organosodium reagents. We hope to perform experiments leading to the solution of these questions.

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(8) This process had been considered and rejected as unlikely by Brink, Lane and Wallis.[9] After our work had been completed, evidence for such a mechanism and reconsideration of it was set forth.[10,11,12]

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(14) It is, of course, possible that the isomerization is intramolecular —compare W. G. Young, S. Winstein and H. L. Goering, Abstracts of the 117th Meeting of the American Chemical Society, April, 1950, p. 70L.

(15) Ulrich and Lane[11] do not consider the possibility of isomerization of the butenyl chlorides in the reaction with ethylsodium.

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Experimental

Materials.—The phenylsodium was prepared under a nitrogen atmosphere in pentane[18] in a three-necked flask fitted with a mercury-sealed stirrer, condenser and gas-inlet tube. A 10% excess of chlorobenzene was added dropwise with stirring to a suspension of sodium sand in pentane, and the mixture was heated at reflux for four hours. The pentane was decanted and replaced with fresh pentane in order to remove excess chlorobenzene and soluble by-products. Carbonation with solid carbon dioxide indicated a 84% yield of phenylsodium using this method of preparation. Crotyl chloride [b.p. 78° (630 mm.), n^{20}D 1.4346–1.4354] was prepared from butadiene and hydrochloric acid using zinc chloride as catalyst[19] and converted to α-methylallyl chloride [b.p. 57° (630 mm.), n^{20}D 1.4150–1.4156] by refluxing with 2 mole per cent. of ferric chloride.[20] Each chloride was distilled carefully through a center-rod column (rated at 60 theoretical plates at maximum efficiency) and center fractions were used.

Crotyl Chloride or α-Methylallyl Chloride and Phenylsodium.—Crotyl chloride (45.3 g., 0.5 mole) was added dropwise to approximately 0.6 mole of phenylsodium in 500 ml. of pentane. After the mixture had been heated at reflux for two hours, the solid material was allowed to settle, and most of the liquid was removed by decantation. Ethyl alcohol was carefully added to the remaining suspension to decompose the reaction mixture. The resulting solution was washed several times with water and was then added to the main pentane solution and dried over magnesium sulfate. A center-rod column (rated at 60 theoretical plates at maximum efficiency) was used to separate the mixture to give a 10% yield of butenylbenzenes, of which 90–95% was crotylbenzene, b.p. 172° (630 mm.), and 5–10% was α-methylallylbenzene, b.p. 157–162° (630 mm.). Better yields of the coupling products were obtained if neither reactant was in large excess during the course of the reaction. Small portions of the suspension of phenylsodium were forced by means of nitrogen pressure into a second reaction flask while the chloride was slowly dropped into the flask. Approximately 1500 ml. of pentane was required to transfer the phenylsodium. Using this method, 15.2 to 16.6 g. (23–25% yield) of the butenylbenzenes was obtained with the percentages of the two products as before. The products were identified as described earlier.[7] A higher boiling product [95–120° (50 mm.)], about twice the weight of the butenylbenzenes, which was not biphenyl, was obtained. The material did not contain an appreciable amount of chlorine, and had a density less than one. A Kuhn–Roth oxidation with chromic acid gave the following molar ratios: benzoic acid, 0.23; other volatile acid, 1; original dimer or polymer calculated as butenylbenzene, 1. If the mixture was entirely a polymer or dimer of butenylbenzene, the benzoic acid to polymer ratio should be 1.

Almost identical results were obtained with α-methylallyl chloride and phenylsodium.

Mixture of α-Methylallyl and Crotyl Chlorides with Phenylsodium.—An equal mixture by weight of crotyl and α-methylallyl chlorides (1.0 mole, 90.6 g.) was treated with phenylsodium (0.6 mole) as described previously. Approximately 70% of the unreacted chloride was recovered of which 90% was crotyl chloride and 10% was α-methylallyl chloride. Since the crotyl chloride was contaminated with benzene formed as a by-product in the reaction, the amount of chloride present was determined from refractive indices ratios and quantitative chloride analysis.

Excess α-Methylallyl Chloride with Phenylsodium.—One mole (90.6 g.) of α-methylallyl chloride reacted with 0.6 mole of phenylsodium as described above. Approximately 85% of the unreacted chloride was recovered of which 65% was crotyl chloride and 35% was α-methylallyl chloride.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Sodium Borohydride as a Reducing Agent for Sugar Lactones[1]

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Sodium borohydride is an effective and convenient reagent for reducing aldonic acid lactones to the aldose or the glycitol.

Ordinarily one reduces an aldonic lactone to an aldose by means of sodium amalgam[2,3] at acid reaction. Yields are often low and the method is time-consuming. Platinum-catalyzed hydrogenation has also been reported.[4] The lactone, ester,[5] or, preferably, the aldose,[6] may be reduced to the glycitol by high pressure catalytic hydrogenation.

We have found that sodium borohydride is an effective reagent with which to convert an aldonic lactone into either an aldose or a glycitol in *ca.* 65% yields (established for the case of D-gluco-D-*gulo*-heptonic γ-lactone). The fact that sodium borohydride[7,8] may be used in aqueous solution makes it a useful reducing agent for the water-soluble carbohydrate derivatives. Although the yield of glycitol is less than when Raney nickel is used on the aldose, the simple equipment is definitely an advantage. It may be noted that lithium aluminum hydride is not suitable for these reductions, since it must be used in ether.

Experimental

Reduction of D-Gluco-D-*gulo*-heptono-γ-lactone to D-Gluco-D-*gulo*-heptose.—A solution of sodium borohydride[9] (2 g.) in 50 ml. of water was added dropwise to a solution of D-gluco-D-*gulo*-heptono-γ-lactone (15.00 g.) in 100 ml. of water, previously cooled to near 0°, at such a rate that the temperature was maintained at 0–3°. The reaction mixture was stirred slowly and continuously by a wide sweep mechanical stirrer. Simultaneously with the addition of the so-

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