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THE PLATINUM COMPLEX CATALYZED REDUCTIVE CARBONYLATION OF NITROARENE TO URETHANE

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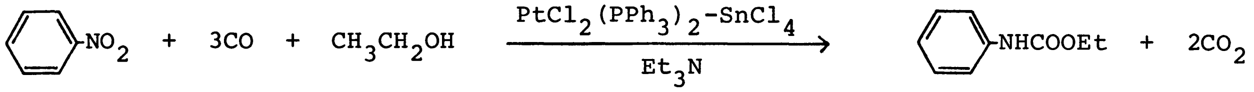
The reductive carbonylation of nitrobenzene to a urethane(ethyl phenylcarbamate) is catalyzed by platinum(II)-tin(IV) systems. The catalytic activities are drastically enhanced by addition of a tertiary amine.

The conventional commercial methods for preparation of isocyanates have consisted of phosgenation of the corresponding amines. Recently the catalytic method for the carbonylation of nitro compounds is of interest. Catalysts for the carbonylation of nitro compounds have been described in several patent literatures, which include rhodium and palladium catalysts.[1)] It is known that a platinum(II)-tin(II) system is a good catalyst for the hydrogenation,[2)] hydroformylation,[3)] and carbonylation[4)] of olefins. However, no studies on the reductive carbonylation of nitro arenes effected by platinum catalysts have been reported.

In this letter, we wish to report preliminary results of an investigation on platinum(II) complex-catalyzed reductive carbonylation of nitrobenzene to urethane.



A typical procedure was as follows. A mixture of nitrobenzene(4.92 g, 40 mmol), dry ethanol(20 ml), $PtCl_2(PPh_3)_2$(158 mg, 0.2 mmol, 0.5 mol% based on nitrobenzene), $SnCl_4$(0.52 g, 2.0 mmol), and triethylamine(1.0 ml) was stirred at 180°C for 4 h under a carbon monoxide pressure(60 atm at 25°C).

The results are shown in Table. In this study, tin(IV) chloride was much more effective as an additive than tin(II) chloride (Runs 1 and 8). This result presents a striking contrast to the platinum-tin chloride catalyst system reported for carbonylations of olefins,[3,4)] where tin(II) chloride was much more favorable than tin(IV) chloride. The urethane was not produced in the absence of the platinum(II) complex or tin chloride additives. Essentially similar results were obtained when $PtCl_2(PPh_3)_2$ in place of $PtCl_2(PhCN)_2$-PPh_3 pair was employed as a catalyst (Runs 1 and 2). The addition of triethylamine to the catalyst system drastically enhanced yield of the urethane (Runs 1 and 6). Without triethylamine as an additive a considerable amount of aniline was generated by reduction of nitrobenzene with ethanol and carbon monoxide.[5)] Elimination of PPh_3 from the catalyst system led to a low yield of the urethane (Run 5). As shown by the equation, carbon monoxide functions as both a deoxygenating and a carbonylating reagent. Therefore, in this

Table. Reductive carbonylation of nitrobenzene by use of Pt complex catalysts[a)]

Run	Tin Halide	Amine	CO (atm)	Temp. (°C)	Conv.[b)] (%)	Yields of Products[b)] (%) Urethane	Aniline
1	$SnCl_4$	Triethylamine	60	180	97	83	8
2[c)]	$SnCl_4$	Triethylamine	60	180	98	78	12
3	$SnCl_4$	Triethylamine	60	200	93	69	5
4	$SnCl_4$	Triethylamine	40	180	97	68	7
5[d)]	$SnCl_4$	Triethylamine	60	180	90	8	32
6	$SnCl_4$	————	60	180	96	19	42
7	$SnCl_4$	Triethylamine	60	160	62	30	5
8	$SnCl_2$	Triethylamine	60	180	97	5	60
9	$SnCl_4$	N-Methylpiperidine	60	180	∿100	76	10
10	$SnCl_4$	Piperidine	60	180	96	46	26
11	$SnCl_4$	n-Butylamine	60	180	90	13	31

a) A mixture of $PtCl_2(PPh_3)_2$(0.2 mmol), tin halide(2.0 mmol), amine(1.0 ml), nitrobenzene(40 mmol), and ethanol(20 ml) was heated for 4 h.

b) Based on the amount of nitrobenzene used and determined by GLC.

c) $PtCl_2(PhCN)_2$(0.2 mmol) and PPh_3(0.4 mmol) were used in place of $PtCl_2(PPh_3)_2$.

d) $PtCl_2(PhCN)_2$(0.2 mmol) was used in place of $PtCl_2(PPh_3)_2$.

study, at least 40 atm of an initial carbon monoxide pressure is required for the reaction. Under the 40 atm of initial carbon monoxide pressure the urethane was also produced in high yield (Run 4). This shows high reactivity of the catalyst system. The highest yield of the urethane was obtained at 180°C in a temperature range of 160∿200°C (Runs 1, 3, and 7). Other amine additives also affected a yield of the urethane (Runs 9, 10, and 11). Generally, the yield of the urethane was improved by using a tertiary amine of high basicity.

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