*On the Formation of Benzoin by the Reaction of Carbon Monoxide with Organometallic Compounds**

By Membo RYANG and Shigeru TSUTSUMI

(Received July 20, 1961)

In the previous papers, the present authors reported that the reaction of carbon monoxide with organometallic compounds produced a coordinate complex as an intermediate, followed by the formation of the carbon monoxide adducts A.

$$RM+CO \longrightarrow (\text{Coordinate complex}) \longrightarrow R-\overset{\overset{O}{\|}}{C}-M$$

where M=MgX[1], Li[2], Na[3]. (A)

The adduct A is reactive and further reacts with excess of organometallic compounds, producing various reaction products, in which included acyloin, the dimerization product of the adducts A.

$$2\ R\overset{\overset{O}{\|}}{C}-M \longrightarrow 2\ R-\overset{\cdot\cdot}{C}-OM \longrightarrow$$

$$R-\underset{\underset{M}{|}}{\overset{\overset{O}{|}}{C}}=\underset{\underset{M}{|}}{\overset{\overset{O}{|}}{C}}-R \longrightarrow R-\overset{\overset{O}{\|}}{C}-\underset{\underset{OH}{|}}{CH}-R \qquad (1)$$

Fisher and Stoffers already reported the formation of acyloin by the reaction of carbon monoxide with Grignard reagents at high temperature and elevated pressure[4].

This report deals with an attempt to prepare acyloin under more mild conditions and it was found that, in the reaction of carbon monoxide with phenylmagnesium bromide in ethyl ether solution at −35°C, the addition of cobalt(II) chloride led to the formation of benzoin as a main product (Table run 3).

TABLE. THE REACTION OF CARBON MONOXIDE WITH PHENYLMAGNESIUM BROMIDE IN THE PRESENCE OF COBALT(II) CHLORIDE

	Temp. °C	Time hr.	Theoretical yields of products, % Diphenyl	Benzoin	Benzophenone	Triphenylcarbinol
1.	−10	1	80	trace	5.5	trace
2.	−25	2	44.2	12.5	22	12
3.	−35	2	30	35	trace	5

On the other hand, the absence of cobalt(II) chloride under the same conditions gave a very poor yield.

From the above results, it is considered that although phenylcobalt chloride, which is formed by the reaction of phenylmagnesium bromide with cobalt(II) chloride (Eq. 2), is unstable, it reacts with carbon monoxide at low temperature, producing benzoin as a main product.

$$PhMgBr+CoCl_2 \longrightarrow PhCoCl+MgBrCl \qquad (2)$$

On the other hand, when reaction temperature is rather high (−10 or −20°C), phenyl radical is formed as a result of homolytic cleavage of the carbon-cobalt bond and dimerizes to diphenyl (run 1) or reacts with carbon monoxide in producing benzophenone (run 2).

$$PhCoCl \longrightarrow Ph\cdot + \cdot CoCl$$

$$2\ Ph\cdot \longrightarrow Ph-Ph$$

$$2\ Ph\cdot + CO \longrightarrow Ph-\overset{\overset{O}{\|}}{C}-Ph$$

Furthermore, in the reaction of carbon monoxide with phenyl potassium, which is prepared by the reaction of anisole with metallic potassium in pentane solution, benzoin (25%), benzhydrol (2.3%), benzoic acid (4%) and benzaldehyde (trace) are produced.

All these results mentioned above seem to support the opinion that, in the reaction of carbon monoxide with organometallic compounds, the carbon monoxide adduct A is formed and dimerizes to acyloin or further reacts with excess of organometallic compounds, producing various reaction products.

Department of Chemical Technology
Faculty of Engineering
Osaka University
Miyakojima-ku, Osaka

---

* Presented at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

1) M. Ryang and S. Tsutsumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 878 (1961).

2) M. Ryang and S. Tsutsumi, ibid., **82**, 880 (1961).

3) M. Ryang and S. Tsutsumi, ibid., in press; M. Ryang and S. Tsutsumi, *Tech. Rep. Osaka Univ.*, **11**, 181 (1961).

4) F. G. Fisher and O. Stoflers, *Ann.*, **500**, 253 (1930).