

## Reductive Carbonylation of Mono- and Dinitroarenes Catalyzed by Montmorillonitebipyridinylpalladium(II) Acetate and Ruthenium Carbonyl

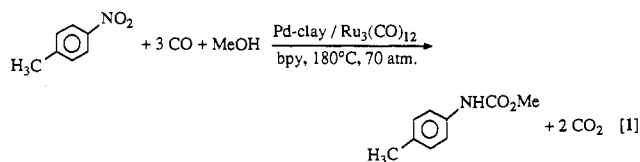
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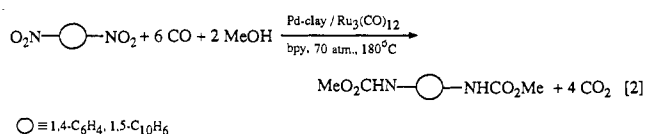
Industrially important materials, such as high-performance plastics, polyurethane elastomers, adhesives, etc., are usually obtained from isocyanates. Phosgene has been used to prepare isocyanates on a commercial basis, and non-phosgene routes have attracted considerable attention in the last two decades.<sup>1-4</sup> One of the approaches being advanced is to first synthesize the urethane, either by oxidative carbonylation of amines<sup>4,5</sup> or by reductive carbonylation of nitro compounds in the presence of an alcohol, followed by thermal elimination of alcohol to form isocyanates.<sup>6,7</sup> While it is well known that various transition-metal catalysts can catalyze the reaction to some extent, little has been reported in the literature on the reductive carbonylation of nitro aromatics using solid supports<sup>7</sup> and, in particular, smectite clays. Transition-metal complexes immobilized on a montmorillonite support, a class of smectite clay, are known to induce enhanced selectivities toward a variety of organic transformations, due to their high surface Brønsted as well as Lewis acidic sites or redox properties.<sup>8</sup> Recently Choudary and co-workers<sup>9</sup> described the use of montmorillonitebipyridinylpalladium(II) acetate for the conversion of amines to *N,N'*-disubstituted ureas in the presence of carbon monoxide. We now report our findings on the highly selective reductive carbonylation of mono- and dinitro aromatic compounds to their corresponding mono- and diurethanes in good yields using montmorillonitebipyridinylpalladium(II) acetate [Pd-clay] coupled with Ru<sub>3</sub>(CO)<sub>12</sub> as catalysts in the presence of bidentate nitrogen donor ligands such as 2,2'-bipyridine. Pd-clay is prepared by the method reported by Choudary et al.<sup>8c,10</sup> reacting chloromontmorillonite (obtained from commercial montmorillonite K10) with *n*-BuLi, followed by treatment with 2,2'-bipyridine and subsequent complexation with Pd(OAc)<sub>2</sub>.

Treatment of *p*-nitrotoluene with carbon monoxide and methanol in the presence of catalytic amounts of Pd-clay, Ru<sub>3</sub>(CO)<sub>12</sub>, and 2,2'-bipyridine (bpy) in dry benzene at 180 °C and 70 atm for 12 h afforded *N-p*-tolylmethylcarbamate in 84% isolated yield (eq 1).



The reaction is highly selective, and no side products such as azo-, azoxytoluene or *N*-methylanilines were detected. However, the formation of the amine is dependent on the proportion and extent of dryness of the methanol. The importance of each component of the catalytic system was examined with *p*-nitrotoluene as a model substrate. 2,2'-Bipyridine is necessary for this reaction, since in its absence the reaction takes longer (up to 48 h) for complete conversion. The monodentate nitrogen donors *N*-methylpyrrolidine (afforded 52% urethane, 48% amine) and tetramethylethylenediamine (75% urethane, 25% amine) gave inferior selectivities, while 1,10-phenanthroline (87% urethane) can be used instead of 2,2'-bipyridine. Control experiments in the absence of Ru<sub>3</sub>(CO)<sub>12</sub> showed that virtually no reaction occurred in 18 h, while 74% conversion of the starting material with 94% selectivity to the urethane resulted after 48 h. However, there was no urethane (<5%) observed in the absence of Pd-clay, with *N,N*-dimethyl-*p*-toluidine (84%) formed instead. Note that the use of 2,2'-bipyridinylpalladium acetate and Ru<sub>3</sub>(CO)<sub>12</sub> or a mixture of Pd(OAc)<sub>2</sub>, 2,2'-bipyridine, and Ru<sub>3</sub>(CO)<sub>12</sub> afforded the urethane and amine in a 7:3 ratio, i.e., much less selective than the clay system.

To our knowledge, there are no publications in the literature to prepare the dicarbamate precursors of *p*-phenylene diisocyanate (PPDI) and 1,5-naphthalene diisocyanates (NDI) by direct carbonylation methods. A recent report by Moore and co-workers<sup>3</sup> advocates the utility of PPDI as a replacement for methylenediphenyl diisocyanate (MDI) in the manufacture of polyurethanes in terms of its performance as a polymer. They described the synthesis of PPDI by the conventional method using toxic phosgene. The method reported herein is very selective toward the formation of diurethanes directly by the carbonylation of dinitro compounds (eq 2).



A series of dinitro compounds were subjected to carbonylation in the same manner as *p*-nitrotoluene to form diurethanes [Table I], the precursors of industrially valuable diisocyanates, in good to excellent yields, including toluene diisocyanate (TDI), *p*-phenylene diisocyanate (PPDI), and 1,5-naphthalene diisocyanate (NDI). Small quantities of monocarbamates were also obtained in each case. Attempts to prepare methylenediphenyl methyl-dicarbamate (MDI precursor) were unsuccessful, with the intermediate diamine undergoing facile polymerization.

The mechanism of the reaction is not clear at this stage. However, it is conceivable that the role of Pd-clay is to initially reduce the nitro compound to the amine, which in turn experiences Ru<sub>3</sub>(CO)<sub>12</sub>-catalyzed carbonylation to the urethane, promoted by the surface Brønsted and Lewis acidities of the smectite clay. Other supported montmorillonite catalysts were examined as catalysts, including Ru(bpy)-montmorillonite (1), Pd(bpy)-montmorillonite (2), and RuPd(bpy)-montmorillonite (3), which were prepared by the method reported by Kiiski et al.<sup>11</sup> Catalysts 2 and 3 are completely inactive, whereas catalyst 1 afforded the urethane with 56% selectivity along with 44% amine. Palladium on carbon was comparable with catalyst 1 and gave 55% carbamate

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**Table I.** Reductive Carbonylation of Nitro Compounds Catalyzed by Pd-Clay and  $\text{Ru}_3(\text{CO})_{12}$ 

nitroarene	alcohol <sup>a</sup>	products <sup>b</sup>		yield by NMR (isolated), %	
		mono-/diurethane	amine/monourethane	urethane	amine
	A			97(84)	
	A			82(65)	18(7)
	A			94(75)	
	A			88	12
	A			75(62)	25(18)
	B			64	35
	C			trace	82(62)
	D			trace	c
	A			96(67)	<5
	A			68(46)	32(18)
	A			67	33
	A			72(64)	28(12)

<sup>a</sup> A = MeOH; B = EtOH; C = *i*-PrOH; D = *t*-BuOH. <sup>b</sup> Products were identified by comparison of spectral data (IR, NMR (<sup>1</sup>H, <sup>13</sup>C), MS) with authentic material. <sup>c</sup> Major product after 12 h. Converted to unidentified product on prolonged reaction.

ester. The results indicate that the unique combination of Pd-clay with  $\text{Ru}_3(\text{CO})_{12}$  and 2,2'-bipyridine displays high selectivity, and this may be due to the enhanced surface acidities of the clay upon anchoring compared with the supported catalysts.

The following general procedure was used: a mixture of the substrate (2 mmol), Pd-clay (40 mg, contains 0.008 mmol of Pd),  $\text{Ru}_3(\text{CO})_{12}$  (10 mg, 0.014 mmol), 2,2'-bipyridine (32 mg, 0.2 mmol), and dry methanol (30 mmol) in benzene (12 mL) was placed in a 30-mL autoclave. The autoclave was flushed with carbon monoxide, subsequently pressurized to 70 atm, and then subjected to heating overnight at 180 °C. The reaction mixture was cooled to room temperature, passed through neutral alumina, and then concentrated by rotary evaporation. Recrystallization from a 9:1 mixture of hexane and chloroform afforded pure

urethane. In the case of dinitro compounds, double the amounts of Pd-clay,  $\text{Ru}_3(\text{CO})_{12}$ , 2,2'-bipyridine, and methanol were used, and the reactions were carried out for 24 h. Mono- and diurethanes were separated by fractional recrystallization from 4:1 hexane–chloroform.

In conclusion, the dual catalytic system consisting of Pd-clay and  $\text{Ru}_3(\text{CO})_{12}$  is very useful for the synthesis of mono- and especially diurethanes from nitro compounds. This research both is of fundamental interest and has considerable commercial potential.

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