Carbonylation of aromatic dinitro compounds with carbon monoxide to respective dicarbamates in the presence of the PdCl$_2$/Fe/I$_2$/Py catalytic system

Monika Karpińska*, Jadwiga Skupińska, Piotr Baran

Laboratory of Physicochemical Fundamentals of Chemical Technology, Department of Chemistry, The University of Warsaw, 02-093 Warsaw, Pasteura 1, Poland

ABSTRACT

The object of this study was the reductive carbonylation of 1,3-dinitrobenzene, 1,4-dinitrobenzene and 2,4-dinitrotoluene to respective dicarbamates in the presence of the PdCl$_2$/Fe/I$_2$/Py catalytic system. By increasing the catalyst amount and extending the carbonylation reaction time a 100% conversion of dinitrobenzene to the corresponding dicarbamates was achieved with a selectivity of 87, 68, and 55%, for 1,4-, 1,3-dinitrobenzene and 2,4-dinitrotoluene, respectively.

1. Introduction

The catalytic carbonylation of nitro compounds has been gaining considerable interest for a long time. The reactions may be useful in affording numerous valuable products, i.e.: isocyanates, carbamates, ureas, azo compounds, azoxy compounds, amines, amides and Schiff's bases [1,2]. Carbamates and ureas are important intermediates and end products in the manufacture of medicines, pesticides and isocyanates. Diisocyanates are major intermediates in the synthesis of polyurethanes, pesticides, artificial leather, adhesives and paints. Commercially, isocyanates are produced by the phosgene process from respective amines in the reaction of condensation with phosgene [3,4]. These amines, used in the condensation reactions, are obtained in the reaction of respective nitrobenzenes reduction. However, these reactions have certain drawbacks, of which the major ones are the need to use phosgene and the formation of waste HCl in great quantity. Therefore, already the 1970s witnessed the beginning of research aimed at finding such methods of isocyanates syntheses in which toxic phosgene could be eliminated. Among the new methods obtained the most promising are those based on catalytic reaction of nitro compounds [5–14] and of amines [15–25] carbonylation to isocyanates or to carbamates in the presence of alcohol. Direct carbonylation of nitro compounds to the corresponding isocyanates, however, is a process that requires high pressure and high temperature. Carbamates, instead, can be obtained under much milder conditions. Thermal decomposition of dicarbamates produces the isocyanates [26].

Reductive carbonylation of aromatic dinitro compounds is an attractive way to obtain the major products like diisocyanates and dicarbamates and, in particular, 2,4-tolylenediisocyanate. There are not many reports in the literature on the carbonylation of dinitro aromatics. Since the 1970s just a few papers have been published on the subject. In one of the first relevant patents, palladium deposited on carbon Pd/C [27,28] and Pd/Al$_2$O$_3$ [29,30] with a Lewis acid (FeCl$_3$) as a co-catalyst were used in the carbonylation of dinitro aromatics. Pd/C with the addition of some chelating amines like phenanthroline or its derivative, e.g. 4,7-diphenyl-1,10-phenanthroline and Brönsted acids like 2,4,6-trimethylbenzenesulfonic acid were active catalysts [31]. Palladium compounds, such as Pd(OAc)$_2$, [Pd(dppp)]Cl$_2$, [Pd(PPh$_3$)$_2$]Cl$_2$ [32]; Pd(phen)$_2$(OTf)$_2$ [33]; Pd-clay/Ru(CO)$_{12}$ [34]; Pd(phen)$_2$(PF$_6$)$_2$ [35]; and [(Ph$_3$P)$_4$Rh$_2$(μ-OH)$_2$]·2C$_6$H$_6$ [36] display catalytic activity in the carbonylation of the dinitro aromatics.

In 2005, a comprehensive article on the carbonylation of 2,4-dinitrotoluene in the presence of [Pd(phen)$_2$]$^{2+}$ catalyst (where phen = phenanthroline) was published. The addition of diphenylphosphinic acids [37] and phosphorus acids [38] were found to improve the carbonylation yield. These data prompted us to investigate the nitro compounds carbonylation over the original catalyst which consists of PdCl$_2$ and a redox cocatalyst: a mixture of Fe/I$_2$ with tertiary amine, pyridine. In our earlier works, the course of nitrobenzene carbonylation over the PdCl$_2$/Fe/I$_2$/Py (Py = pyridine) catalytic system was described. The effect of the catalyst components on catalyst activity was determined [39] and the

* Corresponding author. Fax: +48 22 822 59 96.
  E-mail address: monka@chem.uw.edu.pl (M. Karpińska).

Table 1
Physical and analytical data of carbamates and ureas.

No.	Compound	Melting point (°C)		IR (KBr) (cm^{-1})	ES-MS	Elemental analysis (%)	
		Found	Requires			Found	Requires
1	Ethyl N-(3-nitro)phenylcarbamate	66	64–66 [46]	3345, 1702, 1600, 1548, 1253, 1060, 702		51.40%C, 13.31%N, 4.79%H	51.43%C, 13.33%N, 4.76%H
2	Ethyl N-(4-nitro)phenylcarbamate	128–129	128–129 [47]	3350, 1701, 1600, 1546, 1250, 1060, 703		51.43%C, 13.28%N, 4.80%H	51.43%C, 13.33%N, 4.76%H
3	Diethyl N,N-1,4-phenylenedicarbamate	198–199	198–200 [49]	3350, 1698, 1539, 1265, 1069		57.10%C, 10.99%N, 6.39%H	57.14%C, 11.12%N, 6.35%H
4	Ethyl N-(2-methyl-5-nitro)phenylcarbamate	137	137 [50]	3350 1699,1600, 1550, 1460, 1250, 1059, 695		53.60%C, 12.49%N, 5.38%H	53.57%C, 12.50%N, 5.36%H
5	Ethyl N-(4-methyl-3-nitro)phenylcarbamate	76	76–78 [51]	3395, 1700, 1610, 1550, 1455, 1245, 1062, 690		53.62%C, 12.53%N, 5.31%H	53.57%C, 12.50%N, 5.36%H
6	Diethyl N,N-1,3-phenylenedicarbamate	145	143–145 [48]	3345, 1695, 1540, 1263, 1069	275 (M+Na$^+$), 253 (M+H$^+$), 225, 197	57.04%C, 11.08%N, 6.38%H	57.14%C, 11.12%N, 6.35%H
7	Diethyl N,N-(4-methyl-1,3-phenylene)dicarbamate	135–136	135–137 [48]	3355, 1698, 1540, 1250, 1064, 660	289 (M+Na$^+$), 267 (M+H$^+$), 284, 221, 193	58.84%C, 10.55%N, 6.80%H	58.65%C, 10.53%N, 6.76%H
8	Ethyl N-(3-amino-4-methyl)phenylcarbamate	89	89 [44]	3449, 3368, 1728,1607, 1523, 1242, 1060	195 (M+H$^+$), 167, 157, 149 (EI-MS)	61.96%C, 14.46%N, 7.16%H	61.86%C, 14.43%N, 7.21%H
9	Ethyl N-(5-amino-2-methyl)phenylcarbamate	92	91.5 [44]	3432, 3392, 1713,1592, 1464, 1230, 1061	194 (M), 166, 148, 121, 94, 29 (EI-MS)	61.81%C, 14.45%N, 7.25%H	61.86%C, 14.43%N, 7.21%H
10	Ethyl N-(3-amino)phenylcarbamate	Oil			181 (M+H$^+$), 153,135 (EI-MS)		
11	Ethyl N-(4-amino)phenylcarbamate	70	74 [52]		180 (M), 134, 107, 80, 53, 29 (EI-MS)		
12	[N,N'-(3,3'-Diethyldicarbamate)-(4,4'-dimethyl)]diphenylurea				437 (M+Na$^+$), 415 (M+H$^+$), 194		
13	[N,N'-(3,3'-Diethyldicarbamate)]diphenylurea				409 (M+Na$^+$), 404, 387 (M+H$^+$), 297, 181		
14	[(3-Amino)-N-(3'-ethylcarbamate)-(4,4'-dimethyl)]diphenylurea				365 (M+Na$^+$), 343 (M+H$^+$), 123		
15	[(3-Amino)-N-(3'-ethylcarbamate)]diphenylurea				337 (M+Na$^+$), 353, 315 (M+H$^+$), 217, 109		
16	[(3-Nitro)-N-(3'-ethylcarbamate)]diphenylurea				367 (M+Na$^+$), 345 (M+H$^+$), 299, 207		

carbonylation reaction mechanism was proposed [40,41]. Since the reaction yields were high, this catalyst was applied in the reaction of carbonylation of substituted nitro compounds in order to obtain the defined products. Thus, in this paper, we present the results of study on the carbonylation of dinitro compounds: 1,3-dinitrobenzene, 1,4-dinitrobenzene and 2,4-dinitrotoluene in the presence of the $Pd/Fe/I_2$ catalytic system. A comprehensive analysis of the carbonylation reaction products and the course of that reaction is also made.

2. Experimental

2.1. Materials

All operations were carried out using standard Schlenk techniques under oxygen-free argon. Ethanol was distilled from CaH_2 ($5\,g/dcm^3$), aniline and pyridine from KOH. They were stored under argon. 1,3-Dinitrobenzene, 1,4-dinitrobenzene and 2,4-dinitrotoluene commercial reagents from Aldrich, were dried over phosphorus pentoxide. 1,3- and 1,4-phenylenediamine and 2,4-toluenediamine were of commercial (Aldrich) analytical reagent grade, and dried over 3A molecular sieves in a desiccator. Ethyl chloroformate, 2,4-toluene diisocyanate and 1,3-phenylene diisocyanate were commercial (Aldrich) reagents.

$PdCl_2$, iodine and iron powder, from POCh Poland, were used as received. Carbon monoxide of 99.9% purity as supplied by Multax was directly used as received.

2.2. Reaction procedure

The reaction was carried out in a 200-ml stainless-steel autoclave equipped with a magnetic stirrer, under water-free and oxygen-free conditions. Then $PdCl_2$ (catalyst) 0.01 g (0.056 mmol) and Fe-powder (co-catalyst) 0.15 g (2.68 mmol) were placed in the autoclave, which was evacuated and subsequently filled with purified argon. Then, under an argon stream, 0.03 g (0.12 mmol) iodine, 0.5 g (6.2 mmol) pyridine; 4 or 6 g of dinitrobenzene, 20 ml ethanol as solvent and reagent were introduced. Carbon monoxide (4 MPa) was fed directly into the reaction mixture from the cylinder. Then the autoclave was fixed and placed in an oil bath preheated to $180\,°C$. On completion of the reaction the autoclave was cooled in a water bath, vented, and a liquid sample of the reaction mixture was taken for further analysis. The yield of the reaction was calculated from the HLPC data using a Waters liquid chromatograph with a (Waters) Nova-pack C_{18} column and a UV 486 detector. A water/acetonitrile (36:65) mixture was used as eluent. The eluent flow rate was established at 0.5 ml/min.

For quantitative analysis of the reaction mixtures, ethyl N-3-chlorophenylcarbamate was used as internal standard. The response factors of the starting materials, the intermediates and the reaction products were determined by using pure substances.

Qualitative analysis of the reaction products was performed with a HP-1100 liquid chromatograph coupled with an API 365 mass spectrometer and with the use of a Merck C_{18} (250 mm × 2 mm) column. A water/acetonitrile (36:65) mixture was used as eluent. The eluent flow rate was established at 0.2 ml/min.

Elemental analysis of the synthesized compounds was made using a PerkinElmer model 2400 mark II CHNS/O microanalyser.

Identification of the compounds synthesized was accomplished with a Shimadzu FT-IR 8201 PC instrument.

2.3. Carbamates synthesis

2.3.1. Ethyl N-(4-methyl-3-nitro)phenylcarbamate, ethyl N-(2-methyl-5-nitro)phenylcarbamate, ethyl N-(3-nitro)phenylcarbamate, ethyl N-(4-nitro)phenylcarbamate, ethyl diethyl 1,4-phenylenedicarbamate

The carbamates were obtained as described previously [42]. A mixture of nitroaniline (20 mmol), K_2CO_3 (20 mmol), ethyl chloroformate (60 mmol) and dioxane (30 ml) was refluxed for 2 h. The ethyl chloroformate in excess was evaporated under reduced pressure and insoluble potassium salts were discarded by filtration. The filtrate was diluted with H_2O (90 ml), and the precipitate formed was collected, washed with H_2O and dried. Crystallization from a mixture of ethyl alcohol–H_2O (5:1) afforded the title compounds.

The chemical names, physical and analytical data of carbamates are given in Table 1.

2.3.2. Ethyl N-(3-amino-4-methyl)phenylcarbamate, ethyl N-(5-amino-2-methyl)phenylcarbamate, ethyl N-(3-amino)phenylcarbamate, ethyl N-(4-amino)phenylcarbamate

The carbamates were obtained as described previously[43,44]. Into a mixture of 1 g of ethyl N-(4-methyl-3-nitro)phenylcarbamate and 2 g of granulated tin, 10 ml of concentrated hydrochloric acid was added portionwise. On reaction completion the solution was heated on a steam bath until complete conversion of the nitro groups. Then the reaction mixture was cooled and 20 ml of 30% sodium hydroxide solution was added to solubilize the stannous hydroxide precipitate. Next, the amine formed was extracted from the solution with ether and then the ether was evaporated. The precipitate formed was recrystallized from chloroform. The chemical names, physical and analytical data of carbamates are given in Table 1.

Table 2
Effect of the 1,3-dinitrobenzene carbonylation conditions on the selectivity of the products formed.

No.	$PdCl_2$ (mmol)	1,3 DNB/Pd (molar ratio)	Time (min)	1,3DNB conversion (%)	Yield %				
					1,3 DC	3NC	3AC	3NA	3DA
1	0.056	714	45	30	–	18	Trace	3	–
2	0.056	714	90	90	2.5	68	Trace	15	10
3	0.056	714	120	90	2.5	68	Trace	10	Trace
4	0.056	714	240	90	4	70	Trace	8	7,5
5	0.056	428	240	100	37	39	16	7	Trace
6[a]	0.056	428	360	100	42	35	15	8	Trace
7[a]	0.168	238	120	90	25	60	Trace	8	Trace
8	0.168	238	240	98	52	2	37	6	–
9[a]	0.168	142	120	99	43	9	35	Trace	5
10[a]	0.168	142	240	99	50	9	37	Trace	Trace
11[a]	0.168	142	360	99	68	6	26	Trace	Trace

Reaction conditions: catalyst system $Pd:Fe:I_2 = 1:48:2,1$ molar ratio; 1,3-dinitrobenzene 40 mmol. 1,3 DNB = 1,3-dinitrobenzene; 1,3 DC = diethyl 1,3-phenylenedicarbamate; 3NC = ethyl N-(3-nitro)phenylcarbamate; 3AC = ethyl N-(3-amino)phenylcarbamate; 3NA = 3-nitroaniline; 3DA = 1,3-phenylenediamine.

[a] 1,3-Dinitrobenzene 24 mmol; pyridine 6.2 mmol, T $180\,°C$; $P(CO)$ 4 MPa; ethanol 20 ml; trace = less than 0.5%.
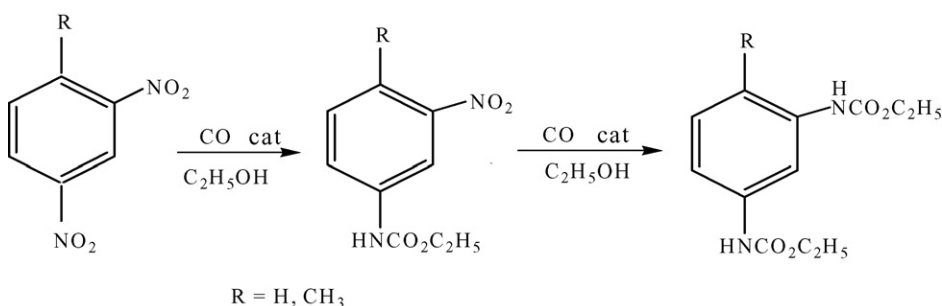
2.3.3. Diethyl N,N-(4-methyl-1,3-phenylene)dicarbamate, diethyl 1,3-phenylenedicarbamate

The synthesis was performed as described previously [45]. Into 20 ml ethanol 7.5 mmol 2,4-toluene diisocyanate was added portionwise. The solution was stirred for 4 h under argon at room temperature. On concentrating the mixture a snow-white product formed that was subsequently filtered off.

The chemical names, physical and analytical data of carbamates are given in Table 1.

3. Results

Catalysts known to be active in carbon monoxide carbonylation of dinitro aromatic compounds are limited in number. During the reaction of carbonylation the nitro groups are converted to amino and carbamato groups and, as a result, the electron interactions in the aromatic ring change, which affects the reactivity of the intermediates (reaction (1)).

lation reaction of 1,3-dinitrobenzene (1,3 DNB), 1,4-dinitrobenzene (1,4 DNB) and 2,4-dinitrotoluene (2,4 DNT).

3.1. 1,3-Dinitrobenzene (1,3 DNB) carbonylation

The results of the 1,3 DNB carbonylation reaction are presented in Table 2. The major product of this reaction is ethyl *N*-phenyl-1,3-dicarbamate (1,3 DC). In addition, in the reaction mixture the intermediates were identified as shown in Fig. 1.

The products presented in Fig. 1 occur in the product mixture in variable quantities. The ureas were found in trace amounts. The product mixture composition was also found to vary depending on the reaction conditions. For a low catalyst concentration (1,3 DNB/PD mole ratio = 714) after 45 min 1,3 DNB conversion was 30%, nitroaniline yield was 3%, and nitrocarbamate yield was 18% (Table 2, entry 1). As early as after 90 min of the reaction 1,3 DNB conversion reached 90% and remained constant during a

$$R = H, CH_3$$

$$(1)$$

The PdCl$_2$/Fe/I$_2$/Py catalytic system is an active and selective catalyst in the reductive carbonylation of nitrobenzene to carbamate [40,41]. We expected the catalyst to be also active in the reaction of carbonylation of dinitro aromatics. It was used in the carbony-

prolonged reaction time. As the reaction progressed, the nitroaniline yield increased to 15% after 90 min, to decline to 8% after 240 min. The carbamate rose to 68% in yield after 90 min and its concentration remained at that level despite an extended reaction
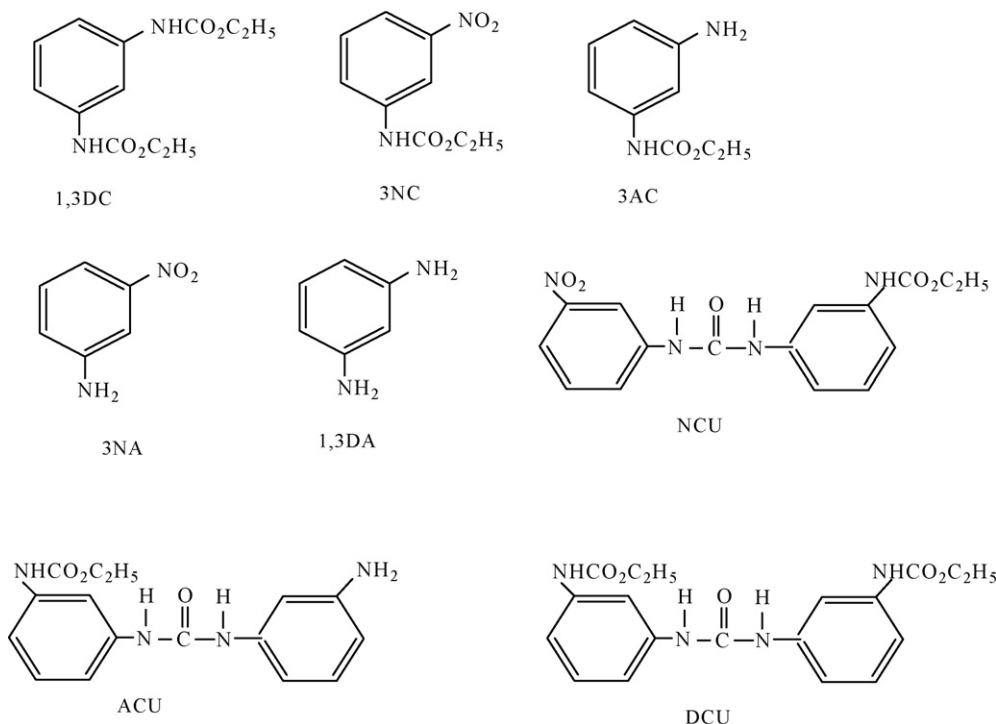
Fig. 1. The 1,3-dinitrobenzene carbonylation reaction products. Abbreviations: 1,3 DC = diethyl 1,3-phenylenedicarbamate; 3NC = ethyl *N*-(3-nitro)phenylcarbamate; 3AC = ethyl *N*-(3-amino)phenylcarbamate; 3NA = 3-nitroaniline; 1,3 DA = 1,3-phenylenediamine; NCU = [(3-nitro)-*N*-(3′-ethylcarbamate)]diphenylurea; ACU = [(3-amino)-*N*-(3′-ethylcarbamate)]diphenylurea; DCU = *N*,*N*′-(3,3′-diethyldicarbamate)]diphenylurea.

Table 3
Effect of the 1,4-dinitrobenzene carbonylation conditions on the selectivity of the products formed.

No.	PdCl$_2$ (mmol)	1,4 DNB/Pd (molar ratio)	Time (min)	1,4 DNB conversion (%)	Yield %				
					1,4 DC	4NC	4AC	4NA	1,4DA
1	0.056	428	240	100	58	29	1	13	Trace
2	0.168	142	120	97	67	<1	25	2	Trace
3	0.168	142	240	100	79	Trace	17	2	Trace
4	0,168	142	360	100	87	Trace	13	1	Trace

Reaction conditions: catalyst system Pd:Fe:I$_2$ = 1:48:2,1 molar ratio; 1,4-dinitrobenzene 24 mmol; pyridine 6.2 mmol, T 180 °C; P(CO) 4 MPa; ethanol 20 ml, trace = less than 0.5%; 1,4 DNB = 1,4-dinitrobenzene; 1,4 DC = diethyl 1,4-phenylenedicarbamate; 4NC = ethyl*N*-(4-nitro)phenylcarbamate; 4AC = ethyl *N*-(4-amino)phenylcarbamate; 4NA = 4-nitroaniline; 1,4 DA = 1,4-phenylenediamine.

time. After 90 min dicarbamate appeared in the products (2.5%) and its quantity varied insignificantly after 240 min (up to 4%). Minor aminocarbamate traces were detected in the products (Table 2, entries 2–4).

To achieve higher conversion, the amount of the catalyst was increased in the reaction mixture. For higher catalyst concentrations and for all the reactions studied the dicarbamate yield increased, while 1,3 DNB conversion reached 100%. For a molar ratio of 1,3 DNB/Pd = 428 after 240 min, 37% DC, 39% nitrocarbamate and 7% nitroaniline were obtained and aminocarbamate appeared in the reaction product in a 16% yield (Table 2, entry 5). For the reaction time extended to 360 min, with the catalyst concentration kept constant, the dicarbamate yield increased to 42%, while the quantity of the other intermediates remained unaffected (Table 2, entry 6).

Next, the catalyst concentration was increased so that the molar ratio was 1,3 DNB/Pd = 238. After 120 min the dicarbamate yield was 25%, nitrocarbamate and nitroaniline yields were 60% and 7.5%, respectively, and aminocarbamate was found in a trace amount. Extension of the reaction time to 240 min increased the yields of dicarbamate to 52% and aminocarbamate to 37%, while the yields of nitrocarbamate and nitroaniline dropped to 2% and 6%, respectively (Table 2, entries 7 and 8). A further increase in catalyst concentration led to a higher reaction rate; as soon as after 120 min the dicarbamate yield reached 43%. In the reaction products nitrocarbamate (9%) and aminocarbamate (35%) were also found. Extension of reaction time to 240 min yielded 50% dicarbamate, 37% aminocarbamate, and 9% nitrocarbamate. After 360 min the dicarbamate yield increased to 68%, nitrocarbamate decreased to 6% and aminocarbamate decreased to 26% (Table 2, entries 9–11). Thus, it can be concluded that with the increase in catalyst concentration, the yields of dicarbamate and aminocarbamate rise whereas those of nitroaniline and nitrocarbamate drop.

3.2. 1,4-Dinitrobenzene (1,4 DNB) carbonylation

The carbon-monoxide carbonylation of 1,4-dinitrobenzene in the presence of the PdCl$_2$/Fe/I$_2$/Py catalytic system occurs rapidly as compared with that of 1,3-dinitrobenzene. Composition of the products obtained for various reaction conditions is summarized in Table 3. The major product is diethyl *N*,*N*-1,4-phenyldicarbamate. The other products are presented in Fig. 2.

The carbonylation reactions were carried out for two catalyst concentrations: at a molar ratio 1,4 DNB/Pd = 428 or 142. Under the reaction conditions no unreacted 1,4 DNB was found in the reaction products. For a lower catalyst concentration in addition to dicarbamate (58%), nitrocarbamate (29%) and nitroaniline (13%) were also found among the reaction products (Table 3, entry 1). A higher catalyst concentration brought about a radical change in the products composition. Nitrocarbamate and nitroaniline were found to occur in trace amounts. Additionally, apart from dicarbamate (67%) aminocarbamate (25%) was formed. Extension of the reaction time to 360 min resulted in an increase in the dicarbamate yield to 87%, and in a decrease in the aminocarbamate yield to 13% (Table 3, entries 2–4).

The carbonylation of 1,3-dinitro- and 1,4-dinitrobenzene follows the same reaction pathway. Extension of the reaction time and a higher catalyst concentration results in an increase in the yields of dicarbamate and aminocarbamate, respectively, and a decrease in those of nitrocarbamate and nitroaniline formed.

3.3. 2,4-Dinitrotoluene (DNT) carbonylation

In the carbon monoxide carbonylation of DNT over the PdCl$_2$/Fe/I$_2$ catalytic system, in addition to the desirable dicarbamate a mixture of intermediates was formed. Products of the reaction are shown in Fig. 3. Ureas in trace amounts were found in the reaction products.

The reaction mixture composition observed varied with reaction conditions (Table 4). For low catalyst concentrations, a molar ratio DNT/Pd = 714, the DNT conversion after 90 min was 59% and extension of reaction time hardly affected the DNT conversion. The dicarbamate (TDC) yield increased from 3 to 10%. Apart from that, methylnitroanilines (7% 4M3NA and 8% 2M5NA), methylnitrocarbamates (37% 4M3NC and 5% 2M5NC) and trace amounts of diamine and aminocarbamates were formed (Table 4, entries 1–3).

A higher catalyst concentration (DNT/Pd = 428) caused a rise of the dicarbamate yield to 20% (Table 4, entry 4). At the same time the
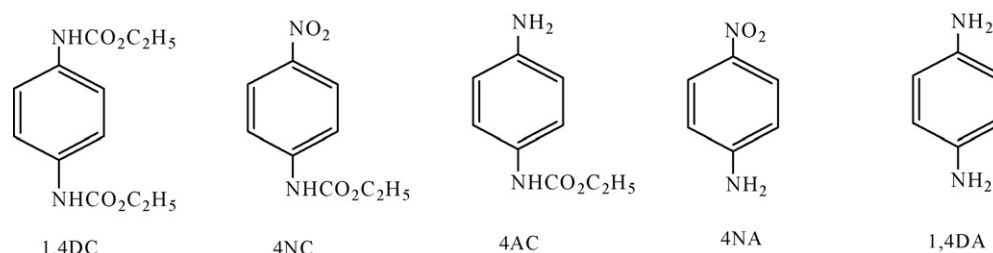

Fig. 2. The 1,4-dinitrobenzene carbonylation reaction products. Abbreviations: 1,4 DC = diethyl 1,4-phenylenedicarbamate; 4NC = ethyl *N*-(4-nitro)phenylcarbamate; 4AC = ethyl *N*-(4-amino)phenylcarbamate; 4NA = 4-nitroaniline; 1,4 DA = 1,4-phenylenediamine.
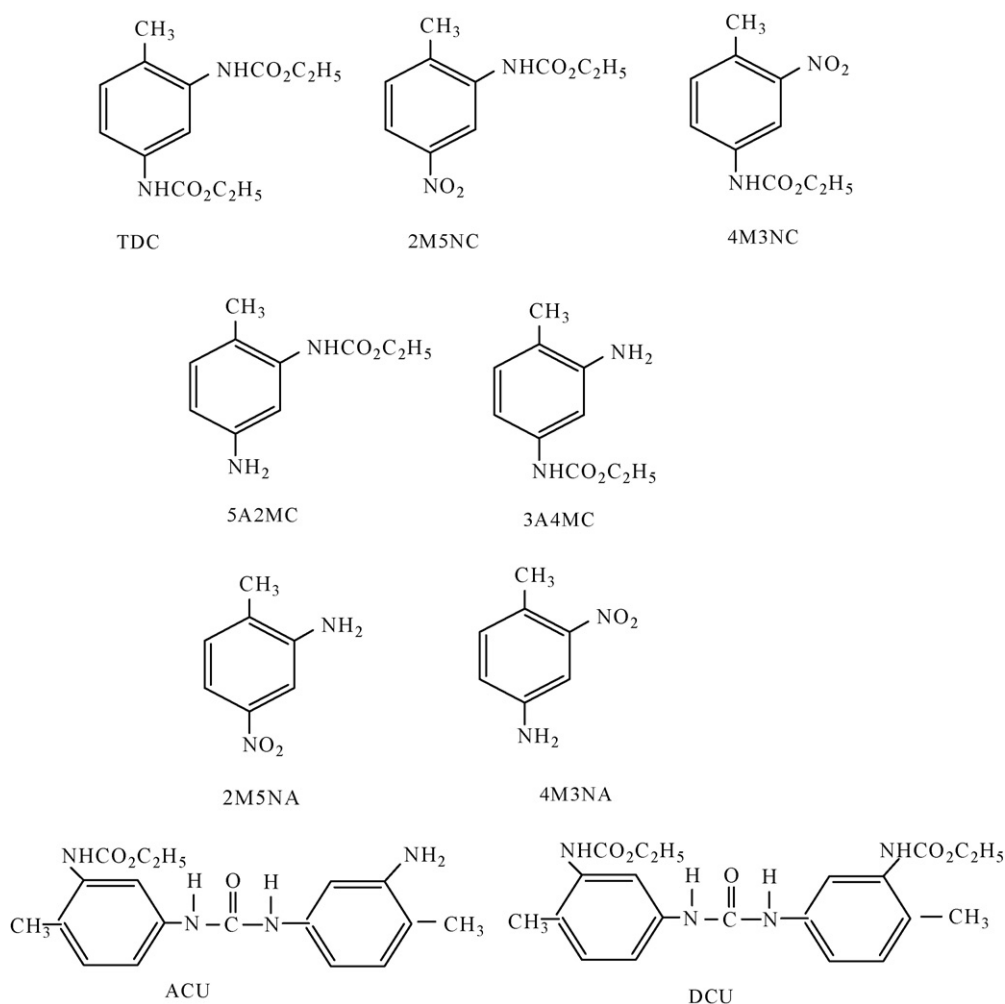
Fig. 3. The 2,4-dinitrotoluene carbonylation reaction products. Abbreviations: TDC = diethyl *N,N*-(4-methyl-1,3-phenylene)dicarbamate; 2M5NC = ethyl *N*-(2-methyl-5-nitro)phenylcarbamate; 4M3NC = ethyl *N*-(4-methyl-3-nitro)phenylcarbamate; 5A2MC = ethyl *N*-(5-amino-2-methyl)phenylcarbamate; 3A4MC = ethyl *N*-(3-amino-4-methyl)phenylcarbamate; 2M5NA = 2-methyl-5-nitroaniline; 4M3NA = 4-methyl-3-nitroaniline; ACU = [(3-amino)-*N*-(3′-ethylcarbamate)-(4,4′-dimethyl)]diphenylurea; DCU = [*N,N*′-(3,3′-diethyldicarbamate)-(4,4′-dimethyl)]diphenylurea.

yield of nitrocarbamate decreased while the amount of aminocarbamate increased.

An increased catalyst concentration to 0.168 mmol (DNT/Pd = 238 mol) resulted in the DNT conversion of 79% in the reaction conducted for 120 min. The dicarbamate was 23%. When the reaction time was extended to 240 min, the carbamate yield increased to 45% (Table 4, entries 5 and 6). At the same time the amount of nitrocarbamate and nitroaniline decreased,

Table 4
Effect of the 2,4-dinitrotoluene carbonylation conditions on the selectivity of the products formed.

No.	PdCl$_2$ (mmol)	2,4 DNT/Pd (molar ratio)	Time (min)	2,4 DNT conversion (%)	Yield %						
					TDC	2M5NC	4M3NC	5A2MC	3A4MC	2M5NA	4M3NA
1	0.056	714	90	59	3	9	22	Trace	Trace	5	10
2	0.056	714	180	62	8	7	37	Trace	Trace	5	8
3	0.056	714	240	65	10	5	37	Trace	3	8	7
4[a]	0.056	428	240	72	20	3	19	2	11	5	6
5	0.168	238	120	79	23	8	38	Trace	Trace	5	3
6	0.168	238	240	90	45	5	3	3	27	1	Trace
7	0.168	238	22h	100	25	3	5	Trace	45	3	Trace
8[a]	0.168	142	60	96	45	1	2	4	28	1	Trace
9[a]	0.168	142	120	99	50	1	2	5	33	1	Trace
10[a]	0.168	142	240	99	53	1	2	5	35	2	2
11[a]	0.168	142	360	100	55	Trace	2	3	40	1	Trace

Reaction conditions: catalyst system Pd:Fe:I$_2$ = 1:48:2,1 molar ratio; 2,4-dinitrotoluene 40 mmol. 2,4 DNT = 2,4-dinitrotoluene; TDC = diethyl *N,N*-(4-methyl-1,3-phenylene)dicarbamate; 2M5NC = ethyl *N*-(2-methyl-5-nitro)phenylcarbamate; 4M3NC = ethyl *N*-(4-methyl-3-nitro)phenylcarbamate; 5A2MC = ethyl *N*-(5-amino-2-methyl)phenylcarbamate; 3A4MC = ethyl *N*-(3-amino-4-methyl)phenylcarbamate; 2M5NA = 2-methyl-5-nitroaniline; 4M3NA = 4-methyl-3-nitroaniline.

[a] 2,4-Dinitrotoluene 24 mmol; pyridine 6.2 mmol, *T* 180 °C; *P*(CO) 4 MPa; ethanol 20 ml; trace = less than 0.5%.

and 3-amino-4-methylcarbamate was formed in a 27% yield. Extension of the reaction time to 22 h is not recommended, because after that time the amount of dicarbamate in the products was found to decrease from 45 to 25% while the amount of 3-amino-4-methylcarbamate increased to 45% (Table 4, entry 7).

A further increase in catalyst concentration (DNT/Pd = 142; Table 4, entries 8–11) resulted in an impaired reaction selectivity with a complete conversion just after 60 min. The dicarbamate yield achieved a maximum of 55% after 360 min. At the same time, 3-amino-4-methylcarbamate was formed in a 40% yield.
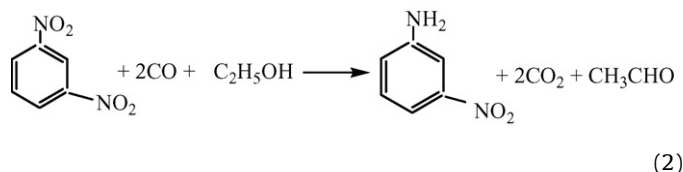
4. Discussion of results

The results indicate that the reaction of carbonylation of dinitro compounds is a multistage reaction in the course of which a host of intermediates are formed as shown in Figs. 1–3 and in Tables 2–4. This stems from the fact that depending on the reaction time a large variety of products are present in the reaction mixture. Should the reaction be stopped at the initial stage, nitrocarbamate and nitroaniline are present in considerable quantity, with minor quantity of carbamate in the reaction mixture. When the reaction proceeds to completion, the products are dicarbamate and aminocarbamate.
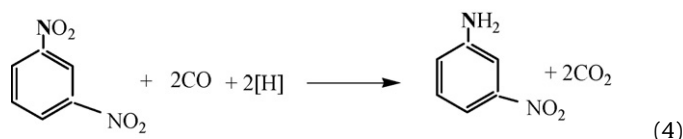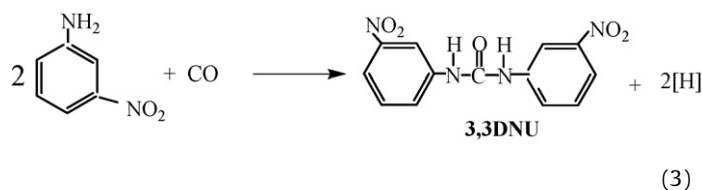
It was found that by extending the reaction time and by increasing catalyst concentration the dicarbamate yield was increased. A 100% carbamate yield, however, could not be obtained. Invariably, in addition to dicarbamate the corresponding aminocarbamate was found in the reaction mixture in considerable quantity as well as other intermediate products in minor quantities. An excessive extension of the reaction time is unfavorable. When the reaction is allowed to proceed for too long time, the dicarbamate quantity decreases, probably on account of dicarbamate decomposition to aminocarbamate, the amount of which increases. By increasing the catalyst quantity and by extending the carbonylation reaction time a 100% conversion of dinitrobenzene to dicarbamates was obtained with a selectivity of 87%, 68%, 55% for 1,4,- 1,3- dinitrobenzene and 2,4-dinitrotoluene, respectively.

From our previous study the carbonylation of aromatic nitro compounds in the presence of the PdCl$_2$/Fe/I$_2$ catalytic system is known to proceed via the aniline formation step [38]. As could be expected, the reaction of nitro compounds in the presence of this catalyst follows the same mechanism. Subsequently, the

a reaction initiation period during which the amino groups are formed in minor quantity that is required to start the reaction. Nitroaniline is produced by dinitrobenzene reduction as a result of hydrogen transfer from ethanol (reaction (2)) or the reaction of dinitrobenzene with trace water introduced as an impurity with the reactants.

$$ \text{(NO}_2\text{)(NO}_2\text{)C}_6\text{H}_4 + 2CO + C_2H_5OH \longrightarrow \text{(NH}_2\text{)(NO}_2\text{)C}_6\text{H}_4 + 2CO_2 + CH_3CHO \tag{2}$$

This initial nitroaniline quantity suffices to initiate the carbonylation reaction which proceeds according to Eqs. (3) and (4).

$$ 2\,\text{(NH}_2\text{)(NO}_2\text{)C}_6\text{H}_4 + CO \longrightarrow \mathbf{3,3DNU} + 2[H] \tag{3}$$

$$ \text{(NO}_2\text{)(NO}_2\text{)C}_6\text{H}_4 + 2CO + 2[H] \longrightarrow \text{(NH}_2\text{)(NO}_2\text{)C}_6\text{H}_4 + 2CO_2 \tag{4}$$

In reaction (3) nitroaniline reacts with one CO molecule in the presence of the PdCl$_2$/Fe/I$_2$ catalytic system to yield 3,3-dinitrophenylurea, with concomitant detachment of two hydrogens. In reaction (4) two CO molecules react with dinitrobenzene, which is converted to CO$_2$ and, on addition of two hydrogens, nitroaniline is formed. The presence of another nitro group, which is strongly electron-accepting in character, accelerates the reduction of dinitrobenzene to nitroaniline. Thus the nitrobenzene reduction reaction proceeds fast and already in the early reaction stage nearly all nitrobenzene reacts to form nitroaniline and others products. Dinitrophenylurea formed in reaction (3) immediately reacts with ethanol to afford nitroaniline and nitrocarbamate according to reaction (5). In the initial reaction stage, therefore, nitroaniline and nitrocarbamate are the major components in the reaction mixture.
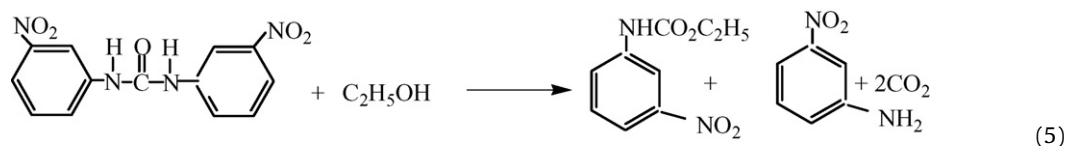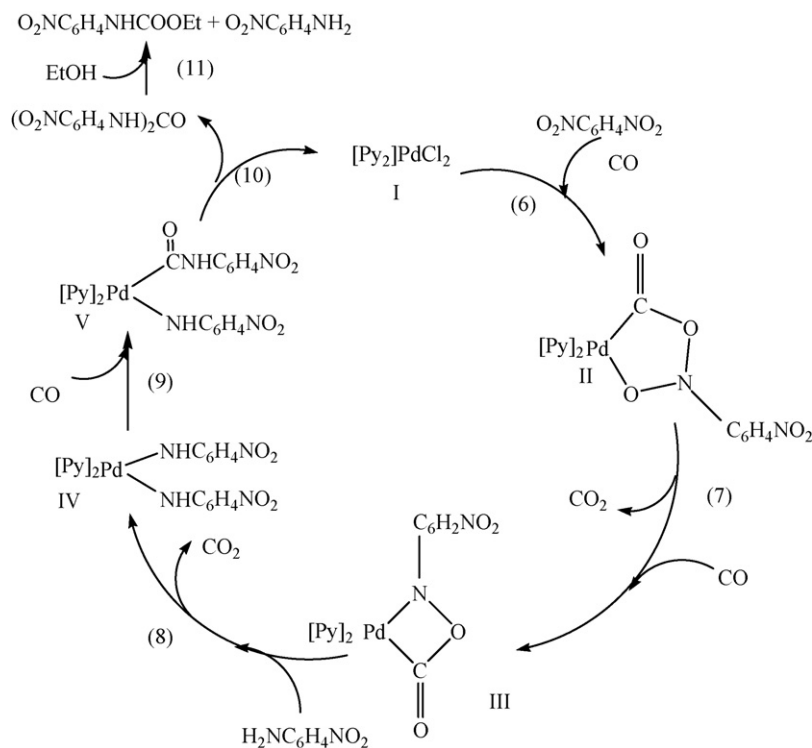
nitro groups react to form amino groups which in turn are converted into carbamino groups, and then the interactions between the substituents in the benzene ring are altered. These electronic interactions of the ring substituents have a significant effect on the carbonylation reaction.

From our earlier study on the carbonylation of substituted nitrobenzenes [40] and from the knowledge of the carbonylation of substituted anilines [53,54] it follows that the electron-donating substituents in the aromatic ring accelerate the carbonylation of amino groups, whereas the electron-accepting substituents speed up the rate of reduction of nitro groups to the respective amines. By considering mutual interactions of the substituents in the ring and analyzing the composition of the reaction mixture that is undergoing change throughout the reaction process, the mechanism of the dinitro compound carbonylation reaction can be advanced.

For simplicity, 1,3-dinitrobenzene was taken as a model dinitro compound. The dinitrobenzene carbonylation reaction features

$$ \text{3,3DNU} + C_2H_5OH \longrightarrow \text{(NHCO}_2\text{C}_2\text{H}_5\text{)(NO}_2\text{)C}_6\text{H}_4 + \text{(NO}_2\text{)(NH}_2\text{)C}_6\text{H}_4 + 2CO_2 \tag{5}$$

At this initial moment there is nitroaniline produced in reactions (4) and (5) in the reaction mixture. The nitroaniline thus formed undergoes the carbonylation reaction in the subsequent reaction cycle according to Eqs. (3) and (5).

As the carbonylation reaction proceeds and dinitrobenzene is depleted, nitroaniline or nitrocarbamate may act as an oxidant in a type of reaction (4). Diamine and aminocarbamate will be formed, respectively, as products of this reaction, which react with CO according to Eq. (3). Electron-donating substituents accelerate the amine carbonylation reactions, in other words, aminocarbamate and in particular, diamine will undergo the carbonylation reaction at a higher rate, as compared with nitroaniline. That is why in the initial stage of the carbonylation reaction only trace diamine and minor quantities of aminocarbamate are detected. Instead, nitrocarbamate accumulates in the reaction system. This is because the carbamate, being the electron-donating substituent, lowers the rate of nitrocarbamate reduction to the respective aminocarbamate.

$O_2NC_6H_4NHCOOEt + O_2NC_6H_4NH_2$

EtOH (11)

$(O_2NC_6H_4NH)_2CO$

(10)

$[Py_2]PdCl_2$ I

$O_2NC_6H_4NO_2$ CO

(6)

$[Py]_2Pd$ II (metallacycle) $C_6H_4NO_2$

CO_2 (7) CO

$[Py]_2Pd$ III $C_6H_2NO_2$ (N, O, C=O)

$H_2NC_6H_4NO_2$

(8) CO_2

$[Py]_2Pd$ IV $NHC_6H_4NO_2$ / $NHC_6H_4NO_2$

(9) CO

$[Py]_2Pd$ V $CNHC_6H_4NO_2$ (C=O) / $NHC_6H_4NO_2$

Scheme 1.

As mentioned earlier, dinitrobenzene carbonylation reaction is a multistage reaction. The reaction pattern is shown in Scheme 1. In the first stage the palladium chloride/pyridine complex reacts with dinitrobenzene (6). Reaction (6) begins with the stage of electron transfer from palladium atom to the nitrobenzene molecule. This is the slowest step in the nitrobenzene carbonylation process, which was treated in some detail in our earlier paper [41]. Possibly, much like for phenanthroline or dipyridine, the metal cyclic compound II forms [55]. As a result of elimination of carbon dioxide molecule from this complex II, a palladium complex III forms. Aniline present in the reaction mixture gives the hydrogen atoms away to III and form the amide complex IV (reaction (8)). Complex IV reacts with carbon monoxide to afford the carbamoyl complex V, from which ureas are produced in reaction (10).

The mechanism of dinitrobenzene carbonylation in the presence of PdCl₂/Fe/I₂/Py catalyst system depicted in Scheme 1 consists of a cycle of reactions of reductive nitro-group carbonylation and of the oxidative amine-group carbonylation. To sum up, the catalytic cycles of dinitro compounds carbonylation, alternately reductive and oxidative, occur until the nitro groups, which are oxidants in the amine carbonylation reaction, disappear. Then the main products, which are dicarbamate and aminocarbamate, remain in the reaction mixture.

An alternative oxidant suitable for use in carbonylation reaction is iodine. It will also participate in the reaction. When the nitro group concentration in the reaction system falls to 0–2%, the aminocarbamate carbonylation reaction occurs in the presence of iodine. This explains why a rise in the dicarbamate yield is observed, which is higher than the presence of nitro groups in the system.

It should be emphasized that on completion of the dinitro compounds carbonylation in the reaction mixture only the end products and intermediate products are found. The intermediate products in that mixture can be converted to the end product by adding a suitable oxidant. Iodine and oxygen are good choices in this respect.

5. Conclusion

Major products of the carbonylation of 1,2- and 1,4-dinitrobenzene and 2,4-dinitrotoluene in the presence of the PdCl₂/Fe/I₂/Py catalytic system were identified.

By increasing the catalyst quantity and by extending the carbonylation reaction time a 100% conversion of dinitrobenzene was achieved with a selectivity for the dicarbamates of 87, 68, and 55%, for 1,4-, 1,3-dinitrobenzene, and 2,4-dinitrotoluene, respectively.

The respective aminocarbamates, which are intermediate products, are major by-products in the reaction.

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