s-Triazolo-*N*-oxides from Sulphimides and Nitrile Oxides. Valence Tautomerism of 5,7-Dimethyl-2-*p*-tolyl-*s*-triazolo[1,5-*a*]pyrimidine 1-Oxide

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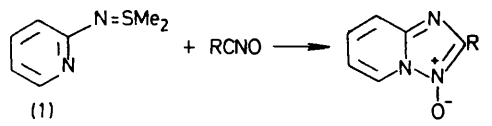
Summary The pyrido-, pyrimidino-, and amidino-sulphimides (**1**)—(**3**) react with nitrile oxides at room temperature to give the *s*-triazolo-*N*-oxides (**4**)—(**6**); the *N*-oxide (**5c**) undergoes a reversible, degenerate valence tautomerism at 90—110°.

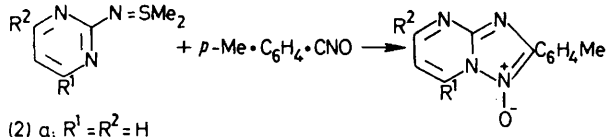
1,2,4-BENZOXADIAZINES are the products of the reaction between *N*-aryl-*SS*-dimethylsulphimides and *p*-toluonitrile oxide.[1] *SS*-Dimethylsulphimides (**1**)—(**3**) derived from 2-aminopyridine, 2-aminopyrimidines, and 1,2-diphenylamidine also react readily with *p*-toluonitrile oxide and with other nitrile oxides, but here the products are *s*-triazolo-*N*-oxides (**4**)—(**6**).

The sulphimides were prepared by reaction of the amines with t-butyl hypochlorite at −60°, followed by treatment with dimethyl sulphide and sodium methoxide.[2] The pyrido- and pyrimidino-sulphimides were used directly without further purification; the more stable amidine derivative (**3**), m.p. 167—169°, was recrystallised from pentane–dichloromethane.

The sulphimide (**1**) reacted readily with *p*-toluonitrile oxide to give 2-*p*-tolyl-*s*-triazolo[1,5-*a*]pyridine 3-oxide (**4a**) (70%), m.p. 161—162°. The structure of the product was supported by its ready deoxygenation with phosphorus trichloride to 2-*p*-tolyl-*s*-triazolo[1,5-*a*]pyridine (90%), m.p. and mixed m.p. 168—169° (lit.,[3] 173°), and by its

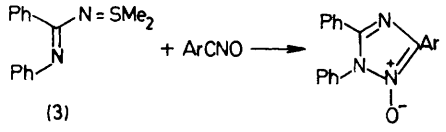


(1) (4) a; R = p-MeC_6H_4
b; R = CO_2Et



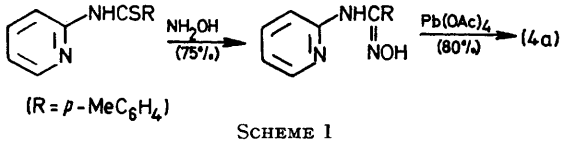
(2) a; $R^1 = R^2 = H$
b; $R^1 = H$, $R^2 = Me$
c; $R^1 = R^2 = Me$

(5)



(3) (6) a; Ar = p-Me C_6H_4
b; Ar = Ph

independent synthesis by the route outlined in Scheme 1. Similarly, 2-ethoxycarbonyl-*s*-triazolo[1,5-*a*]pyridine 3-oxide (**4b**) (37%), m.p. 143—144°, was formed from the sulphimide (**1**) and ethyl chloroglyoxylate 2-oxime[4] in the presence of triethylamine.

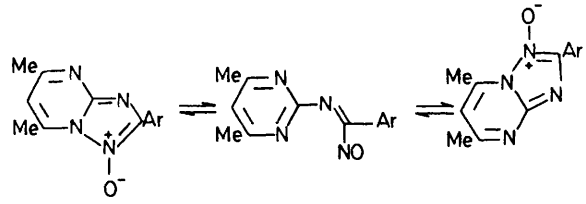


(R = p-MeC_6H_4)

SCHEME 1

The synthesis of this hitherto unknown class of *N*-oxides was extended to the pyrimidine derivatives (**5a**) [(50%), m.p. 202—204°], (**5b**)[(50%), m.p. 228—229°], and (**5c**) [(45%), m.p. 184—185°]. Only one isomer (**5b**) of the two possible, was obtained from the sulphimide (**2b**). The monocyclic 1,2,4-triazole 2-oxides (**6a**) [(20%), m.p. 260°] and [(**6b**) (30%), m.p. 252°] were prepared in the same way. The structure of 1,3,5-triphenyl-1,2,4-triazole-2-oxide (**6b**) was supported by its deoxygenation with phosphorus trichloride to 1,3,5-triphenyl-1,2,4-triazole, m.p. 104—105°, which was identified by comparison with an authentic specimen.[5]

The *N*-oxides (**4a**) and (**5**) are slowly deoxygenated by heating in xylene. The dimethyl derivative (**5c**) was found



(5c)

SCHEME 2

to have a temperature-dependent n.m.r. spectrum; the singlets at τ 7·45 and 6·76 assigned to the methyl groups on the pyrimidine ring broadened when (**5c**) in dichlorobenzene was heated above 90°, and collapsed to a singlet (τ7·10) above 110°.† The original spectrum reappeared when the solution was cooled. The change in the spectrum is attributed to a reversible valence tautomerism (Scheme 2) involving a nitrosoimine tautomer as intermediate.

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† $\Delta G^{\ddagger}$ for the process is calculated as 85 ± 10 kJ mol^{-1}.

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