Synthesis of 3-Substituted 1-Mesitylenesulfonyloxyureas

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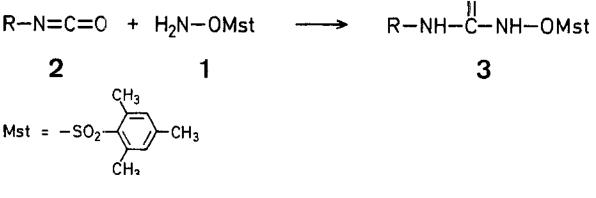
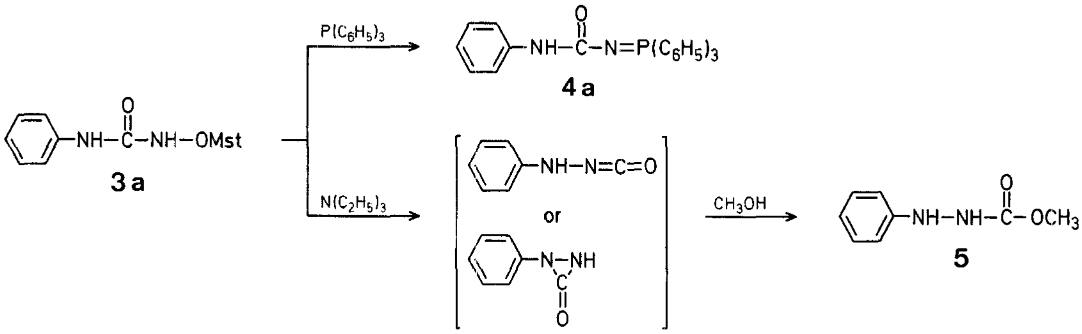
We report here a synthesis of new urea derivatives, 3-substituted 1-mesitylenesulfonyloxyureas (**3**), which are expected not only to react as aminocarbonylaminating agents[1], but also to be potential precursors of aminocarbonyl nitrenes[4], aminoisocyanates[5], or oxodiaziridines[5].

In general, compounds **3** were prepared by the reaction of equimolar quantities of the isocyanates **2** and *O*-mesitylenesulfonylhydroxylamine[6] (**1**) in dichloromethane at room temperature. The structures of **3** were determined by the elemental and spectral analyses and the chemical evidence: for example, the infrared spectrum of **3a** showed strong absorption bands at 1680 (C=O), 3370, and 3150 cm^{-1} (NH). Treatment of **3a** with potassium iodide in acetic acid liberated iodine. Treatment of **3a** with triphenylphosphine in dichloromethane followed by addition of 5% sodium hydroxide gave *N*-phenylaminocarbonyliminotriphenylphosphorane (**4a**) in 61% yield. Similarly **3b** gave *N*-*p*-bromophenylaminocarbonyliminotriphenylphosphorane (**4b**) in 58% yield.





The behavior of **3a** as a precursor of an aminoisocyanate (or an oxodiaziridine) was demonstrated by the reaction with triethylamine in methanol at room temperature to give 1-methoxycarbonyl-2-phenylhydrazine (**5**) in 39% yield. Similar treatment of **3g** in chloroform or methanol, however, gave 2-phenyl-5-oxo-4,5-dihydro-1,3,4-oxadiazole (**7**), the formation of which may involve an initial formation of benzamidoisocyanate (or *N*-benzoyloxodiaziridine) (**6**) followed by an intramolecular cyclization.

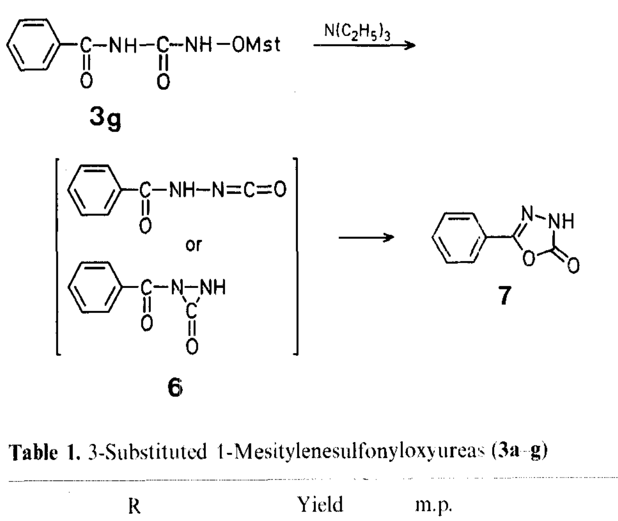
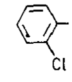
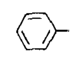


Table 1. 3-Substituted 1-Mesitylenesulfonyloxyureas (**3a**-**g**)

	R	Yield (%)	m.p. (from CH_3OH)	Elemental Analyses				
3a		65	161–163°	$C_{16}H_{18}N_2O_4S$	calc.	C 57.48	H 5.43	N 8.38
				(334.39)	found	57.74	5.52	8.30
3b		46	188–190°	$C_{16}H_{17}BrN_2O_4S$	calc.	C 46.50	H 4.15	N 6.78
				(413.30)	found	46.40	4.17	6.72
3c		34	190–191°	$C_{17}H_{20}N_2O_4S$	calc.	C 58.61	H 5.79	N 8.04
				(348.42)	found	58.55	5.84	7.91
3d		67	177–178°	$C_{16}H_{17}ClN_2O_4S$	calc.	C 52.10	H 4.65	N 7.60
				(368.84)	found	52.11	4.64	7.54
3e		36	165–166°	$C_{16}H_{17}ClN_2O_4S$	calc.	C 52.10	H 4.65	N 7.60
				(368.84)	found	52.15	4.69	7.55
3f	*n*-$C_{18}H_{37}$–	60	94–95°	$C_{28}H_{56}N_2O_4S$	calc.	C 65.85	H 9.87	N 5.49
				(510.78)	found	65.92	9.97	5.42
3g		55	182–184°	$C_{17}H_{18}N_2O_5S$[a]	calc.	C 56.35	H 5.01	N 7.73
				(362.40)	found	56.12	5.14	7.59

[a] I.R. (KCl): ν_{max} = 1720, 1670 (C=O) cm^{-1}.

Further studies on the chemical properties of compounds **3** are in progress.

Reaction of *O*-Mesitylenesulfonylhydroxylamine with Phenyl Isocyanate (2a):

To a solution of phenyl isocyanate **2a** (2.4 g, 20 mmol) in dichloromethane (10 ml) was added dropwise a solution of *O*-mesitylenesulfonylhydroxylamine (**1**) (4.3 g, 20 mmol) in dichloromethane (5 ml). The reaction mixture was allowed to stand at room temperature for 20 min and then the solvent was removed under reduced pressure below 30°. The residual solid was recrystallized from methanol to give white crystals of **3a**; yield: 4.3 g (65%).

1-Methoxycarbonyl-2-phenylhydrazine (5):

To an ice-cooled solution of **3a** (334 mg, 1 mmol) in methanol (100 ml) was added dropwise a solution of triethylamine (101 mg, 1 mmol) in methanol (10 ml). After evaporation of methanol, compound **5** was isolated by preparative T.L.C. on alumina (Alumina PF_{254}) using chloroform as solvent; yield: 64 mg (39%); m.p. 114–115° (from methanol) (lit.[7] m.p. 115–117°). Its I.R. spectrum (KCl) was identical with that of an authentic sample prepared by a known procedure[7].

2-Phenyl-5-oxo-4,5-dihydro-1,3,4-oxadiazole (7):

To an ice-cooled solution of **3g** (362 mg, 1 mmol) in chloroform (5 ml) was added dropwise triethylamine (101 mg, 1 mmol). After 5 min, ether was added and precipitated triethylaminium mesitylenesulfonate was filtered off. The filtrate was concentrated to dryness and the residual solid was recrystallized from ether/petroleum ether to give **7**; yield: 103 mg (64%); m.p. 137° (lit.[8] m.p. 139°).

Mass spectrum: *m/e* = 162 (M$^+$), 118, 105, 91, 77.

Reaction of 3a with Triphenylphosphine:

To an ice-cooled solution of **3a** (167 mg, 0.5 mmol) was added a solution of triphenylphosphine (131 mg, 0.5 mmol) in dichloromethane (5 ml) and the reaction mixture was stirred for 10 min and then treated with 5% sodium hydroxide (5 ml). The organic layer was separated and dried over magnesium sulfate. After evaporation of the solvent, a residual mass was recrystallized from benzene/ether to give **4a**; yield: 120 mg (61%); m.p. 178–179° (lit.[9] m.p. 178–179°).

Similarly **4b** was obtained from **3b** in 58% yield; m.p. 175–176° (lit.[9] m.p. 169–171°).

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