

# Addition of ethyl urethane to olefins: A new approach to the synthesis of aliphatic carbamates

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## Abstract

Several different palladium-based catalytic systems have been investigated for the addition of urethane ( $\text{NH}_2\text{COOEt}$ ) to olefins. A catalytic system based on  $\text{PdCl}_2(\text{CH}_3\text{CN})_2/\text{CuCl}/\text{O}_2$  gave good results only in the case of the activated olefin methyl acrylate. Catalytic systems of the type  $\text{Pd}(\text{acac})_2/\text{phosphorus ligand/acid}$ , previously used to catalyse the telomerisation of conjugated olefins with amines, gave the desired adduct, together with the product of addition of one molecule of urethane and two molecules of diolefin, in the case of isoprene and 2,3-dimethylbutadiene. The main by-products were the dimers of the diolefin, whereas the selectivity in urethane appears to be high. In no case could the addition of urethane to an unactivated non-conjugated olefin be achieved.

## 1. Introduction

Organic isocyanates are important industrial products, employed in the manufacture of polymers and other organic derivatives such as fertilizers and pesticides. The actually employed technology for their synthesis requires the reaction of an amine with the highly toxic and corrosive phosgene and much effort has been devoted in recent years towards the development of phosgene-free routes to these products. Since isocyanates can also be obtained by thermolysis of the corresponding carbamates ( $\text{RNHCOOR}'$ ) or ureas ( $\text{RNHCONHR}$ ), the synthesis of these products have also been the

object of considerable attention. Among the alternative routes which have been investigated, the direct carbonylation of organic nitro compounds is essentially limited to aromatic derivatives [1]. However, aliphatic isocyanates are also important intermediates, since the corresponding polyurethanes are stable to sunlight degradation. Moreover, carbamates derived from aliphatic isocyanates are used as pesticides. Among the processes potentially applicable to the production of aliphatic isocyanates, the oxidative carbonylation of amines [2] and their reaction with dimethyl carbonate [3] have been both considered interesting, but neither of the two has been applied on an industrial scale. On the other hand, the addition of isocyanate ion or isocyanic acid to an olefin [4] appears to be inadequate, at least at the actual stage of development, for large scale production and it does

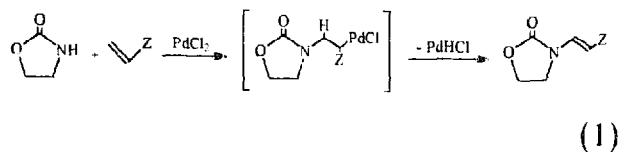
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not completely solve the problem of the use of dangerous reagents.

In the aim of investigating a new approach to the synthesis of aliphatic isocyanates via their corresponding carbamates, we investigated the possibility of effecting the addition of urethane ( $\text{NH}_2\text{COOR}$ ) to an olefin. Urethane is a cheap, large scale industrial product whose production does not involve the use of phosgene [5]. This approach is in the line of the recent world-wide efforts to find efficient ways of catalysing the addition of N–H bonds to C=C double bonds. In a previous paper, we have shown that several ruthenium complexes can activate urethane, to afford isocyanate complexes, but these last complexes failed to afford organic isocyanates when treated with olefins [6]. To the best of our knowledge, the addition of urethane to an olefin has been achieved in only one case [7], but the reaction was only stoichiometric. Catalytic addition of urethane to benzene has also been reported, but only two turnovers were obtained after several hours at high temperature [8]. In this paper, we report our preliminary results on the use of some different palladium-based catalytic systems by which the title reaction could be successfully performed, albeit only for some substrates.

## 2. Results and discussion

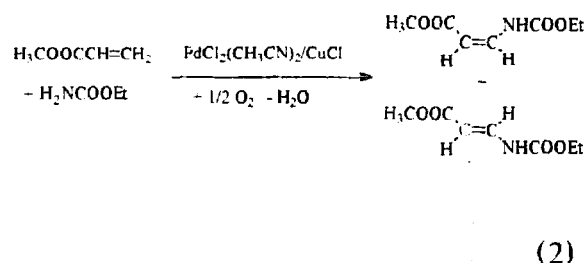
Although only the previously mentioned system [7] has been reported for the addition of urethane to olefins, a catalytic system has been reported for the addition of a cyclic carbamate to activated olefins [9],



We thus started our investigation by applying the same catalytic system to the reactions of urethane. Since we experienced some difficulty in obtaining precise quantitative gaschromato-

graphic analyses for urethane and even a small error in its conversion would completely alter the selectivity values, especially in cases where the conversion was low, we will report the amounts of obtained products as mol product/mol palladium catalyst throughout this paper (the analysis of all other products was reproducible). In any case, from experiments in which the analysis of the final solution was repeated many times in order to mediate the errors, it appears that the selectivity of all reported reactions with respect to the converted urethane is always very high, close to 100%, although the selectivity with respect to the converted olefin may be much lower (see later).

Reaction of urethane with methyl acrylate in the presence of 5 mol%  $\text{PdCl}_2(\text{CH}_3\text{CN})_2/\text{CuCl}$  ( $\text{Cu}/\text{Pd} = 1.1:1$ ) at  $50^\circ\text{C}$  in dry 1,2-dimethoxyethane (DME), under a dioxygen atmosphere for 16 h, led to the formation of the desired adduct (16.3 mol/mol Pd) in a 21:79 *cis/trans* ratio,



The reaction shows a similar selectivity to the one previously reported for cyclic carbamates, but is much slower. Interestingly, no evidence could be obtained by GC or GC–MS for the formation of products derived from any following reaction of the obtained carbamate and it appears that only one of the two nitrogen-bound hydrogen atoms can be involved in the interaction with the substrate. Note that the final result of reaction (2) is not the simple addition of an N–H bond across the double bond of the olefin and the C=C double bond is still present in the final product.

Although these results are interesting, the same catalytic system proved to be inadequate to the functionalisation of less activated sub-

strates. Styrene, which affords good results with cyclic carbamates, only afforded some methylphenylketone (by direct oxidation by  $O_2$ ) but no adduct. Simple olefins such as 1-hexene did not react at all under mild conditions and afforded only oxidation products when subjected to more forcing conditions (up to  $160^\circ C$  and 4 atm  $O_2$  in an autoclave). Conjugated olefins afforded a mixture of unidentified products, but again no adduct could be observed by GC-MS. Several modifications of the catalytic system, such as the use of a quinone as an oxidant in place of  $CuCl/O_2$ , the addition of ligands, or changes in the solvent did not improve the results. When ligands such as phenanthroline were added, the formation of palladium complexes containing the isocyanato ligand was evidenced by IR spectroscopy. Such complexes have been previously shown by us to derive from attack of the urethane molecule directly on the metal, rather than on a coordinated olefin, and to be inactive towards further reactions [6].

Several catalytic systems exist which are able to catalyse the telomerisation of conjugated diolefins (especially butadiene or isoprene) with amines [10–13]. These reactions generally afford, in addition to the adduct of one molecule of amine and one of diolefin, the adduct of one molecule of amine and two (or even three) molecules of diolefin and several dimers of the diolefin. The selectivity towards the 1:1 with

respect to the 1:2 adduct can be switched by suitable modifications in the catalytic system and the experimental conditions. Several nucleophiles, such as alcohols or water, have also been employed in place of amines. We found that urethane can also act as a suitable nucleophile in this type of reaction.

In order to avoid problems arising from different isomeric products, we started our investigation by using the symmetric 2,3-dimethylbutadiene. In a previous work, Roper et al. have shown that  $[Pd(DPPE)(Py)_2][BF_4]_2$  (DPPE = 1,2-bis(diphenylphosphino)ethane) is an active catalyst for the telomerisation of isoprene (2-methylbutadiene) with diethylamine even under mild conditions [11]. However, when the same catalytic system was employed with our substrates, no adduct was formed. Better results were instead obtained with the catalytic system  $Pd(acac)_2$ /phosphorus ligand/acid (even Lewis acid) previously reported by some of the same authors [12] (Table 1). The addition of an acid has been reported to increase the selectivity in the 1:1 adduct. The data reported in Table 1 shows that the 1:1 adduct is always the main product, accompanied by only minor amounts of the 1:2 adduct. However, GC-MS analysis of the reaction solutions allowed us to evidence also the formation of two different isomeric dimers of the starting diolefin and even two isomeric trimers. The total amount of the trimers

Table 1  
Addition of urethane to 2,3-dimethylbutadiene catalysed by  $Pd(acac)_2$ <sup>a</sup>

Run	Pd (mmol)	Lig (Lig/Pd)	Acid (acid/Pd)	$NH_2COOEt/Pd$	Olefin/ $NH_2COOEt$	T (°C)	1:1 add/Pd	1:2 add/Pd	Dimers/ total adducts
1	0.068	$PCy_3$ (1)	$BF_3 \cdot Et_2O$ (5)	50	2	120	1.39	0.24	1.18
2	0.068	$PCy_3$ (1)	$BF_3 \cdot Et_2O$ (5)	50	2	90	1.40	0.31	0.60
3	0.034	$PCy_3$ (4)	$BF_3 \cdot Et_2O$ (10)	50	2	80	1.38	0.11	0.52
4	0.034	$PCy_3$ (4)	$BF_3 \cdot Et_2O$ (10)	200	2	90	7.82	0.56	0.21
5 <sup>b</sup>	0.034	$PCy_3$ (4)	$BF_3 \cdot Et_2O$ (10)	200	2	90	10.0	0.70	0.24
6	0.034	$PCy_3$ (4)	$BF_3 \cdot Et_2O$ (10)	200	0.5	90	8.65	2.41	0.63
7	0.034	$PCy_3$ (4)	TsOH (10)	200	2	90	—	—	—
8	0.034	$P(OBu)_3$ (4)	$BF_3 \cdot Et_2O$ (10)	200	2	90	8.79	0.79	0.22

<sup>a</sup> Experimental conditions:  $t = 8$  h, in  $CH_3CN$  (10 ml) as solvent and under 10 atm  $N_2$ . A small amount ( $\sim 1:1$  with respect to the starting complex) of a product derived from coupling of two olefin molecules with one molecule of acetylacetonone was also always observed. All ratios are molar ratios. TsOH = *p*-toluenesulfonic acid.

<sup>b</sup>  $t = 16$  h.

is low, typically around 5 mol% with respect to the amount of the dimers. A small amount (about 1:1 with respect to the starting complex) of a product identified as the adduct of two olefin molecules and one molecule of acetylacetonone was also always observed.

Both  $\text{PCy}_3$  and  $\text{P}(\text{O}i\text{Bu})_3$  were suitable ligands, but, at least in the case of  $\text{PCy}_3$ , use of *p*-toluenesulphonic acid in place of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  completely inhibited any reaction. A large urethane/Pd ratio was beneficial to the reaction, although the conversion was low, whereas the temperature appears to play a minor role. High temperatures tend to increase the amount of dimers anyway. As previously said, the selectivity with respect to the consumed urethane is high, but a relatively large amount of olefin is lost in the dimers formation.

Next we examined the use of isoprene as a substrate, with the same catalytic system (Table 2). Due to the possibility of isomeric products, two forms of the 1:1 adduct were observed, together with one 1:2 and one 1:3 adduct. Three isomeric dimers, one of which was identified as the cyclic dimer 1-methyl-5-(1-methylethenyl)-cyclohexene by comparison of its mass fragmentation pattern with the one reported in the

library of the GC-MS instrument, were also detected. Several other products were always present in the high molecular weight part of the gas-chromatograms, but their very low abundance prevented their identification. They are probably a mixture of other isomers of the 1:2 and 1:3 adducts and of trimeric derivatives of the diolefin.

Examination of the data in Table 2 shows that some trends are similar to the ones found in the case of 2,3-dimethylbutadiene. In addition, it appears that the acid amount plays an important role. Under a certain amount (runs 6, 7), only the cyclic dimer of the diolefin, but no adduct was observed. Use of chelating phosphines (runs 10, 11) afforded results close to the one observed with  $\text{PCy}_3$ . Chelating phosphines have been reported to lead to increased amounts of 1:1 adduct in telomerisation reactions with amines [13], but this does not appear to be the case in the present reaction. Finally, the use of  $\text{P}(\text{O}i\text{Bu})_3$  coupled with  $\text{CF}_3\text{SO}_3\text{H}$  (run 12) gave the largest amounts of adducts. The selectivity with respect to the consumed diolefin is similar to the one found for 2,3-dimethylbutadiene and is little sensitive to the experimental conditions.

In conclusion, we have shown for the first

Table 2  
Addition of urethane to isoprene catalysed by  $\text{Pd}(\text{acac})_2$ <sup>a</sup>

Run	Pd (mmol)	Lig (lig/Pd)	Acid (acid/Pd)	$\text{NH}_2\text{COOEt}/\text{Pd}$	1° 1:1 add/ Pd	2° 1:1 add/ Pd	1:2 add/ Pd	1:3 add/ Pd	Dimers/ total adducts
1	0.2	$\text{PCy}_3$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10)	50	0.62	0.032	0.12	0.034	0.66
2	0.1	$\text{PCy}_3$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10)	100	4.08	0.38	0.28	0.13	0.33
3	0.05	$\text{PCy}_3$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10)	200	5.30	0.52	0.26	0.22	0.31
4 <sup>b</sup>	0.05	$\text{PCy}_3$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10)	200	3.48	0.44	—	—	0.53
5 <sup>c</sup>	0.05	$\text{PCy}_3$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10)	200	5.12	0.26	0.24	0.30	0.46
6	0.1	$\text{PCy}_3$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (5)	100	—	—	—	—	Cycl. dim/ Pd = 0.62
7	0.05	$\text{PCy}_3$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (5)	200	—	—	—	—	Cycl. dim/ Pd = 0.96
8	0.05	$\text{PCy}_3$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (20)	200	5.36	0.22	0.28	0.28	0.40
9	0.05	$\text{PCy}_3$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10)	100	1.14	1.18	0.18	0.174	0.58
10	0.05	$\text{DCyPE}$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10)	200	5.88	0.32	0.12	0.24	0.48
11	0.05	$\text{DPPE}$ (4)	$\text{BF}_3 \cdot \text{Et}_2\text{O}$ (10)	200	4.50	0.20	0.062	0.28	0.49
12	0.05	$\text{P}(\text{O}i\text{Bu})_3$ (4)	$\text{CF}_3\text{SO}_3\text{H}$ (10)	200	12.1	5.6	0.44	0.38	0.42

<sup>a</sup> Experimental conditions:  $T = 90^\circ\text{C}$ ,  $\text{NH}_2\text{COOEt}/\text{olefin} = 2$ , in  $\text{CH}_3\text{CN}$  (2 ml) as solvent, for 8 h. All ratios are molar ratios.  $\text{DCyPE} = 1,2\text{-bis}(\text{dicyclohexylphosphino})\text{ethane}$ ,  $\text{DPPE} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$ .

<sup>b</sup>  $t = 5$  h.

<sup>c</sup>  $t = 16$  h.

time that the catalytic addition of urethane to olefins is possible, but much work has still to be done in order for the selectivity and activity of these catalytic systems to become interesting for possible industrial applications.

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