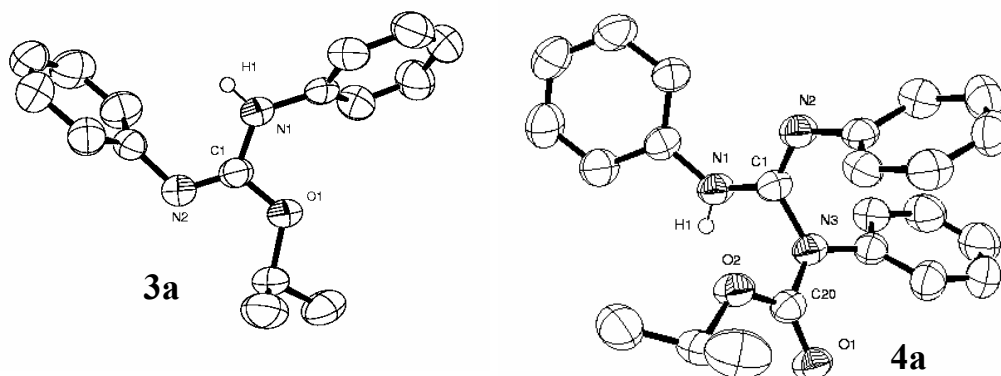


### Supporting Information

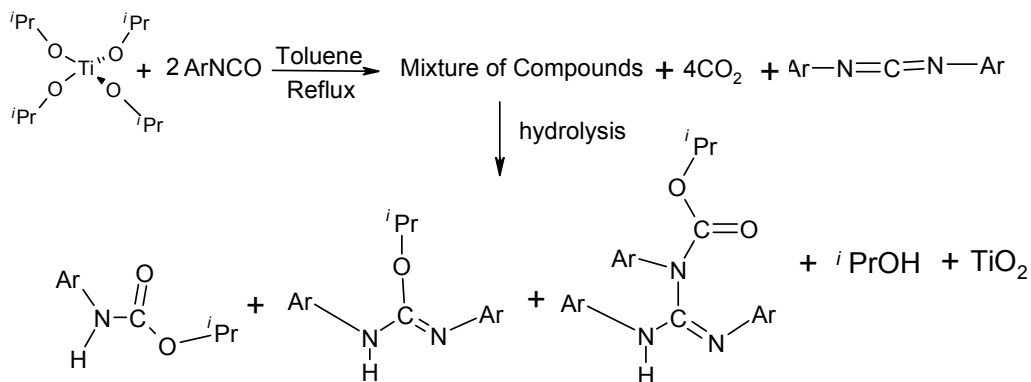
#### Catalytic Metathesis of Carbon Dioxide with other Heterocumulenes Mediated by Titanium isopropoxide

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**Figure 1.** ORTEP diagrams of the insertion product of titanium isopropoxide and diphenyl carbodiimide (**3a**) and the product from insertion of titanium carbamate into carbodiimide (**4a**) with 50% thermal ellipsoids. Hydrogen atoms on carbons have been omitted for clarity



**Scheme 1:** Metathesis of two equivalents of aryl isocyanate with titanium isopropoxide and the products on hydrolysis (Scheme 2 in the manuscript).

**Table 1:** Product obtained by metathesis of aryl isocyanate with titanium isopropoxides as shown in Scheme 1

Entry	Ratio of Ti(O <sup>i</sup> Pr) <sub>4</sub> : ArNCO	Solvent	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
1 <sup>a</sup>	1 : 1	Toluene	67	31	-	2
2 <sup>a</sup>	1 : 2	Toluene	46	49	2	2
3 <sup>a</sup>	1 : 3	Toluene	40	49	9	2
4 <sup>a</sup>	1 : 4	Toluene	47	48	2	2
5 <sup>b</sup>	1 : 2	Toluene	39	47	12	3
6 <sup>b</sup>	1 : 2	THF	46	41	9	3
7 <sup>c</sup>	1 : 2	Toluene	23	70	3	4
8 <sup>c</sup>	1 : 2	THF	82	17	0	2

<sup>a</sup> Reaction of phenyl isocyanate under reflux. <sup>b</sup> Reaction of phenyl isocyanate in a sealed vial maintained at 110°C. <sup>c</sup> Reaction of 4-methylphenyl isocyanate under reflux.

**Table 2:** Crystallographic data for compound **3a** and **4a**.

Compound	<b>3a</b>	<b>4a</b>
Empirical formula	C <sub>16</sub> H <sub>18</sub> N <sub>2</sub> O	C <sub>23</sub> H <sub>23</sub> N <sub>3</sub> O <sub>2</sub>
Formula weight	254.32	373.44
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	a = 8.9335(18) Å	a = 9.505(5) Å
	b = 9.5181(19) Å	b = 10.689(6) Å
	c = 9.5609(19) Å	c = 10.748(6) Å
	α = 110.127(3)°.	α = 81.385(9)°.
	β = 99.664(3)°.	β = 71.862(9)°.
	γ = 101.080(3)°.	γ = 88.352(9)°.

Volume	724.5(3) Å <sup>3</sup>	1025.9(10) Å <sup>3</sup>
Z	2	2
Color, Shape	Colorless, block	Colorless, box type
Density (calculated)	1.166 Mg/m <sup>3</sup>	1.209 Mg/m <sup>3</sup>
Absorption coefficient	0.074 mm <sup>-1</sup>	0.078 mm <sup>-1</sup>
F(000)	272	396
Crystal size	0.43 x 0.36 x 0.32 mm <sup>3</sup>	0.40 x 0.32 x 0.28 mm <sup>3</sup>
Theta range for data collection	2.35 to 26.01°.	1.93 to 26.10°.
Reflections collected	7559	10794
Independent reflections	2835 [R(int) = 0.0594]	4038 [R(int) = 0.0563]
Completeness to theta = 26.01°	99.2 %	99.0 %
Absorption correction	Empirical (SADABS)	Empirical (SADABS)
Max. and min. transmission	0.9702 and 0.71	1 and 0.7814
Data / restraints / parameters	2835 / 0 / 245	4038 / 0 / 345
Goodness-of-fit on F <sup>2</sup>	1.063	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1292	R1 = 0.0398, wR2 = 0.0982
R indices (all data)	R1 = 0.0597, wR2 = 0.1371	R1 = 0.0544, wR2 = 0.1053
Largest diff. peak and hole	0.174 and -0.195 e.Å <sup>-3</sup>	0.158 and -0.192 e.Å <sup>-3</sup>

**Table 3:** Important bond length and bond angles in compound **3a**.

O(1)-C(1)	1.343(2)	N(2)-C(1)-O(1)	122.76(12)
N(1)-C(1)	1.367(2)	N(2)-C(1)-N(1)	126.35(12)
N(2)-C(1)	1.266(2)	O(1)-C(1)-N(1)	110.89(11)

**Table 4:** Important bond length and bond angles in compound **4a**.

O(1)-C(20)	1.211(1)	N(2)-C(1)-N(1)	124.26(10)
O(2)-C(20)	1.331(2)	N(2)-C(1)-N(3)	123.87(10)
N(1)-C(1)	1.368(2)	N(1)-C(1)-N(3)	111.69(10)
N(2)-C(1)	1.269(2)	O(1)-C(20)-O(2)	125.58(12)
N(3)-C(1)	1.451(2)	O(1)-C(20)-N(3)	124.80(11)

N(3)-C(20)	1.380(2)	O(2)-C(20)-N(3)	109.62(10)
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### Experimental Details:

All manipulations were carried out under an inert nitrogen atmosphere using a standard double manifold. Tetrahydrofuran and petroleum ether were freshly distilled from sodium/benzophenone prior to use. Titanium tetraisopropoxide, phenyl isocyanate, 4-methoxyphenyl isocyanate, 4-fluorophenylisocyanate, 2-methylphenyl isocyanate were obtained from Aldrich and 4-methylphenyl isocyanate was obtained from Lancaster and used as supplied. Diphenyl carbodiimide was synthesised by the literature procedure<sup>[34]</sup>.

### Physical Measurements:

<sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} spectra were recorded either on a Bruker ACF 200 MHz operating at 200 MHz for <sup>1</sup>H NMR and 50 MHz for <sup>13</sup>C NMR or on a Bruker AMX400 / Bruker Avance 400 operating at 400 MHz and 100 MHz, with tetramethylsilane (TMS) as the internal reference. All samples were recorded in CDCl<sub>3</sub> as the solvent. For compounds **3a**, **3b** and **3ab** representative coupled <sup>13</sup>C NMR was recorded as an evidence for identity of the compounds. In the case of compound **1**, the reported NMR is for a mixture as no purification could be accomplished. In the case of compounds **3a**, **3b**, **3c**, **3d**, **3ab** the <sup>1</sup>H NMR at room temperature contains broad peaks due to the 1-3 migration of the proton on nitrogen, so the <sup>1</sup>H NMR was recorded at -40° C to improve the resolution. HRESMS was recorded on a Micromass Q-ToF micro instrument. Elemental analyses were done on a Carlo Erba elemental analyser model 1106. GC measurements were made using a Chemito GC 7610 instrument with a flame ionisation detector and a packed column (0.32 mm i.d., 2.44 m length) having 5% SE-30 as the liquid phase and Ch-W(HP) as the solid phase. Nitrogen was used as a carrier gas at a flow rate of 30 cm<sup>3</sup> min<sup>-1</sup>. A temperature program (1 min. at 150 °C ramp to 270 °C @ 20 °C/min and hold at 270 °C for 4 min) run was employed with the injector being maintained at 250 °C and the detector at 270 °C, to analyze the organic products in the mixed metathesis and catalytic experiments.

X-Ray Crystallography: Good quality crystal of **3a** and **4a** were chosen and glued to the tip of a glass fiber along the largest dimension for indexing and data collection. Data was

collected on a Bruker AXS single crystal diffractometer equipped with SMART APEX CCD detector and a sealed Mo K $\alpha$  source working at 1.75 kW. Intensity data were collected at 293(2) K. The SMART software was used for data acquisition and the SAINT software for data extraction. The data were corrected for Lorentz and polarization effects. Absorption correction was carried out with SADABS.<sup>[35]</sup> All computations were performed using the WINGX package.<sup>[36]</sup> The positions of heavy atoms were determined by SHELXS-86.<sup>[37]</sup> The remaining atoms were located from the difference Fourier map using SHELXL-97.<sup>[38]</sup>

In the following discussion, 'work up' involved redissolving in methylene chloride and the organic part was extracted after addition of water. The organic compound is then evaporated to dryness and the mixture extracted with petroleum ether.

Reaction of titanium isopropoxide with 2 eq. of phenyl isocyanate under toluene reflux: Titanium tetraisopropoxide (1 ml. 3.38 mmol) was dissolved in 20 ml of toluene. Into this solution phenyl isocyanate (0.74 ml. 3.38 mmol) was added. The mixture was stirred under reflux for 24 hrs and the solvent evaporated to dryness under vacuum to give a yellow paste. This was characterized as a mixture of compounds. NMR analysis <sup>1</sup>H NMR (200 MHz.)  $\delta$ 7.36 – 6.75 (m, 10H), 6.96 – 6.75 (m, 20H), 4.69 (sept, 5H, J = 6.3 Hz.), 4.42 (sept, 8H, J = 6.3 Hz.), 4.12 (sept, 3H, J = 6.3 Hz.), 1.18 (d, 48H, J = 6.3 Hz.), 1.04 (sept, 30H, J = 6.3 Hz.), 0.83 (d, 18H, J = 6.3 Hz.).

Compound **3a** : Carbamimidic acid, N,N'-diphenyl-, 1-methylethyl ester: Compound 1 dissolved in methylene chloride was taken in a separating funnel and extracted from water. The organic part was evaporated to dryness under vacuum. The compound was isolated by eluting with a mixture of ethyl acetate and petroleum ether (5 : 95) through a silica column to get a white waxy solid (yield 70%). Crystals suitable for single crystal x-ray were obtained by slow evaporation of the solvent from a solution of the compound in petroleum ether. <sup>1</sup>H NMR (400 MHz.)  $\delta$ 7.39 (t, 2H, J = 7.6 Hz.), 7.29 (t, 2H, J = 7.6 Hz.), 7.11 (t, 1H, J = 7.6 Hz.), 7.10 (d, 2H, J = 7.6 Hz.), 7.05 (t, 1H, J = 7.6 Hz.), 7.01 (d, 2H, J = 7.6 Hz.), 5.88 (s, NH), 5.29 (sept, 1H, J = 6.0 Hz.), 1.45 (d, 6H, J = 6.0 Hz.). <sup>13</sup>C NMR

(100 MHz.)  $\delta$ 149.4, 148.3, 138.9, 129.8 (d,  $^1J_{\text{CH}} = 156.0$  Hz.), 129.1 (d,  $^1J_{\text{CH}} = 158.5$  Hz.), 122.9 (dt,  $^1J_{\text{CH}} = 159.4$  Hz.,  $^2J_{\text{CH}} = 6.8$  Hz.), 120.4 (d,  $^1J_{\text{CH}} = 159.4$  Hz.), 118.8 (d,  $^1J_{\text{CH}} = 154.3$  Hz.), 70.0 (d sept,  $^1J_{\text{CH}} = 149.2$  Hz.,  $^2J_{\text{CH}} = 4.2$  Hz.), 22.1 (dd,  $^1J_{\text{CH}} = 125.5$  Hz.,  $^2J_{\text{CH}} = 4.2$  Hz.). HRESMS  $[\text{M} + \text{Na}]^+$  obsd.  $m/z$  277.1337, calcd. for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{ONa}$  277.1317. GC retention time: 5.9 min.

Compound **4a**: Carbanilic acid, N-(N,N'-diphenylamidino)-, 1-methylethyl ester: After the isolation of compound **3** on a silica column, elution with a mixture of ethyl acetate and petroleum ether (10 : 90) gave the compound (7 mg). Crystals suitable for single crystal x-ray were obtained by slow evaporation of the solvent from a solution of the compound in hexane.  $^1\text{H}$  NMR (400 MHz.)  $\delta$ 7.21 (m, 6H), 7.10 (t, 5H,  $J = 7.1$  Hz.), 7.01 (t, 4H,  $J = 7.1$  Hz.), 4.95 (sept, 1H,  $J = 6.3$  Hz.), 1.18 (d, 6H,  $J = 6.3$  Hz.).  $^{13}\text{C}$  NMR (100 MHz.)  $\delta$ 152.81, 138.76, 128.84, 128.55, 125.81, 124.25, 123.29, 120.52, 70.73, 21.73. Anal. Calcd for  $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_2$ : C, 73.96; H, 6.21; N, 11.25. Found: C, 73.98; H, 6.32; N, 10.92.

Compound **3b**: Carbamimidic acid, N,N'-bis(4-methylphenyl)-, 1-methylethyl ester:  $^1\text{H}$  NMR (400 MHz.)  $\delta$ 7.12 (d, 2H,  $J = 8$  Hz.), 7.04 (d, 2H,  $J = 8$  Hz.), 6.94 (d, 2H,  $J = 8$  Hz.), 6.84 (d, 2H,  $J = 8$  Hz.), 5.77 (s, NH), 5.22 (sept, 1H,  $J = 6.4$  Hz.), 2.30 (s, 3H), 2.26 (s, 3H), 1.38 (d, 6H,  $J = 6.4$  Hz.).  $^{13}\text{C}$  NMR (100 MHz.)  $\delta$ 149.7, 145.6, 136.5, 132.2, 130.3 (d,  $^1J_{\text{CH}} = 158.5$  Hz.), 129.3 (d,  $^1J_{\text{CH}} = 155.1$  Hz.), 122.6 (d,  $^1J_{\text{CH}} = 156.8$  Hz.), 120.5 (d,  $^1J_{\text{CH}} = 160.2$  Hz.), 69.6 (d sept,  $^1J_{\text{CH}} = 149.2$  Hz.,  $^2J_{\text{CH}} = 4.2$  Hz.), 22.0 (dd,  $^1J_{\text{CH}} = 126.3$  Hz.,  $^2J_{\text{CH}} = 4.2$  Hz.), 20.7 (d,  $^1J_{\text{CH}} = 126.3$  Hz.). HRESMS  $[\text{M} + \text{H}]^+$  obsd.  $m/z$  283.1851, calcd. for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}$  283.1810. GC retention time: 7.0 min.

Compound **3ab**: Carbamimidic acid, N-phenyl, N'-(4-methylphenyl)-, 1-methylethyl ester:  $^1\text{H}$  NMR (400 MHz.)  $\delta$ 7.39 (t, 2H,  $J = 7.6$  Hz.), 7.29 (t, 2H,  $J = 7.6$  Hz.), 7.12 (d, 2H,  $J = 8$  Hz.), 7.11 (t, 1H,  $J = 7.6$  Hz.), 7.10 (d, 2H,  $J = 7.6$  Hz.), 7.05 (t, 1H,  $J = 7.6$  Hz.), 7.04 (d, 2H,  $J = 8$  Hz.), 7.01 (d, 2H,  $J = 7.6$  Hz.), 6.94 (d, 2H,  $J = 8$  Hz.), 6.84 (d, 2H,  $J = 8$  Hz.), 5.85(s, 2H, NH), 5.29(sept, 2H,  $J = 6.4$  Hz.), 2.30 (s, 3H), 2.26 (s, 3H), 1.40(d,

12H,  $J = 6.4$  Hz.).  $^{13}\text{C}$  NMR (100 MHz.)  $\delta$ 149.5, 145.6, 136.5, 132.2, 130.3 (d,  $^1J_{\text{CH}} = 158.5$  Hz.), 129.3 (d,  $^1J_{\text{CH}} = 155.1$  Hz.), 122.6 (d,  $^1J_{\text{CH}} = 156.8$  Hz.), 120.5 (d,  $^1J_{\text{CH}} = 160.2$  Hz.), 69.8 (d sept,  $^1J_{\text{CH}} = 149.2$  Hz.,  $^2J_{\text{CH}} = 4.2$  Hz.), 22.0 (dd,  $^1J_{\text{CH}} = 126.3$  Hz.,  $^2J_{\text{CH}} = 4.2$  Hz.), 20.7 (d,  $^1J_{\text{CH}} = 126.3$  Hz.). HRESMS  $[\text{M} + \text{H}]^+$  obsd.  $m/z$  269.1678, calcd. for  $\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}$  269.1654. GC retention time: 6.5 min.

Compound **3c**: Carbamimidic acid,  $N,N'$ -bis(4-methoxyphenyl)-, 1-methylethyl ester:  $^1\text{H}$  NMR (400 MHz.)  $\delta$ 7.03(d, 2H,  $J = 8.8$  Hz.), 6.95 (d, 2H,  $J = 8.8$  Hz.), 6.91 (d, 2H,  $J = 8.8$  Hz.), 6.83 (d, 2H,  $J = 8.8$  Hz.), 5.74 (s, NH), 5.24 (sept, 1H,  $J = 6.4$  Hz.), 3.83 (s, 3H), 3.80 (s, 3H), 1.40(d, 6H,  $J = 6.4$  Hz.).  $^{13}\text{C}$  NMR (100 MHz.)  $\delta$ 155.6, 155.4, 150.3, 141.2, 131.8, 123.5, 122.5, 114.9, 113.9, 69.4, 55.4, 21.9. HRESMS  $[\text{M} + \text{H}]^+$  obsd.  $m/z$  315.1712, calcd. for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_3$  315.1708.

Compound **3d**: Carbamimidic acid,  $N,N'$ -bis(4-fluorophenyl)-, 1-methylethyl ester:  $^1\text{H}$  NMR (400 MHz.)  $\delta$ 7.07 (dd, 2H,  $J = 8.8$  Hz.,  $^3J_{\text{HF}} = 7.8$  Hz.), 7.03 (dd, 2H,  $J = 8.8$  Hz.,  $^4J_{\text{HF}} = 5.9$  Hz.), 7.01 (dd, 2H,  $J = 8.8$  Hz.,  $^3J_{\text{HF}} = 8.4$  Hz.), 6.94 (dd, 2H,  $J = 8.8$  Hz.,  $^4J_{\text{HF}} = 5.9$  Hz.), 5.74 (s, NH), 5.24 (sept, 1H,  $J = 6.8$  Hz.), 1.41 (d, 6H,  $J = 6.8$  Hz.).  $^{13}\text{C}$  NMR (100 MHz.)  $\delta$ 159.0 (d,  $^1J_{\text{FC}} = 241.5$  Hz.), 149.7, 143.9, 134.5, 123.7, 122.5, 116.1, 115.6, 70.0, 21.9. HRESMS  $[\text{M} + \text{H}]^+$  obsd.  $m/z$  291.1318, calcd. for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}$  291.1309.

Compound **3e**: Carbamimidic acid,  $N,N'$ -bis(2-methylphenyl)-, 1-methylethyl ester:  $^1\text{H}$  NMR (400 MHz.)  $\delta$ 7.35 (d, 1H,  $J = 7.8$  Hz.), 7.18 (m, 3H), 7.07 (d, 1H,  $J = 7.8$  Hz.), 6.96 (m, 2H), 6.91 (d, 1H,  $J = 7.8$  Hz.), 5.49 (NH), 5.33 (sept, 1H,  $J = 6.4$  Hz.), 2.23 (s, 3H), 1.99 (s, 3H), 1.39 (d, 6H,  $J = 6.4$  Hz.).  $^{13}\text{C}$  NMR (100 MHz.)  $\delta$ 148.9, 146.5, 136.7, 130.8, 130.7, 130.2, 129.1, 127.0, 126.7, 123.6, 122.9, 122.6, 122.1, 69.4, 22.0, 17.9, 17.5. HRESMS  $[\text{M} + \text{H}]^+$  obsd.  $m/z$  283.1825, calcd. for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}$  283.1810.

Cross metathesis reaction: Single step reaction: To a solution of titanium tetrakisopropoxide (0.5 ml. 1.69 mmol.) dissolved in 20 ml of toluene, phenyl isocyanate (0.18 ml. 1.69 mmol.) and 4-methylphenyl isocyanate (0.21 ml. 1.69 mmol) are added as a

mixture dissolved in 10 ml. toluene. The mixture is stirred and refluxed for 24 hours and the solvent evaporated to dryness under vacuum. The mixture is worked up and analysed by GC.

Cross metathesis reaction: Two step reaction: To a solution of titanium tetraisopropoxide (0.5 ml. 1.69 mmol.) dissolved in 30 ml of toluene, phenyl isocyanate (0.18 ml. 1.69 mmol.) was added. The mixture was stirred at room temperature for 24 hours. To this solution 4-methylphenyl isocyanate (0.21ml. 1.69 mmol) was added and the solution stirred in refluxing toluene for 24 hours. The solvent is then evaporated to dryness under vacuum. The mixture is worked up and analysed by GC.

Reactions done with CO<sub>2</sub>: Into 6 ml. of tetrahydrofuran in a sealable vial flushed with nitrogen, requisite amount of CO<sub>2</sub> from a gas burette was condensed. A mixture of titanium isopropoxide (0.5ml 1.69mmol.) and diphenyl carbodiimide (0.32ml 1.69 mmol.) in 2 ml of tetrahydrofuran was added while maintaining the vial at liquid nitrogen. The vial was subsequently evacuated and sealed. The sealed vial was heated in an oil bath maintained at 115°C for 24 hours. The vial was broken open and the reaction mixture evacuated to dryness under vacuum. The mixture was then worked up and analysed by GC.

Catalytic reactions: With only phenyl isocyanate: To a solution of titanium tetraisopropoxide (0.05 ml. 0.17 mmol.) dissolved in 30 ml of toluene, phenyl isocyanate (0.37 ml. 3.4 mmol.) was added. The mixture was stirred and refluxed for 24 hours. The solvent was then evaporated to dryness under vacuum. The mixture was worked up and analysed by GC. Retention time: diphenyl carbodiimide : 5.1 min.

Catalytic reactions: With 4-methylphenyl isocyanate and phenyl isocyanate: To a solution of titanium tetraisopropoxide (0.1 ml. 0.34 mmol.) dissolved in 30 ml of toluene, 4-methylphenyl isocyanate (0.04 ml. 0.34 mmol.) was added. The mixture was stirred at room temperature for 24 hours. To this solution phenyl isocyanate (0.56ml. 5.1 mmol) was added and the solution stirred in refluxing toluene for 24 hours. The solvent is then



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evaporated to dryness under vacuum. The mixture is worked up and analysed by GC.

Retention time: Di(4-methylphenyl)carbodiimide: 6.4 min., Phenyl  
4-methylphenylcarbodiimide: 5.8 min.