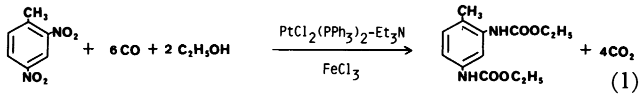
The Platinum Complex-catalyzed Reductive *N*-Carbonylation of Dinitroarenes to the Biscarbamates

Yoshihisa WATANABE,* Yasushi TSUJI, and Ryo TAKEUCHI
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606

(Received December 21, 1984)

Synopsis. Dichlorobis(triphenylphosphine) platinum(II) shows good catalytic activity for the reductive *N*-carbonylation of dinitroarenes in ethanol in the presence of a Lewis acid and triethylamine. From 2,4-dinitrotoluene, diethyl 4-methyl-1,3-phenylenebiscarbamate is obtained in 50% yield at 190 °C under carbon monoxide pressure of 60 kg cm^{-2}.

Much attention has been paid to the reductive *N*-carbonylation of dinitroarenes and intensive effort is focused on finding an effective catalyst system.[1)] We have recently demonstrated that a homogeneous platinum catalyst system including tertiary amine and a Lewis acid has high catalytic activity for the reductive *N*-carbonylation of mononitroarenes,[2)] where ethyl phenylcarbamate derivatives are obtained in high yields in ethanol medium. In the present paper, dinitroarenes such as 2,4-dinitrotoluene, 2,6-dinitrotoluene, and *m*-dinitrobenzene are employed as a substrate (Eq. 1).



(1)

Results and Discussion

Dichlorobis (triphenylphosphine) platinum(II) is effective for the catalytic transformation of 2,4-dinitrotoluene into diethyl 4-methyl-1,3-phenylenebiscarbamate in the presence of tertiary amine and a Lewis acid. The combination of the platinum complex with a Lewis acid, tertiary amine, and triphenylphosphine is essential for the high catalytic activity , as in the previous paper.[2)] The effectiveness of the catalyst system is highly affected by the nature of and the ratio between those components.

The most dominant factor is the nature of a Lewis acid (Table 1). Without a Lewis acid, the platinum catalyst system does not show any catalytic activity and dinitroarenes are recovered unchanged. Iron(III) chloride is the most favorable for giving the biscarbamate, diethyl 4-methyl-1,3-phenylenebiscarbamate, in a good yield (Run 1). Different from the previous paper,[2)] tin(IV) chloride and aluminum chloride are less effective. The additions of vanadium(V) trichloride oxide or titanium(IV) chloride were also less effective. With iron(II) chloride trihydrate or pentacarbonyliron(0) or molybdenum(V) chloride, the biscarbamate is not obtained.

The catalytic activity is strongly influenced by the amount of the Lewis acid in the catalytic system (Table 2). The yield of the biscarbamate was nearly zero and only 8% with a small amount of iron(III) chloride. In order to maintain the high catalytic activity, more than tenfold excess of the Lewis acid to the platinum complex is required.

The molar ratio of triethylamine to iron(III) chloride is also a major factor determining the catalytic activity (Fig. 1). The yield of the biscarbamate showed a maximum at the molar ratio of 1.8. The biscarbamate was not obtained at all at the molar ratio over 3. Excess triethylamine would coordinate the platinum complex and saturate the active catalyst sites.

The reaction proceeded with reasonable conversion at 180 °C and 190 °C. At lower temperatures, the yield of the biscarbamate is low and cannot be improved by prolonging the reaction time. The reaction completed at 190 °C for 4 h. Elevating the reaction temperature to 200 °C decreased the yield of biscarbamate to 37%. The optimum initial carbon monoxide pressure is 60 kg cm^{-2}. Under both lower and higher pressures the yield of biscarbamate decreased (yield 29% both under 85 and 45 kg cm^{-2}). The reaction was performed with other dinitroarenes. *m*-Dinitrobenzene and 2,6-dinitrotoluene were converted to the corresponding biscarbamate, although the yields were rather low (diethyl 1,3-phenylenebiscarbamate 28%, diethyl 2-methyl-1,3-phenylenebiscarbamate 30%).

TABLE 1. THE PLATINUM- COMPLEX- CATALYZED REDUCTIVE *N*-CARBONYLATION OF 2, 4- DINITROTOLUENE[a)]. THE EFFECT OF VARIOUS LEWIS ACIDS

Run	Lewis acid	Temp	Time	Yield[b)]
		°C	h	%
1[c)]	$FeCl_3$	190	4	50
2[c)]	$FeCl_3$	190	8	40
3	$FeCl_3$	180	4	44
4	$SnCl_4$	180	4	27
5	$AlCl_3$	180	4	6
6	$TiCl_4$	180	4	13

a) A mixture of 2, 4-dinitrotoluene(10 mmol), [$PtCl_2(PPh_3)_2$](0.1 mmol; 1 mol% based on 2, 4-dinitrotoluene used), Lewis acid(2.0 mmol), triethylamine(3.6 mmol) and ethanol(20 ml) was stirred under 60 kg cm^{-2} carbon monoxide. b) Product: Diethyl 4-methyl-1, 3-phenylenebiscarbamate. Determined by HPLC based on the amount of 2, 4-dinitrotoluene charged. c) Iron(III) chloride(1.0 mmol), triethylamine(1.8 mmol).

Table 2. The effect of molar ratio of iron(III) chloride to platinum complex[a)]

Run	Molar ratio of $[PtCl_2(PPh_3)_2]$ to Iron(III) Chloride	Yield[b)]/%
7	1: 2	0
8	1: 5	8
9	1:10	44
3	1:20	44
10	1:40	40

a) 2, 4-Dinitrotoluene(10 mmol), $[PtCl_2(PPh_3)_2]$(0.1 mmol), iron(III) chloride(0.2-4 mmol), triethylamine(0.36-7.2 mmol; fixing $FeCl_3/Et_3N=1/1.8$), EtOH(20 ml) at 180 °C for 4 h under 60 Kg cm^{-2}. b) Product: Diethyl 4-methyl-1, 3-phenylenebiscarbamate. Determined by HPLC based on the amount of 2, 4-dinitrotoluene charged.

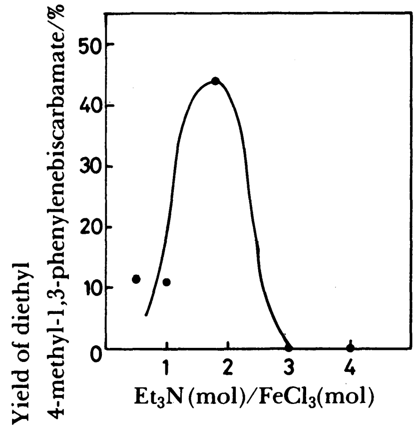


Fig 1. The *N*-Carbonylation of 2,4-Dinitrotoluene. The Effect of the Molar Ratio, $Et_3N/FeCl_3$. 2,4-Dinitrotoluene (10 mmol), $PtCl_2(PPh_3)_2$ (0.1 mmol), $FeCl_3$ (1.0 mmol), triethylamine (0.5—4.0 mmol), EtOH (20 ml) at 180 °C for 4 h under the initial pressure of 60 kg cm^{-2} carbon monoxide. Yields are determined by HPLC based on the amount of 2,4-dinitrotoluene charged.

In the present *N*-carbonylation, the nitrene intermediate would be generated by the deoxygenation of dinitroarene with carbon monoxide, and the carbonylation of the nitrene intermediate will follow (Eq. 2).[2)]

$$\mathrm{ArNO_2} \xrightarrow[-\mathrm{CO_2}]{+\mathrm{CO}} \mathrm{(ArN)[Pt]} \xrightarrow{+\mathrm{CO}} \mathrm{(ArNCO)[Pt]} \xrightarrow{+\mathrm{EtOH}} \mathrm{ArNHCOOEt} + \mathrm{[Pt]} \qquad (2)$$

Experimental

General Procedure. A glass liner was set in a 100 ml stainless steel autoclave. The reagents were charged in the following order: Dinitroarene (10 mmol), ethanol (20 ml), triethylamine (0.25 ml, 1.8 mmol), $[PtCl_2(PPh_3)_2]$ (79 mg, 0.1 mmol), and $FeCl_3$ (162 mg, 1.0 mmol). After being sealed and flushed with carbon monoxide, the reactor was pressurized with carbon monoxide to 60 kg cm^{-2}. The autoclave was heated to 190 °C in 20 min and then held at this temperature for 4 h.

Product Isolation. Ethanol was removed from the reaction mixture *in vacuo* at 50 °C. Then, benzene was added to the residue. Aminoarenes were extracted by 60 ml of 10% HClaq three times and the aqueous layer was discharged. Evaporation of benzene afforded the biscarbamate.

Analytical Procedure. The melting points were uncorrected. The HPLC analysis was performed on a Shimadzu LC-5A equipped with a column (μ-Bondapak C_{18}) and $MeOH/H_2O=6/4$ as an eluent. Naphthalene was employed as an internal standard and the yield of the product was determined according to the calibration curve obtained for each sample. The IR spectra were measured on a Hitachi model 215 grating spectrophotometer. The ^{13}C and ^1H-NMR spectra were recorded at 25.05 MHz and 100 MHz respectively with a JEOL JNM FX- 100 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. The mass spectra were recorded on a JMS OISG mass spectrometer.

The analytical data of the products are described below. The phenyl carbon resonances in the ^{13}C-NMR spectra were tentatively assigned by calculating their chemical shifts with additive parameters.[4)]

Diethyl 4-Methyl-1,3-phenylenebiscarbamate. White crystals, mp 136—138 °C. (lit,[4)]mp 137 °C) ^1H-NMR (100 MHz) ($CDCl_3$): 1.29 (t, 3H, $-OCH_2C\underline{H}_3$), 1.30 (t, 3H, $-OCH_2C\underline{H}_3$), 2.18 (s, 3H, $-C\underline{H}_3$), 4.20 (q, 2H, $-OC\underline{H}_2CH_3$), 4.21 (q, 2H, $-OC\underline{H}_2CH_3$), 4.74 (br, 1H, $-N\underline{H}$), 6.42 (br, 1H, $-N\underline{H}$), 7.14 (d, 1H, phenyl), 7.30 (d, 1H, phenyl), 7.76 (d, 1H,penyl). ^{13}C-NMR (25.05 MHz) ($CDCl_3$): 14.6 (q, $-OCH_2\underline{C}H_3$), 16.7 (q, $-\underline{C}H_3$), 61.1 (t, $-O\underline{C}H_2CH_3$), 61.4 (t, $-O\underline{C}H_2CH_3$), 111.3 (d, phenyl 2), 114.3 (d, phenyl 6), 121.9 (s, phenyl 4), 130.7 (d, phenyl 5), 136.3 (s, phenyl 1), 136.7 (s, phenyl 3), 153.6 (s, C=O). IR (KBr): 3330 cm^{-1} (ν_{N-H}), 3280 cm^{-1} (ν_{N-H}), 1690 cm^{-1} ($\nu_{C=O}$), 1680 cm^{-1} ($\nu_{C=O}$). MS (*m/z*): 266 (M^+). Calcd for $C_{13}H_{18}N_2O_4$: C, 58.64; H, 6.81; N, 10.52%. Found: C, 58.50, H, 6.81, N, 10.05%.

Diethyl 2-Methyl-1,3-phenylenebiscarbamate. White crystals, mp 168—169 °C. ^1H-NMR (100 MHz) ($CDCl_3$): 1.30 (t, 6H, $-OCH_2C\underline{H}_3$), 2.10 (s, 3H, $-C\underline{H}_3$), 4.20 (q, 4H, $-OC\underline{H}_2CH_3$), 6.39 (br, 2H, $-N\underline{H}$), 7.09—7.49 (m, 3H, phenyl). ^{13}C-NMR (25.05 MHz) ($CDCl_3$): 12.0 (q, $-\underline{C}H_3$), 14.5 (q, $-OCH_2\underline{C}H_3$), 61.3 (t, $-O\underline{C}H_2CH_3$), 119.5 (d, phenyl 4,6), 126.3 (d, phenyl 5), 135.9 (s, phenyl 1, 2, 3), 153.9 (s, C=O). IR (KBr): 3270 cm^{-1} (ν_{N-H}), 1685 cm^{-1} ($\nu_{C=O}$). MS (*m/z*): 266 (M^+). Calcd for $C_{13}H_{18}N_2O_4$: C, 58.64; H, 6.81; N; 10.52%. Found: C, 58.89; H, 6.69; N, 10.00%.

Diethyl 1,3-Phenylenebiscarbamate. White crystals, mp 142—145 °C. (lit,[5)] mp 143—145 °C) ^1H-NMR (100 MHz) ($CDCl_3$): 0.95 (t, 6H, $-OCH_2C\underline{H}_3$), 4.00 (q, 4H, $-OC\underline{H}_2CH_3$), 7.04—7.16 (m, 4H, phenyl), 7.82 (br, 2H, $-N\underline{H}$). ^{13}C-NMR (25.05 MHz) ($CDCl_3$): 14.6 (q, $-OCH_2\underline{C}H_3$), 61.4 (t, $-O\underline{C}H_2CH_3$), 109.1 (d, phenyl 2), 113.5 (d, phenyl 4,6), 129.5 (d, phenyl 5), 139.5 (s, phenyl 1,3), 153.4 (s, C=O). IR (KBr): 3270 cm^{-1} (ν_{N-H}), 1700 cm^{-1} ($\nu_{C=O}$), 1680 cm^{-1} ($\nu_{C=O}$). MS (*m/z*): 252 (M^+). Calcd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.1%. Found: C,57.39; H, 6.37; N, 10.97%.

References

1) a) V. I. M. Yuvenskii and B. K. Nefedov, *Russ. Chem. Rev.*, **50**, 470, (1980); b) K. Miyata, *Shokubai*, **23**, 29, (1980).

2) Y. Watanabe, Y. Tsuji, R. Takeuchi, and N. Suzuki, *Bull. Chem. Soc. Jpn.*, **56**, 3343 (1983).

3) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York (1972). p. 197.

4) Beilsteins Handbuch der Organischen Chemie, **13**, 137 (1930).

5) M. Michman, S. Patai, and Y. Wiesel, *J. Chem. Soc. Perkin I*, **1977**, 1705.