CHEMISTRY LETTERS, pp. 1073 - 1076, 1984.

# CARBONYLATION OF AMINES CATALYZED BY ORGANOZINC COMPOUND

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Diethylzinc was found to catalyze the carbonylation of amines including aromatic amines to give the corresponding formamides in good yields.

In recent years, considerable attention has been paid to develop new synthetic reactions with carbon monoxide.[1)] In the course of our studies on the reaction of metal amides and $C_1$ compounds such as carbon dioxide,[2,3)] we found a novel insertion reaction of carbon monoxide to the Zn-N bond of alkylzinc amide and the carbonylation of amines catalyzed by organozinc compound to produce selectively the corresponding formamide derivatives.

In the reaction of ethylzinc N,N-diethylamide[4)](2.88 g, 17 mmol) and carbon monoxide (40 atm ; $4.1 \times 10^6$ Pa) in benzene (8 $cm^3$) at room temperature for 18 h, the IR spectrum of the reaction mixture showed a new carbonyl absorption at 1650 $cm^{-1}$. $^1H$ NMR spectrum of the reaction mixture in benzene showed signals at $\delta$ 0.3 (2H, q), 0.9 (6H, t), 1.3 (3H, t), and 3.2 (4H, q), which are considered to be assigned to $CH_3C\underline{H}_2Zn$, $NCH_2C\underline{H}_3$, $C\underline{H}_3CH_2Zn$, and $NC\underline{H}_2CH_3$ of $EtZnCONEt_2$, respectively, while ethylzinc N,N-diethylamide showed signals at $\delta$ 0.4 (2H, q, $CH_3C\underline{H}_2Zn$), 1.0 (6H, t, $NCH_2C\underline{H}_3$), 1.4 (3H, t, $C\underline{H}_3CH_2Zn$), and 2.8 (4H, q, $NC\underline{H}_2CH_3$). A remarkable downfield shift from 2.8 ppm to 3.2 ppm observed for hydrogens of N-methylene group is considered to correspond to the insertion of carbon monoxide into Zn-N bond. The hydrolysis of the reaction mixture gave diethylformamide in 45% yield. These results indicate that carbon monoxide inserts to Zn-N bond of ethylzinc N,N-diethylamide, as Eq. 1.[5)]

$$\mathrm{EtZnNEt_2} + \mathrm{CO} \longrightarrow (\mathrm{EtZnCONEt_2}) \xrightarrow{\mathrm{H^+}} \mathrm{HCONEt_2} \qquad (1)$$

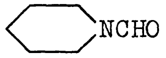
On the basis of the observed insertion of carbon monoxide into Zn-N bond, the carbonylation of amines catalyzed by organozinc compound was attempted. Since organozinc amide, $R\text{-}Zn\text{-}NR'_2$, is known to be obtained easily by the reaction of dialkylzinc with secondary amine at 80-100 °C,[4] diethylzinc was used as catalyst for the carbonylation.

In a typical experiment, N-methylaniline (10.7 g, 98 mmol) and diethylzinc (0.1 g, 0.98 mmol) were placed in a 100 $cm^3$-autoclave flushed with nitrogen gas, pressured with 45 atm. of carbon monoxide, and the mixture was heated in an oil bath at 100 °C for 18 h. After cooling, the pressure was released and the content of the autoclave was subjected to distillation, yielding 4.0 g of N-methylformanilide, bp 137 °C (25 mmHg)(30%, based on amine). Another expected product, i.e., urea, was not detected in the reaction mixture by GLC and IR analyses.

$$\mathrm{C_6H_5NHCH_3} + \mathrm{CO} \xrightarrow{\text{Diethylzinc}} \mathrm{HCON(CH_3)C_6H_5} \qquad (2)$$

The results of the carbonylation of various amines catalyzed by diethylzinc are given in Table 1.[6] The carbonylation of aliphatic secondary amines by diethylzinc catalyst gave the corresponding formamide derivatives in good yields

Table 1. Reaction of CO and Amine with Diethylzinc as Catalyst[a)]

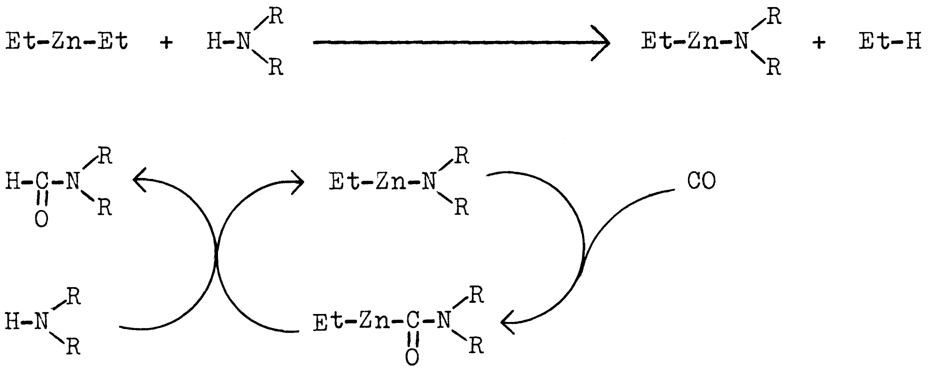
| No. | Amine | Formamide | Yield / %[b)] |
|---|---|---|---|
| 1 | $(CH_3CH_2)_2NH$ | $(CH_3CH_2)_2NCHO$ | 93 |
| 2 | $((CH_3)_2CHCH_2)_2NH$ | $((CH_3)_2CHCH_2)_2NCHO$ | 80 |
| 3 |  |  | 67 |
| 4 | $CH_3CH_2CH_2CH_2NH_2$ | $CH_3CH_2CH_2CH_2NHCHO$ | 6.7 |
| 5 | $C_6H_5(CH_3)NH$ | $C_6H_5(CH_3)NCHO$ | 64 |
| 6 | $C_6H_5(CH_3CH_2)NH$ | $C_6H_5(CH_3CH_2)NCHO$ | 34 |

a) CO, 45 atm; $ZnEt_2$, 0.98 mmol; amine, 98 mmol; temp, 100 °C; time, 18 h.

b) Estimated by GLC; another expected product, i.e., urea derivative, was not detected.

(Table 1, No. 1-3), but in the case of primary amine, the yield of formamide was low (Table 1, No. 4). Diethylzinc was found to be a good catalyst also for the carbonylation of N-alkylaniline (Table 1, No. 5 and 6), although the corresponding formamides were not obtained from aniline or diphenylamine in the presence of diethylzinc. The selective formation of N-formyl derivatives of aromatic amines by the carbonylation has been difficult so far,7-10) except for rather limited examples such as the formation of N,N-diphenylformamide by nickel carbonyl,11) N-methylformanilide by chloroauric acid,12) and p-hydroxyphenylformamide by sodium methoxide or zinc chloride.13)

The reaction is considered to proceed as shown in Scheme 1. Diethylzinc reacts with secondary amine to produce ethylzinc dialkylamide, carbon monoxide inserts to the zinc amide to form a carbamoylzinc compound, and amine attacks the carbamoylzinc compound to give formamide and to regenerate the zinc amide.



Scheme 1.

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( Received March 29, 1984)