The Reaction of Organolithium Compounds with Nickel Carbonyl*

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In previous papers we reported that organolithium compounds reacted smoothly with iron pentacarbonyl at −50—−40°C in an ether solution, giving ketones and acyloins as major produts.[1,2] This communication will deal with similar reactions of organolithium compounds with nickel carbonl.

Organolithium compounds were prepared by the ordinary methods, and nickel carbonyl was added to the ether solutions of organolithium compounds at −70°C. The reaction mixture was hydrolyzed with ethanol and hydrochloric acid.

The results of this reaction are given in Table I.

As a general tendency, acyloins were produced from arillithiums and symmetrical ketone alkyllithiums.

TABLE I.

Organolithium compound	Main product	Yield* %
Phenyllithium	Benzoin	36
m-Tolyllithium	*m*-Toluoin	61
p-Tolyllithium	*p*-Toluoin	71
p-Methoxyphenyllithium	*p*-Anisoin *p*-Anisil	15 23
2,6-Dimethylphenyllithium	2,6-Dimethylbenzaldehyde 2,2′,6,6′-Tetramethylbenzil	22 23
n-Butyllithium	Di-*n*-butyl ketone	29

* The calculations of yields are based on the amounts of organic halides used.

Whereas the reaction mixture obtained from the reaction of *p*-tolyllithium with nickel carboyl at −70°C gave *p*-toluoin in a 71% yield on hydrolysis with ethanol-6N hydrochloric acid at −70°C, the extraction of the reaction mixture with anhydrous benzene in a dry nitrogen box at room temperature, i.e., the isolation of the products without hydrolysis, yielded di-*p*-tolyl ketone in a 29% yield.

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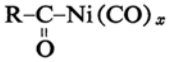
* This work was presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964.

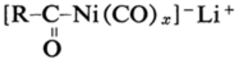
[1] M. Ryang, Y. Sawa, H. Masada and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 66, 1086 (1963).

[2] M. Ryang, I. Rhee and S. Tsutsumi, This Bulletin, 37, 341 (1964).

When the reaction time was prolonged by stirring for a further 5 hr. at 30—60°C, the subsequent hydrolysis gave *p*-toluoin and di-*p*-tolyl ketone in yields of 36 and 25% respectively (at 35°C) and in yields of 34 and 38% respectively (at 60°C). Thus it is evident that the reaction products were markedly affected by the methods of treating the reaction mixture.

The present findings suggest that the ketones and acyloins were produced from the same intermediate complexes, but that the acyloins were produced via the dimerization of the intermediate, followed by hydrolysis, while the ketones were produced by the thermal decomposition of the same intermdiates. Hence, the complicated results in the reaction of organolithium compounds with iron pentacarbonyl or nickel carbonyl can be explained by considering the thermal stabilities and chemical reactivities of the intermediates. As for the intermediates, the following three unstable complexes can be postulated:

(a)

$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}Ni(CO)}_x$

(b)

$[\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}Ni(CO)}_x]^-\mathrm{Li}^+$

(c) R–C–Li

The mechanistic aspects of this reaction will be discussed in detail in a forthcoming paper.

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