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15. The side product of the reaction of 4'-methylacetophenone (entry 5 in Table) was identified as 2,2-dichloro-4'-methylacetophenone by G.C.-M.S. and ^1H nmr (300 MHz).

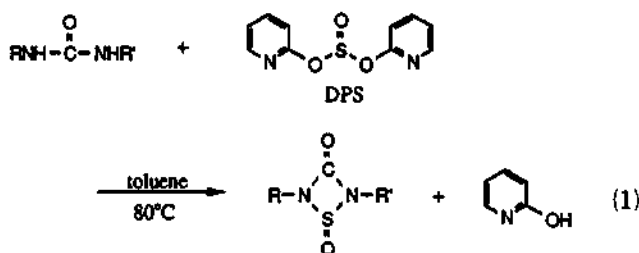
Synthesis of 1,2,4-Thiadiazetid-1-oxide-3-ones by Reaction of Ureas with Di-2-pyridyl Sulfite

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Received February 7, 1990

In the course of studies on the synthetic utilities of di-2-pyridyl sulfite (DPS),^{1,2} we have had an occasion to examine the reaction of ureas with di-2-pyridyl sulfite. Surprisingly, the reaction of *N,N'*-di-*tert*-butylurea with an equimolar amount of DPS in toluene at 80 °C did not yield *N,N'*-di-*tert*-butylcarbodiimide. Instead the product showing a strong IR absorption at 1785 cm^{-1} was isolated in 32% yield. Based on ^{13}C NMR data as well as ^1H NMR and mass spectral data,³ it seems reasonable to assign the product into a new 4-membered heterocyclic compound, 2,4-di-*tert*-butyl-2,4-thiadiazetid-1-oxide-3-one, as shown in Eq. 1.



Although 1,2,4-thiadiazetid-1-oxide-3-ones were once reported as reactive intermediates in exchange reaction of *N*-sulfinylamine with isocyanate,^{4,5} their preparation and structure determination have not been reported.

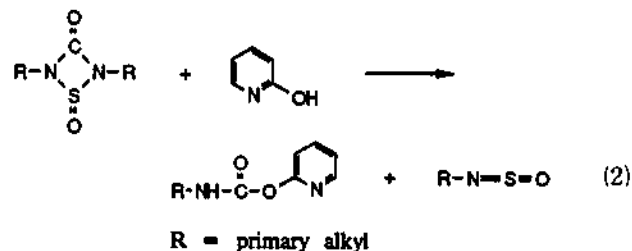
The preparation of 1,2,4-thiadiazetid-1-oxide-3-ones was performed on several structurally different *N,N'*-disubstituted ureas using 1.1 equiv of DPS in toluene at 80 °C and some of experimental results are shown in Table 1. The reaction occurred cleanly and was complete within 30 min. However, the products turned out to be very hygroscopic and unstable. Thus, the products were isolated by passing through a short column of silica gel to remove 2-hydroxypyridine but the products were decomposed to significant extent during isolation. Particularly, the products from *N,N'*-diphenylurea and *N*-phenyl-*N'*-cyclohexylurea were too unstable to be isolated. When *N,N'*-di-*n*-butylurea was treated with di-2-pyridyl sulfite in toluene at 80 °C for 20 min, 20% of 2,4-di-*n*-butyl-1,2,4-thiadiazetid-1-oxide-3-one was isolated together with 22% of 2-pyridyl carbamate. Furthermore, only 2-pyridyl carbamate was obtain-

Table 1. Preparation of 1,2,4-Thiadiazetid-1-oxide-3-ones from *N,N'*-Disubstituted Ureas with DPS^a

R	R'	time, h	isolated yield, %
C ₆ H ₅	(CH ₃) ₃ C	0.5	55
(CH ₃) ₃ C	(CH ₃) ₃ C	0.5	32
CH ₃ CH ₂ CH(CH ₃) ₂	CH ₃ CH ₂ CH(CH ₃) ₂	0.5	33
<i>c</i> -C ₆ H ₁₁	(CH ₃) ₃ C	0.3	71
<i>c</i> -C ₆ H ₁₁	<i>c</i> -C ₆ H ₁₁	0.5	37
<i>c</i> -C ₆ H ₁₁	CH ₃ (CH ₂) ₂ CH ₂	0.5	22
CH ₃ (CH ₂) ₂ CH ₂	CH ₃ (CH ₂) ₂ CH ₂	0.3	20(22) ^b
		1	0(65) ^b
C ₆ H ₅ CH ₂ CH ₂	C ₆ H ₅ CH ₂ CH ₂	1	0(73) ^b

^a 1.1 equiv of DPS was used. ^b Isolated yield of 2-pyridyl carbamate.

ed in 1h, indicating ring-opening by 2-hydroxypyridine, as shown in Eq. 2. Similar results were realized with *N,N'*-diphenylurea.



The typical procedure is illustrated as follows. Di-2-pyridyl sulfite (520 mg, 2.2 mmol) was added to a solution of *N,N'*-di-*tert*-butylurea (345 mg, 2.0 mmol) in toluene (6 ml). After being stirred at 80 °C for 0.5 h under nitrogen, the reaction mixture was allowed to cool to room temperature and concentrated to dryness. The residue was immediately subjected to short column chromatography with hexane and ethyl acetate (6:1) as an eluant, yielding the product (140 mg) in 32% yield.

Acknowledgement. Support of our work by Korea Science and Engineering Foundation is gratefully acknowledged.

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- ^{13}C NMR (CDCl₃) δ 28.3, 55.8, 150.1; ^1H NMR (CDCl₃) δ 1.60(s), Mass *m/e*, 218, 147, 119, 104, 84, 71.
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