Pergamon

Tetrahedron Vol. 50, No. 38, pp. 11235-11238, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00685-7

Cs_2CO_3 or CaO as Promoters of Ethyl *N*-{[(4-Methylphenyl)sulphonyl]oxy}carbamate in Amination Reactions

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Abstract: Replacing triethylamine by heterogeneous inorganic bases makes it possible to aminate benzene or other nitrene acceptors, using the title reagent, previously reported to be scarcely reactive. Products of C-H insertion and/or those coming from intermediate aziridines are also obtained.

There are not many methods available to perform direct formation of carbon-nitrogen bonds. Recently our continuing efforts in this area led us to propose a simplified procedure for amination reactions by ethyl *N*-{[(4-nitrophenyl)sulphonyl]oxy}carbamate[1] ($NsONHCO_2Et$, **1**) in the presence of inorganic bases in heterogeneous phase without catalyst.[2]

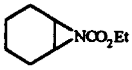
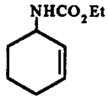
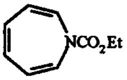
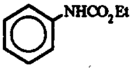
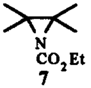
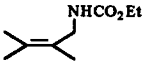
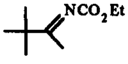
Reports involving insoluble reagents are in rapid growth,[3] because of the advantages offered by reactions performed in such conditions.

We wish to report here the results obtained with a different carbamate, namely ethyl *N*-{[(4-methylphenyl)sulphonyl]oxy}carbamate ($TsONHCO_2Et$, **2**), bearing the tosyl instead of the nosyl moiety. It is noteworthy that **2** is approximately 50 times less expensive than **1**, but it is reported to give amination of benzene, toluene and cyclohexane only in the presence of surfactants and with low yields.[4]

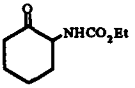
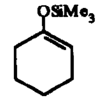
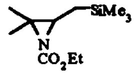
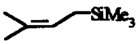
In order to compare the reactivity of the two carbamates we considered the substrates shown in the Table and Cs_2CO_3 or CaO as bases, after a screening of several inorganic bases.

The typical procedure was similar to that employed with **1**. To a stirred solution of substrate (1 M in CH_2Cl_2) at room temperature the base and $TsONHCO_2Et$ were added portionwise with a molar ratio substrate:**2**:base = 1:5:5. With 2,3-dimethylbut-2-ene the molar ratio was 1:3:3 and with the silyl derivatives **10** and **12** it was increased up to 1:7:7. After 1.5 - 24 h petroleum ether was added and cesium[5] or calcium tosylate[6] were isolated as a solid phase.

Table. Comparison of the reactivity of **1** and **2**.

Substrate	Base[a]	Time (h)[b]		Product yields (%)[b]					
				 3		 4			
	Cs_2CO_3	24	7	62	79	5	6		
	CaO	0.5	24	74	51	5	3		
	BaO	24	24	56	30	5	3		
	K_2CO_3	0.7	24	73	10	6	1		
	Et_3N	3	24	57[c]	-	5[c]	-		
				 5		 6			
	Cs_2CO_3		6		57		1		
	CaO	5	24	46	48	14	4		
	K_2CO_3	5		38		10			
	Et_3N	4.3		50[c]					
	NaOH, $RMe_3N^+Br^-$ (R = cetyl)			13[d]					
				 7		 8		 9	
	Cs_2CO_3		1.5		59		2		1
	CaO	0.3	2.5	54	57	10	4	5	1
	K_2CO_3	0.5		54		8		4	
	Et_3N	2	24	57[e]	-	7[e]	-	1[e]	-

(continued)

				**11**			
**10**	Cs_2CO_3		24		51		
	CaO	3.5		67			
	Et_3N	3	24	-	-		
				CO_2Et **13**		**14**	
**12**	Cs_2CO_3		24		65		6
	CaO	1.5	24	65	61	4	6

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[a] In our reactions, the molar ratio substrate:reagent:base was generally 1:5:5, but in the reaction of **1** with benzene and CaO it was 1:3:3 and with 2,3-dimethylbut-2-ene and CaO or K_2CO_3 it was 1:2:2. In the reaction of **2** with 2,3-dimethylbut-2-ene the molar ratio was 1:3:3 and with **10** or **12** it was 1:7:7. [b] The first column refers to reactions run with **1**, the second one refers to those with **2**. [c] Ref. 1. [d] Ref. 4. [e] Nicholas, P. P. *J. Org. Chem.* **1975**, *40*, 3396-3398.

From the results shown in the Table it is concluded that in the reactions with $TsONHCO_2Et$ longer reaction times are required with respect to those with $NsONHCO_2Et$, but the products are the same and the molar ratios as well as the yields are quite similar.

In conclusion, replacing nosyl with tosyl group in the Lwowski's reagent (**1**) and using our improved procedure allow again to perform useful aminations under mild conditions and also with substrates, such as **10**, unreactive in the reactions induced by triethylamine.[7] The reactive intermediate, on the basis of the presence of insertion products (for example **4** and **8**) as well as of product distribution in all reactions, seems to be (ethoxycarbonyl)nitrene. *tert*-Butyl *N*-lithio-*N*-{[(4-methylphenyl)sulphonyl]oxy}carbamate has been found to be an electrophilic aminating reagent toward ester enolates and other organometallic substrates.[8] A similar nitrenoid species, namely *tert*-butyl *N*-lithio-*N*-{[(2,4,6-trimethylphenyl)sulphonyl]oxy}carbamate, has been lately characterised by X-ray structure analysis.[9]

We are continuing our studies on both **1** and **2**, especially with less reactive substrates, in the hope to gain more insight about the process too.

EXPERIMENTAL SECTION

Synthesis of $TsONHCO_2Et$ (2). To a solution of ethyl *N*-hydroxycarbamate[1] (80 mmol) in 120 ml of anhydrous ethyl ether with stirring and ice cooling (4-methylphenyl)sulphonyl chloride (80 mmol) was added in 30 min. Then a solution of anhydrous Et_3N (80 mmol) in 12 ml of ethyl ether was added in 1 h. After addition, the mixture was stirred for 2 h at 0 °C, for 1 h at room temperature and filtered. The ether phase was dried on Na_2SO_4 and the solvent was evaporated. The resulting semi-solid residue was washed with light petroleum ether and crystallised from hexane to give **2** (71% yield) as a white solid after 48 h at 4 °C; mp 58-

59 °C; IR (CCl_4) 3370, 1773, 1338 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (t, 3 H, CH_2CH_3), 2.40 (s, 3 H, CH_3), 3.98 (q, 2 H, CH_2), 7.29-7.32 (d, 2 H, CH), 7.80-7.83 (d, 2H, CH), 8.51 (br, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 13.88 (CH_2CH_3), 21.65 (CH_3), 63.06 (CH_2), 129.45, 129.60 (CH), 130.21 (*C*-CH_3), 146.03 (C-S), 155.74 (CO).

Reaction of **2** *with Cyclohexene, Benzene, 2,3-Dimethylbut-2-ene,* ***10*** *or* ***12****. General Procedure.* To a stirred solution of substrate (6 mmol) in 6 ml of CH_2Cl_2 at room temperature, solid base and **2** were added portionwise in 1.5 h with the molar ratios reported in the Table. After 1.5 - 24 h of stirring, 20 ml of CH_2Cl_2 and 200 ml of petroleum ether (bp 30-50 °C) were added. After filtration, the liquid phase was concentrated *in vacuo*. The yields are reported in the Table.

Presented at the 2nd International Symposium on Supported Reagents and Catalysts in Chemistry, 5-8 July 1994, Swansea (G. B.), Abstracts, P.21.

Acknowledgment. This work was supported by the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) and Consiglio Nazionale delle Ricerche (CNR).

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5. IR (KBr) 3044, 2922, 1398, 1189 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.28 (s, 3 H, CH_3), 7.09-7.13 (d, 2 H, CH), 7.46-7.50 (d, 2 H, CH); ^{13}C NMR (DMSO-d_6) δ 20.79 (CH_3), 125.81, 128.35 (CH), 137.92 (*C*-CH_3), 146.21 (C-S); AAS found Cs^+ 284 ppm, calcd 300 ppm.
6. IR (KBr) 3039, 2917, 1415, 1201 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.28 (s, 3 H, CH_3), 7.10-7.14 (d, 2 H, CH), 7.47-7.51 (d, 2 H, CH); ^{13}C NMR (DMSO-d_6) δ 20.77 (CH_3), 125.83, 128.42 (CH), 138.22 (*C*-CH_3), 146.18 (C-S); ICP-AES found Ca^{2+} 76.4 ppm, calcd 79.0 ppm.
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(*Received in UK* 9 *June* 1994; *revised* 29 *July* 1994; *accepted* 4 *August* 1994)