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Palladium-Catalyzed Generation of O-Allylic Urethanes and Carbonates from Amines/Alcohols, Carbon Dioxide, and Allylic Chlorides

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Addition of preformed carbamate anions RR′NHCO$_2^-$ ($^+$H base), generated from various primary and secondary amines and carbon dioxide, to THF solutions of allylic chlorides under 80–100 psig carbon dioxide at room temperature (or 30 °C) containing a palladium/phosphine catalyst gave high yields and high selectivities of O-allylic urethanes (66–100%). The choice of added base in the generation of carbamate was found to be critical for high yields of O-allylic products. The use of a guanidine (*N*-cyclohexyl-*N′*,*N′*,*N″*,*N″*-tetramethylguanidine) or amidine (1,8-diazabicyclo[5.4.0]undec-7-ene) base is optimal for this system. Use of a diamine (*N*,*N′*-dimethylhexamethylenediamine), carbon dioxide, 2 equiv of base, and 1,4-dichloro-2-butene with added palladium/phosphine catalyst gave polyurethane with M_n = 5400 and M_w = 8900. Substitution of benzyl alcohol for the amines in this catalytic process gave an 88% yield of benzyl allyl carbonate. The rate of appearance of benzylethylcarbamate from benzylethyl amine, carbon dioxide, and allyl chloride catalyzed by a palladium/phosphine complex was determined for four concentrations of catalyst and indicated a first-order dependence on catalyst concentration with a turnover number of 2600 moles per hour per mole of catalyst.

Introduction

Urethane and polyurethane materials find many important applications. These materials are historically made by the addition of an alcohol to an isocyanate (eq 1).[1] The isocyanate in turn is constructed by the addition

$$RN{=}C{=}O + R'OH \rightarrow RNHCO_2R' \qquad (1)$$

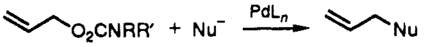
of phosgene to an amine with elimination of 2 equiv of hydrogen chloride (eq 2). This method for the production

$$RNH_2 + COCl_2 \rightarrow RN{=}C{=}O + 2HCl \qquad (2)$$

of urethane compounds has the major drawback of using highly toxic raw materials, phosgene and the isocyanate. Several publications and patents have dealt with either making isocyanates without the use of phosgene or constructing urethanes without the use of either phosgene or isocyanates.[2] These published results have found only limited success.

The introduction of an allylic group into a urethane product gives a product which possesses a reactive group for additional chemistry to take place. The allylic urethane has traditionally been synthesized using the method described above, the addition of allyl alcohol to an isocyanate giving an O-allylic urethane. Several accounts have been reported in which these O-allylic urethanes have been used in radiation-curable coatings systems.[3] Allylic urethanes have also been used as intermediates for organic synthesis,[4] while allylic carbonates have been shown to be important materials (i.e., diethylene glycol bis(allyl carbonate),[5] which has been used in shatter-resistant optical lenses, face shields, and windows).[6]

It is well-known that several transition-metal complexes will activate allylic substrates toward nucleophilic attack, giving new allyl compounds. A well-studied system utilizes palladium, and Scheme I shows the catalytic cycle proposed for this process.[7] Many different allylic substrates (allyl–X) have been utilized as starting materials; among these are allyl–urethanes and allyl carbonates as shown in eq 3.[8,9]



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We are continuing to investigate the use of carbamate anions, generated from amines and carbon dioxide, as useful nucleophiles in the construction of urethane materials.[10] We therefore investigated the use of the carbamate as well as carbonate anions, in the palladium-

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(1) For a discussion of urethane chemistry see: Oertel, G. *Polyurethane Handbook*; Hanser: Munich, 1985.

(2) One recent example which describes the generation of urethanes from amines, alcohols, and urea appears in: Bayer. U.S. Patent 4713476.

(3) Several accounts of these systems have been given in *Chemical Abstracts*; see, for example, diurethane from allyl alcohol and hexamethylene diisocyanate in photocurable insulating varnishes: *Chem. Abstr.* 1977, *86*, 74526y.

(4) Hoppe, D.; Hanko, R.; Bronneke, A. *Angew. Chem., Int. Ed. Engl.* 1980, *19*, 625–627. Hanko, R.; Hoppe, D. *Angew. Chem. Int. Ed. Engl.* 1981, *20*, 127–128. Hoppe, D.; Hanko, R.; Bronneke, A.; Lichtenberg, F.; Hulsen, E.-v. *Chem. Ber.* 1985, *118*, 2822–2851.

(5) Produced by PPG Industries and trade-named CR-39.

(6) For a discussion of the use of diethylene glycol bis(allyl carbonate) see: Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G.; Kroschwitz, J. I. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1990; Vol. 4, pp 781–790.

(7) For a discussion of this chemistry see: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(8) Allyl carbonates: Guibe, F.; M'Leux, S. *Tetrahedron Lett.* 1981, *22*, 3591–3594. Tsuji, J.; Sato, K.; Okumoto, H. *Tetrahedron Lett.* 1982, *23*, 5189–5190. Tsuji, J.; Sato, K.; Okumoto, H. *J. Org. Chem.* 1984, *49*, 1341–1344. Minami, I.; Shimizu, I.; Tsuji, J. *J. Organomet. Chem.* 1985, *296*, 269–280. Consiglio, G.; Scalone, M.; Rama, F. *J. Mol. Catal.* 1989, *50*, L11–L15. Ozawa, F.; Son, T.; Ebina, S.; Osakada, K.; Yamamoto, A. *Organometallics* 1992, *11*, 171–176. Allyl urethanes: Minami, I.; Ohashi, Y.; Shimizu, I.; Tsuji, J. *Tetrahedron Lett.* 1985, *26*, 2449–2452. Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* 1987, *28*, 4837–4840.

(9) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* 1988, *29*, 99–102.

(10) McGhee, W. D.; Riley, D. P. *Organometallics* 1992, *11*, 900–907.

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Scheme I

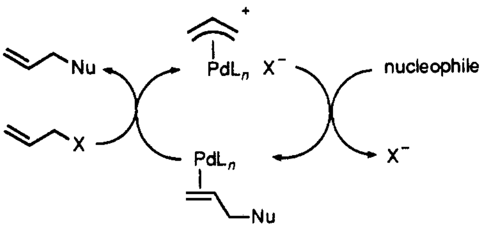


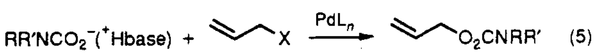
Table I. Tertiary Amine Co-Base Effects: Reaction of Benzylethylamine, Carbon Dioxide, Co-Base, and Allyl Chloride[a]

co-base	reacn time, h	% urethane	% amine[b]
$(i\text{-Pr})_2$NEt[c]	1	2	23
DBN[d]	4	49	13.5
DBU[e]	2	86.5	3
CyTMG[f]	2	100	1
MTBD[g]	2	104	<1

[a] All reactions were run at room temperature under 80–100 psig of carbon dioxide in THF using $Pd_2(dba)_3$/phosphine catalyst (palladium to amine ratio in all cases 1:90) with tridecane or biphenyl as internal standard. All reactions were run to completion on the basis of the disappearance of benzylethyl amine except where noted, and percent yields are GC yields. [b] Amine product: allylbenzylethylamine. [c] Reaction taken to only ca. 50% conversion based on benzylethyl amine. [d] DBN = 1,5-diazabicyclo[4.3.0]non-5-ene. [e] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. [f] CyTMG = *N*-cyclohexyl-*N'*,*N'*,*N''*,*N''*-tetramethylguanidine. [g] MTBD = 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene.

catalyzed allylic nucleophilic substitution system described above, in order to produce useful O-allylic urethanes and allylic carbonates (eqs 4 and 5). The construction of

$$\text{RR'NH} + \text{base} + CO_2 \rightleftharpoons \text{RR'NCO}_2^-({}^+\text{Hbase}) \qquad (4)$$



(5)

urethanes and carbonates using this method is unique and surprising in light of the literature precedent of decarboxylation of these materials in the presence of identical catalytic systems.

Results

Stabilized carbamate anions were generated by the addition of 80–100 psig of carbon dioxide to THF solutions of amines using stoichiometric amounts of nitrogen-containing bases (eq 4). In some cases the carbamate salt solution formed a slurry. The carbamate salt solution was then added under ca. 80–100 psig of carbon dioxide to a preformed solution of a catalytic amount of a palladium complex and an allylic chloride. The reaction was run at room temperature (or 30 °C), during which time a white solid precipitated from solution ($Hbase^+Cl^-$) with the generation of good yields of O-allylic urethanes (eq 5) and high catalytic turnover (typically 100–400 turnovers with no apparent sign of catalyst decomposition). Results as a function of base, solvent, and palladium precatalyst are given in Tables I–III. Table IV gives the results of the use of several different amines and allylic substrates.

Addition of the dicarbamate salt of *N*,*N'*-dimethyl-1,6-hexanediamine to a THF solution of 1,4-dichloro-2-butene with a palladium/phosphene catalyst gave the polyurethane shown in eq 6, isolated as an orange tacky material. GPC HPLC analysis of the isolated polymeric material gave the following molecular weight information (based on polystyrene standards): M_n = 5400, M_w = 8900.

Table II. Solvent Effects: Reaction of Benzylethylamine, Carbon Dioxide, DBU, and Allyl Chloride[a]

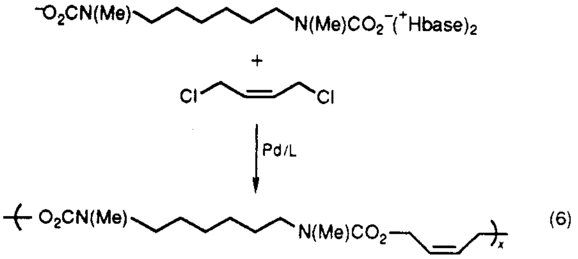
solvent	reacn time, h	% urethane	% amine[b]
CH_2Cl_2	2	49	34
DMSO	2.5	67	3.4
THF	2	86.5	3
glyme	17	82	1

[a] All reactions were run at room temperature under 80–100 psig of carbon dioxide using $Pd_2(dba)_3$/phosphine catalyst (Pd to amine ratio 1:90 in all cases) with tridecane or biphenyl as internal GC standard. All reactions were carried to completion on the basis of the disappearance of benzylethylamine, and percent yields are GC yields. [b] Amine product allylbenzylethylamine.

Table III. Catalyst Effects: Reaction of Diallylamine, Carbon Dioxide, DBU, and Allyl Chloride[a]

catalyst	Pd:diallylamine	reacn time, h	% urethane	% amine[b]
$[allylPdCl]_2/PPh_3$	1:61	2	85	5
$Pd_2(dba)_3/PPh_3$	1:90	2	88	5.5
$Pd(PPh_3)_4$	1:68	2	90	4.5
$Pd_2(dba)_3$/DIPHOS	1:90	2	98	4

[a] All reactions were run at room temperature under 80–100 psig of carbon dioxide in THF with tridecane or biphenyl as internal GC standard. All reactions carried to completion as judged by disappearance of diallylamine. [b] Amine = triallylamine.



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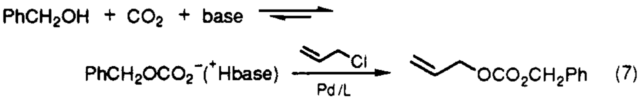
The use of benzyl alcohol in place of amines (eq 7) in the above reaction gave a 88% yield of benzyl allyl carbonate (Table IV).



(7)

The rate dependence of allyl benzylethylcarbamate formation as a function of palladium concentration is shown in Table V, and a plot of the calculated second-order rate vs palladium concentration is shown in Figure 1. From this study a catalyst turnover number of 2600 per hour at 30 °C is calculated.

Discussion

The literature describes the use of allylic urethanes and allylic carbonates as *substrates* for allylic substitution reactions using palladium catalysts (eq 3). The addition of the urethane or carbonate to the palladium complex generates a π-bound allylic palladium intermediate with the evolution of carbon dioxide and either amine or alcohol. This intermediate is then attacked by nucleophiles, generating new allylic materials. Our results have shown that we can use these same catalyst systems to *generate* O-allylic urethanes and carbonates.

We, and others, have been exploring the use of the carbamate anion as a nucleophile in generating ure-

Table IV. Conversion of Amines (Alcohols), Carbon Dioxide, and Allylic Chlorides to O-Allylic Urethanes and Carbonates[a]

reacn no.	nucleophile	co-base	allylic Cl	Pd:substrate[b]	reacn time, h	% urethane or carbonate (% based on Pd)	% amine or ether
1	$PhCH_2N(Et)CO_2^-$	DBU[c]	$CH_2{=}CHCH_2Cl$	1:455	21	86.5 (39 400)	3 (1365)
2	$(CH_2{=}CHCH_2)_2NCO_2^-$	DBU	$CH_2{=}CHCH_2Cl$	1:91	2	95 (8645)	1.5 (136)
3	$(CH_2{=}CHCH_2)_2NCO_2^-$	DBU	$CH_2{=}C(Me)CH_2Cl$	1:91	18	87 (7920)	<1
4	$Et_2NCO_2^-$	DBU	$CH_2{=}CHCH_2Cl$	1:91	2.33	91.5 (8330)	1 (91)
5	$Et_2NCO_2^-$	DBU	$ClCH_2CH{=}CHCH_2Cl$	1:41	18	68 (2790)	<1
6	$Et_2NCO_2^-$	CyTMG[d]	$ClCH_2CH{=}CHCH_2Cl$	1:68	20	90 (6120)	<1
7	$c\text{-}C_6H_{11}NHCO_2^-$	CyTMG[d]	$CH_2{=}CHCH_2Cl$[e]	1:91	18	105 (9555)	<1
8	$^-O_2CN(Me)(CH_2)_6N(Me)CO_2^-$	DBU	$CH_2{=}CHCH_2Cl$	1:45	22	66 (2970)	16[f] (720)
9	$^-O_2CN(Me)(CH_2)_6N(Me)CO_2^-$	CyTMG[d]	$CH_2{=}CHCH_2Cl$	1:45	2.5	86 (3870)	14.5[f] (650)
10	$PhCH_2OCO_2^-$	CyTMG[d]	$CH_2{=}CHCH_2Cl$[e]	1:91	16	88 (8000)	<1

[a] All reactions were run under 80–100 psig of carbon dioxide pressure in THF at room temperature using $Pd_2(dba)_3$/DIPHOS or PPh_3 catalyst with tridecane or biphenyl as internal standard. All reactions were carried out to completion on the basis of the disappearance of limiting reagent; all yields are GC yields. [b] Pd:substrate based on millimoles of palladium vs millimoles of limiting reagent (limiting reagent = nucleophile in reaction numbers 1–4 and 7–10, limiting reagent = 1,4-dichloro-2-butene in reaction numbers 5 and 6). [c] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. [d] CyTMG = *N*-cyclohexyl-*N′*,*N′*,*N″*,*N″*-tetramethylguanidine. [e] Reaction run at 30 °C. [f] Percent amine indicates percent allyl–$N(Me)(CH_6)N(Me)CO_2$–allyl.

Table V. Rate Studies: Rate of Reaction of Benzylethylcarbamate with Allyl Chloride vs Catalyst Concentration[a]

[Pd], mmol	k, 10^3 M^{-1} s^{-1}	[Pd], mmol	k, 10^3 M^{-1} s^{-1}
5	3.80	1.25	1.13
2.5	2.07	0.5	0.53

[a] All reactions run at 30 °C under 80 psig of carbon dioxide pressure. Rates were determined by GC analysis of allyl benzylethylcarbamate vs biphenyl internal standard. In all cases good first-order appearance of the product was observed (correlation coefficient >0.98 in all cases). Pseudo-first-order rate constants were converted to second-order rate constants using $k = k_{obs}[\text{allyl–Cl}]$.

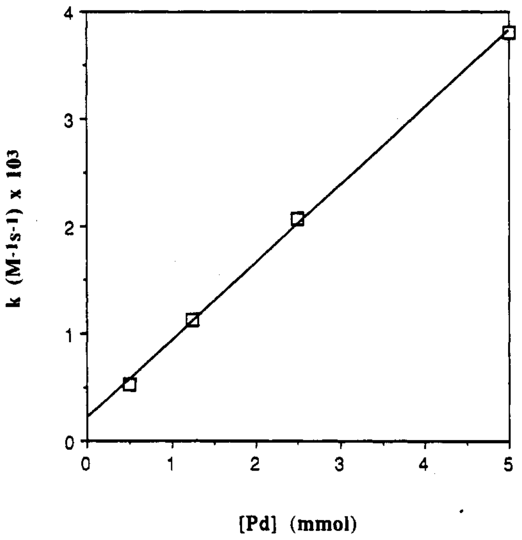
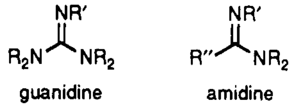


Figure 1. Calculated second-order rate of generation of allyl benzylethylcarbamate from benzylethylamine, carbon dioxide, and allyl chloride vs concentration of palladium catalyst.

thanes.[10,11] We have found that the carbamate anion is about as nucleophilic as the acetate anion in a palladium diolefin system.[10] In the present study we have investigated the carbamate anion as a nucleophile in the palladium-catalyzed conversion of allylic chlorides to allylic urethanes and carbonate anions to allylic carbonates. The carbamate and carbonate anions indeed act as competent nucleophiles in this catalytic system. To obtain high selectivity of urethanes over amine products (oxygen vs nitrogen attack) and high selectivity of carbonates over ethers, stabilization of the anion by the use of a stoichiometric amount of a co-base is required. Addition of this premade carbamate or carbonate anion under carbon dioxide pressure to a solution of an allylic chloride with a suitable palladium/phosphine catalyst gives high yields and selectivities of O-allylic urethanes and carbonates (Table IV). The selection of the co-base in the formation of the carbamate is critical. This co-base cannot simply be a tertiary amine such as diisopropylethylamine, which will give a poor yield of urethane (Table I). We have found that the use of guanidine or amidine bases gives increased



yields and selectivities of urethanes or carbonates (see Table I). Several of these bases are commercially available, and others can be easily synthesized by literature procedures.[12] The use of amidine and guanidine bases to stabilize and enhance the reactivity of anions is not new. The addition of DBU to carboxylic acids, generating carboxylate anions, has been explored in making esters by nucleophilic substitution pathways.[13] It is likely that the enhancement of activity by using these bases arises from greater ion-pair separation, which is facilitated by delocalization of the resulting positive charge on the amidine

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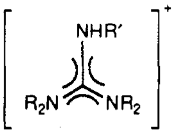
(11) (a) Toda, T. *Chem. Lett.* **1977**, 957–958. (b) Asano, T.; Saito, N.; Ito, S.; Hatakeda, K.; Toda, T. *Chem. Lett.* **1978**, 311–312. (c) Toda, T.; Kitagawa, Y. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 334–335. (d) Yoshida, Y.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 559–560. (e) Yoshida, Y.; Inoue, S. *Chem. Lett.* **1978**, 139–140. (f) Yoshida, Y.; Inoue, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3146–3150. (g) Yoshida, Y.; Inoue, S. *J. Polym. Sci.* **1980**, *12*, 763–766. (h) Yoshida, Y.; Ishii, S.; Yamashita, T. *Chem. Lett.* **1984**, 1571–1572. (i) Yoshida, Y.; Ishii, S.; Kawato, A.; Yamashita, T.; Yano, M.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2913–2916. (j) Ishii, S.; Nakayama, H.; Yoshida, Y.; Yamashita, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 455–458. (k) Yoshida, Y.; Ishii, S.; Watanabe, M.; Yamashita, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1534–1538. (l) Sasaki, Y.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1986**, 790–791. (m) Dixneuf, P. H.; Mahe, R. *Tetrahedron Lett.* **1986**, *27*, 6333–6336. (n) Sasaki, Y.; Dixneuf, P. H. *J. Org. Chem.* **1987**, *52*, 315–316. (o) Sasaki, Y.; Dixneuf, P. H. *J. Org. Chem.* **1987**, *52*, 4389–4391. (p) Bruneau, C.; Dixneuf, P. H.; Lecolier, S. *J. Mol. Catal.* **1988**, *44*, 175–178. (q) Mahe, R.; Sasaki, Y.; Bruneau, C.; Dixneuf, P. H. *J. Org. Chem.* **1989**, *54*, 1518–1523. (r) Mitsudo, T.-A.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 4417–4418. (s) Fournier, J.; Bruneau, C.; Dixneuf, P. H.; Lecolier, S. *J. Org. Chem.* **1991**, *56*, 4456–4458. (t) Tsuda, T.; Washita, H.; Watanabe, K.; Miwa, M.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1978**, 815–816. (u) Belforte, A.; Calderazzo, F. *J. Chem. Soc., Dalton Trans.* **1989**, 1007–1009. (v) Haynes, P.; Slaugh, L. H.; Kohnle, J. F. *Tetrahedron Lett.* **1970**, *5*, 365–368. (w) Schreiner, S.; Yu, Y.; Vaska, L. *J. Chem. Soc., Chem. Commun.* **1988**, 602–603. (x) Hori, Y.; Nagano, Y.; Nakao, J.; Fukuoka, T.; Taniguchi, H. *Chem. Express* **1986**, *1*, 224–227.

(12) (a) Bredereck, H.; Bredereck, K. *Chem. Ber.* **1961**, *94*, 2278–2295. (b) Barton, D. H. R.; Elliott, J. D.; Gero, S. D. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2085–2090. (c) Oszczapowicz, J.; Raczynska, E. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1643–1646.

(13) Ono, N.; Yamada, T.; Saito, T.; Tanaka, K.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2401–2404.

or guanidine counterion through the carbon–nitrogen π system:



In the present case of the carbamate and carbonate anions this ion separation enhances the reactivity of the oxygen center, giving greater yields of O-allylic urethanes and carbonates. Amine side products, derived from nitrogen attack, may be the result of direct attack of the nitrogen in the carbamate anion with concomitant loss of carbon dioxide or may be the result of reaction of free amine in solution with the electrophile.[14] The cyclic amidine base DBU has been utilized to stabilize the carbamate anion toward nucleophilic attack in one literature account.[12v]

A multitude of possible precatalyst systems are known from literature work to activate allylic chlorides toward nucleophilic attack.[7] Table III shows that several palladium complexes act as good precatalyst systems in our urethane and carbonate methodology with little difference in activity. We assume, from prior work in the area, that the chemistry presented here goes through a mechanism similar to that depicted in Scheme I. This involves nucleophilic attack of the carbamate or carbonate anion on a (π-allyl)palladium species, formed by the oxidative addition of an allyl chloride on a palladium(0) intermediate. Our results indicate high catalytic rates (complete reactions within 2 h at room temperature; see Table IV) with high turnover (as high as 455; reaction 1 in Table IV) and high selectivity toward urethane production (quantitative in reaction 7, Table IV).

We have also investigated the rate enhancement in reactivity of the nucleophilic displacement reaction of the carbamate anion on allyl chloride by the use of a palladium catalyst. The results of this study are given in Table V and shown in Figure 1. The linearity of the plot of palladium concentration vs rate (second-order rate constant derived from k_{obs}[allyl–Cl]) indicates a first-order dependence in [catalyst] with a catalytic turnover of 2600 moles per hour per mole of catalyst at 30 °C.

Conclusions

We have demonstrated that O-allylic urethanes and O-allylic carbonates can be synthesized from allylic chlorides, carbon dioxide, and amines or alcohols using palladium/phosphine catalysts. This result has been achieved under mild conditions (80–100 psig of carbon dioxide, at 20–30 °C) with high catalytic turnover.

Experimental Section

Materials. All amines and alcohols used in this account were obtained either from Aldrich Chemical Co. or Kodak Chemical Co. and were used as received. Anhydrous solvents under nitrogen, bis(diphenylphosphino)ethane (DIPHOS), triphenylphosphine, DBN (1,5-diazabicyclo[4.3.0]non-5-ene), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$), tetrakis(triphenylphosphine)palladium, and allylpalladium chloride dimer were purchased from Aldrich Chemical Co.; MTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene) was obtained from Fluka. CyTMG (*N*-cyclohexyl-*N′*,*N′*,*N″*,*N″*-tetramethylguanidine) was synthesized according to a literature procedure.[12a]

Analytical Details. Gas chromatographic analysis was performed on a Varian Model 3400 gas chromatograph with a Model 8000 auto sample using a 30-m Megabore DB-1 (3 μm) J & W Scientific column. Urethane products were purified and were identified by ^{1}H NMR, ^{13}C NMR, mass spectroscopy, IR, and elemental analysis. Nuclear magnetic resonance spectra were obtained on Varian VXR-300 or VXR-400 spectrometers. Mass spectra were obtained by FAB or by chemical ionization techniques using isobutane as reagent gas. Infrared spectra were obtained on a Nicolet FT-IR. Elemental analyses were performed by Galbraith Laboratories, Inc. GPC analysis was run in THF solvent on a Waters-HPLC containing 500-, 10^3-, 10^4-, and 10^5-Å Ultrastyragel columns in series. A Model 410 differential refractometer was used for detection, and in-line analysis was carried out on a Maxima 820 workstation.

Allyl Benzylethylcarbamate (1). Into a Fischer–Porter bottle was added 13.5 g (0.1 mol) of benzylethylamine, 16.1 g (0.106 mol) of DBU, and 1 g (5.38 mmol) of tridecane (as GC internal standard). To this was added 65 mL of anhydrous THF, giving a clear solution. The Fischer–Porter bottle was attached to a pressure head, and ca. 35 psig of carbon dioxide was added above the solution at room temperature with stirring. Upon addition of carbon dioxide the solution warmed slightly, and after 2 h absorption of CO_2 had ceased.

Into a second Fischer–Porter bottle was added 100 mg (0.11 mmol) of $Pd_2(dba)_3$ and 108 mg (0.27 mmol) of DIPHOS (bis(diphenylphosphino)ethane). This Fischer–Porter bottle was attached to a pressure head, and the apparatus was flushed with carbon dioxide. Anhydrous THF (45 mL) was added to this mixture, giving a purple solution which slowly turned yellow. After 15 min 16.35 g (0.214 mol) of allyl chloride was added and the reaction mixture was stirred at room temperature for 15 min.

The carbamate salt solution was added to the palladium–DIPHOS–allyl chloride mixture at room temperature with rapid stirring using excess carbon dioxide pressure to force the carbamate solution into the reactor with the catalyst. A head pressure of 80 psig of carbon dioxide was then added above the reaction mixture, and it was stirred at room temperature for 21 h, during which time a white solid precipitated. After this time the pressure was released and the yellow solution was filtered through silica gel (this inactivates the catalyst). The filtrate was concentrated, leaving a yellow oil. Distillation at 5 Torr (125–130 °C) gave 17.17 g (78.4%) of 1 as a clear oil: ^{1}H NMR ($CDCl_3$) δ 7.39–7.26 (m, 5H), 6.0 (br, 1H), 5.4–5.2 (br, 2H), 4.69 (br d, J = 5 Hz, 2H), 4.54 (s, 2H), 3.32 (br, 2H), 1.13 (br t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.7 (br), 138.6, 133.7, 129.0, 128.3 (br), 127.8, 117.6, 66.5, 50.3 (br), 42 (br), 13.6 (br);[15] IR (film) 1705, 1647 cm^{-1}; MS (CI, methane) m/z 220 (MH^+).[16]

Allyl Diallylcarbamate (2): procedures as in the synthesis of 1; product isolated by distillation at 4 Torr (76–80 °C); 93%; ^{1}H NMR ($CDCl_3$) δ 5.93 (m, 1H), 5.78 (m, 2H), 5.26 (dq, J = 17.2, 1.7 Hz, 1H), 5.15–5.08 (overlapping m, 5H), 4.54 (dt, J = 5.4, 1.5 Hz, 2H), 3.85 (br d, J = 5.5 Hz, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 155.9, 135.1, 134.6, 116.7, 116.9, 66.4, 49.6 (br); IR (film) 1705, 1646 cm^{-1}; MS (CI, methane) m/z 182 (MH^+). Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.27; H, 8.01; N, 7.98.

2-Methylallyl Diallylcarbamate (3): procedures as in the synthesis of 1; product isolated by distillation at 5 Torr (78–85 °C); 67.5%; ^{1}H NMR ($CDCl_3$) δ 5.78 (m, 2H), 5.16 (s, 2H), 5.13 (br, 2H), 4.92 (d, J = 10.3 Hz, 2H), 4.52 (s, 2H), 3.88 (br, 4H), 1.75 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.3, 141.1, 134.0, 117.3 (br), 112.5, 69.1, 49.3 (br), 19.9; IR (film) 1705, 1659, 1646 cm^{-1};

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[14] This point was discussed in: Schroth, V.-W.; Andersch, J.; Schadler, H.-D.; Spitzner, R. *Chem.-Ztg.* **1989**, *113*, 261–271.

[15] Broad peaks in the ^{1}H and ^{13}C NMR spectra of the carbamates derived from secondary amines are the results of hindered rotation about the urethane moiety. At higher temperatures these peaks sharpen significantly.

[16] Elemental analysis gave the following results. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 70.70; H, 7.62; N, 6.36.

MS (CI, methane) *m/z* 196 (MH^+). Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78; N, 7.17. Found: C, 67.31; H, 8.85; N, 7.11.

Allyl Diethylcarbamate (4): known compound,[17] isolated by chromatography on silica gel using 50% CH_2Cl_2/hexane; ^{1}H NMR ($CDCl_3$) δ 5.97 (m, 1H), 5.32 (dq, J = 17.2, 1.7 Hz, 1H), 5.22 (dq, J = 10.5, 1.5 Hz, 1H), 4.61 (dt, J = 5, 1.4 Hz, 2H), 3.32 (q, J = 7.2 Hz, 4H), 1.15 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.2, 133.9, 117.3, 66.1, 42 (br), 14.1 (br); IR (film) 1701, 1649 cm^{-1}. Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 60.81; H, 9.62; N, 8.98.

2-Butene-1,4-diyl Bis(diethylcarbamate) (5): known compound,[18] product isolated by chromatography on silica gel using 20% ethyl acetate/80% hexane (22% isolated as clear oil); ^{1}H NMR ($CDCl_3$) δ 5.78 (m, 2H), 4.72 (d, J = 5 Hz), 3.30 (br q, J = 6.9 Hz, 8H), 1.14 (t, J = 7.1 Hz, 12 H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.2, 128.9, 61.2, 41.9 (br), 14.2 (br); IR (film) 1700 cm^{-1}; MS (CI, methane) *m/z* 287 (MH^+).

Allyl Cyclohexylcarbamate (6): known compound,[19] procedures as in the synthesis of 1 except that CyTMG used as co-base and reaction carried out at 30 °C; product isolated by chromatography on silica gel using 100% CH_2Cl_2 (30% as clear oil); ^{1}H NMR ($CDCl_3$) δ 5.95 (m, 1H), 5.32 (dq, J = 17.2, 1.5 Hz, 1H), 5.23 (dq, J = 10.4, 1.4 Hz, 1H), 4.65 (br s, N–H), 4.57 (br d, J = 5.4 Hz, 2H), 3.52 (br m, 1H), 1.99–1.10 (m, cyclohexyl, 10H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 155.9, 133.6, 118.0, 65.8, 50.4, 33.9, 26.0, 25.3; IR (film) 3325, 1698, 1647 cm^{-1}; MS (CI, methane) *m/z* 184 (MH^+). Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.37; H, 9.40; N, 7.82.

Diallyl Hexamethylenebis(methylcarbamate) (7): product isolated by chromatography using 15% ethyl acetate/85% hexane (50% isolated as clear oil); ^{1}H NMR ($CDCl_3$) δ 5.93 (m, 2H), 5.29 (dq, J = 17.2, 1.5 Hz, 2H), 5.19 (dq, J = 10.4, 1.3 Hz, 2H), 4.57 (dt, J = 5.4, 1.4 Hz, 4H), 3.25 (t, J = 7.3 Hz, 4H), 2.89 (s, 6H), 1.53 (m, 4H), 1.30 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.6, 133.8, 117.5, 66.3, 49.2 (br), 36.5 (br), 28.0 (br), 26.9; IR (film) 1700, 1649 cm^{-1}; MS (CI, methane) *m/z* 313 (MH^+). Anal. Calcd for $C_{16}H_{28}N_2O_4$: C, 61.51; H, 9.03; N, 8.97. Found: C, 61.37; H, 9.01; N, 9.00.

Benzyl Allyl Carbonate (8): procedures as in the synthesis of 1 except that CyTMG used as co-base and reaction carried out at 30 °C; product isolated by chromatography using 100% CH_2Cl_2 (64%); ^{1}H NMR ($CDCl_3$) δ 7.45–7.30 (m, 5H), 5.98 (m, 1H), 5.40 (dq, J = 17.2, 1.5 Hz, 1H), 5.30 (dq, J = 10.4, 1.3 Hz, 1H), 5.22 (s, 2H), 4.68 (dt, J = 5.8, 1.3 Hz, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 155.5, 135.8, 132.1, 129.1, 129.0, 128.8, 119.4, 70.2, 69.1; IR (film) 1754, 1650 cm^{-1}; MS (FAB, *n*-BuOH) *m/z* 181 (MH^+). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.34; H, 6.28.

Polyurethane. Into a Fischer–Porter bottle was added 7.2 g (0.05 mol) of *N,N′*-dimethylhexamethylenediamine and 21.7 g (0.11 mol) of cyclohexyltetramethylguanidine. To this was added 30 mL of anhydrous THF, giving a clear solution. The Fischer–Porter bottle was attached to a pressure head, and ca. 60 psig of carbon dioxide was added above the solution at room temperature with stirring. Upon addition of carbon dioxide the solution warmed slightly and after 2 h absorption of CO_2 had ceased.

Into a second Fischer–Porter bottle was added 250 mg (0.22 mmol) of $Pd(PPh_3)_4$. This Fischer–Porter bottle was attached to a pressure head, and the apparatus was flushed with carbon dioxide. Anhydrous THF (40 mL) was added to this mixture, giving a yellow solution; to this was added. 6.25 g (0.05 mol) of 1,4-dichloro-2-butene, and the raction mixture was stirred at room temperature for 15 min (a small amount of a precipitate formed).

The carbamate salt solution was added to the palladium-containing mixture at room temperature with rapid stirring, using excess carbon dioxide pressure to force the carbamate solution into the reactor with the catalyst. A head pressure of 60 psig of carbon dioxide was maintained above the reaction mixture, and it was stirred at room temperature for 3 days, during which time a white solid precipitated. After this time the pressure was released and the yellow solution was filtered through Celite. The filtrate was concentrated and the orangish residue was slowly dripped into diethyl ether (ca. 500 mL), giving the crude polymeric product as a brown-orange semisolid: ^{1}H NMR ($CDCl_3$) δ 5.75 (br, 2H), 4.71 (d, J = 4.4 Hz, 4H), 3.26 (br, 4H), 2.90 (s, 6H), 1.53, (br, 4H), 1.32 (br, 4H); IR ($CHCl_3$) 1692 cm^{-1}; GPC (polystyrene based) M_n = 5400, M_w = 8900 (M_w/M_n = 1.66).

Rate Studies. A 0.1 M solution of amine was made by diluting 1.35 g (0.01 mol) benzylethylamine and 1.54 g (0.01 mol) of biphenyl (internal GC standard) with 100 mL of THF in the drybox. A stock solution of 0.11 M *N*-cyclohexyl-*N′,N′,N″,N″*-tetramethylguanidine (CyTMG) was made by diluting 2.17 g of the guanidine to 100 mL with THF in the drybox. A 1 M solution of allyl chloride was made by diluting 7.65 g (0.1 mol) of allyl chloride to 100 mL with THF in the drybox. A stock solution of palladium catalyst was made by diluting 0.366 g (0.001 mol) of bis[η^3-allyl)palladium chloride], 0.8 g (0.002 mol) of bis(diphenylphosphino)ethane, and 7.65 g (0.1 mol) of allyl chloride to 100 mL with THF in the drybox.

All reactions were run at 30 °C under 80 psig of carbon dioxide pressure. In the drybox 10 mL of the 0.1 M stock solution of benzylethyl amine and 10 mL of the 0.11 M stock solution of CyTMG were added to a Fischer–Porter bottle. This was attached to a pressure head and 80 psig of carbon dioxide added above the solution.

In the drybox a second Fischer–Porter bottle was charged with 1–10 mL of a stock solution of the palladium catalyst, 9–0 mL of the stock solution of allyl chloride (added to keep all runs at constant allyl–Cl concentration), and 10 mL of THF. This bottle was also attached to a pressure head and 80 psig of carbon dioxide added above the yellow solution.

After 1 h both of the Fischer–Porter bottles were added to an oil bath maintained at 30 °C (±1 °C), and after equilibrium at this temperature the carbamate solution from the first Fischer–Porter bottle was added all at once to the palladium solution. Aliquots were taken periodically, quenched with 0.5 M aqueous HCl, extracted with diethyl ether, and analyzed by GC. The reaction was repeated for a total of four different palladium concentrations, and the results are given in Table V and shown graphically in Figure 1.

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