

Found: C, 63.39; H, 7.31. *Rotation.* 10.3 mg. dissolved in 2.0 cc. of chloroform gave a rotation of $+0.82^\circ$ at 23.6° ; l , 2 dm.; $[\alpha]^{23.6}_D +80^\circ$; $C = 0.515$.

Biological tests on the tetraacetate and deacetylated material are being conducted by Dr. E. S. Gordon of the University of Wisconsin Medical School.

I am indebted to Schering Corporation for supplies of desoxycorticosterone acetate.

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THE EFFECT OF METALLIC HALIDES ON THE REACTION OF ORGANOLITHIUM COMPOUNDS WITH ALKYL AND ARYL HALIDES

Sir:

It has recently been found in this Laboratory¹ that small amounts (2-5 mole per cent.) of metallic halides profoundly affect the reactions of organomagnesium halides with a variety of organic compounds. Specifically, an ether solution of *p*-tolylmagnesium bromide, which does not react with phenyl bromide under the usual conditions, reacts readily with that compound in the presence of cobaltous chloride to give high yields of *p,p'*-bitolyl, along with biphenyl (trace), terphenyl and other polyphenyls. Ethylmagnesium bromide reacts rapidly with phenyl bromide in the presence of cobaltous halides to give ethane, ethylene, biphenyl (trace) and polyphenyls.

This type of catalytic effect has now been observed in reactions of organolithium compounds with alkyl and aryl halides. Whereas, under normal conditions, phenyllithium reacts to a negligible extent with phenyl bromide, reaction proceeds rapidly in the presence of 5 mole per cent. of cobaltous bromide, to give high yields of biphenyl along with smaller quantities of terphenyl and polyphenyls. With ethyl bromide, phenyllithium reacts normally in ether solution to give ethylbenzene. In the presence of 2-5 mole per cent. of cobaltous bromide the products are biphenyl, ethane and ethylene. Butyllithium reacts normally in ether solution with phenyl bromide to give butylbenzene. No biphenyl or

other solid or tarry material is formed. In the presence of 3-5 mole per cent. of cobaltous bromide, however, practically no butylbenzene is formed; the reaction products are biphenyl, terphenyl, and gases that appear to be a mixture of butane and butylene.

Experimental

In a typical experiment, to 100 ml. of a 1.06 *N* ether solution of phenyllithium at 0° was added 1.1 g. of cobaltous bromide (0.005 mole). A black coloration immediately appeared. To this mixture was added 0.1 mole of bromobenzene. A vigorous reaction ensued. The mixture was stirred for three hours, allowed to stand an additional twelve hours, and then poured onto cracked ice and acidified with dilute nitric acid. The layers were separated and the water layer extracted twice with ether. The combined ether layers were then treated with small quantities of bicarbonate solution, which were added to the water layer. Titration of an aliquot of this solution for bromide ion and analysis of the original phenyllithium solution indicated that 54% of the bromobenzene entered into the reaction, due allowance being made for the halide from cobaltous bromide. The ether layer yielded 8.5 g. of biphenyl and 1.0 g. of a mixture of terphenyl and polyphenyls. If corrected for the biphenyl present in the phenyllithium solution (0.9 g.) 7.6 g. of this product was formed in the reaction. In a control experiment and excluding the cobaltous bromide less than 2% of the bromobenzene had reacted and only the amount of biphenyl indicated above was found.

The promotion of the reactions that do not otherwise occur is striking, but it is perhaps even more significant that the nature of the products and, therefore, of the reaction mechanism, is fundamentally altered in the other cases cited.

These reactions will be recorded in greater detail later. It is the intention to study the effect of metallic halides in the condensation of organolithium (as well as other organometallic) compounds with a variety of organic substances (unsaturated compounds, acid halides, aldehydes, ketones).

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(1) For reference see Kharasch and Fields, *THIS JOURNAL*, **63**, 2316 (1941).

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