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INTRAMOLECULAR CYCLIZATION OF N-SULFONYL SUBSTITUTED α-BROMOAMIDINES AND GUANIDINES

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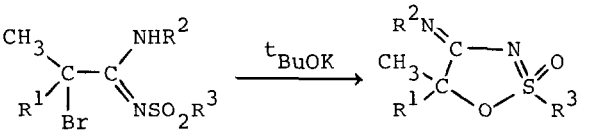
4-Imino-4,5-dihydro-1,2λ^6,3-oxathiazol-2-ones have recently been obtained from the reaction of ketenimines with methanesulfonyl azide.[1] We now wish to report a second approach to this new ring system.

Thus, when α-bromoamidine 1a (mp 85-86°)[2] was treated with two equiv of potassium tert-butoxide in ether at 0°C for 2 h, a compound (mp 67-68°) was obtained in 83% yield which gave spectral data and elemental analysis consistent with structure 2a. The IR spectrum (KBr) shows strong absorptions at 1685, 1650 (doublet, C=N)



1 2

a: R^1 = Me, R^2 = ^{t}Bu, R^3 = Ph

b: R^1 = Me, R^2 = p-$CH_3C_6H_4$, R^3 = Me

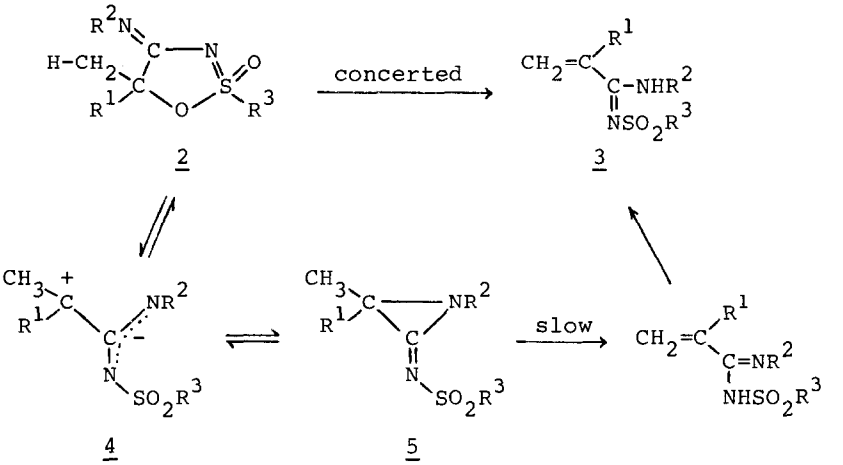
c: R^1 = H, R^2 = ^{t}Bu, R^3 = Ph

and 1050 cm^{-1} (S=O). In the ^{1}H NMR spectrum ($CDCl_3$) the two methyl groups are non-equivalent (at δ 1.52 and 1.7) due to the anisotropic effect of the sulfinyl function. The ring carbon absorptions in the ^{13}C NMR spectrum ($CDCl_3$) are found at δ 96.4 (C^5) and 158.6 (C^4). The mass spectrum exhibits a weak molecular ion peak (5%) and fragment peaks at m/e 222 (7%, $M^{\cdot+}$ - Me_2CO), 141 (90%, $PhSO_2^+$), 125 (50%, $Me_2C{=}C{=}NBu^{t\cdot+}$) and 77 (100%, Ph^+).

Similarly, 1b (mp 128-129°) and 1c (mp 83-84°) reacted with ^{t}BuOK in ether at 0°C to afford respectively 2b (40%, mp 96-97°) and 2c (50%, colourless oil). Compound

2b was identical in all respects with an authentic sample prepared from dimethyl-N-tolylketenimine and methanesulfonyl azide.[1] The ^{1}H NMR spectrum ($CDCl_3$) of 2c shows the presence of an erythro-threo mixture with two doublets at δ 1.42 and 1.6 and two quartets at δ 4.96 and 5.12 ppm. The mixture could not be separated into the two diastereoisomers because it decomposed in solution even at 20°.

The oxathiazolines 2a,b isomerize smoothly and quantitatively into the acrylic amidines 3a,b on warming. Two mechanisms can be considered for this isomerization: (i) a concerted 1,7-hydrogen shift, and (ii) the intermediate formation of dipole 4 in steady-state equilibrium with 2. Dipole 4 subsequently undergoes ring closure and 1,5-sigmatropic hydrogen shift into the amidines. A kinetic study of



2 3 4 5

the thermolysis of 2a was carried out in several solvents. The relative amounts of 2a and 3a during the reaction were estimated from the ^{1}H NMR spectra by integration of the CH_3 and/or ^{t}Bu proton signals. The reactions were strictly first-order and the rate constants are summarized in Table 1. The experiments in benzene-d_6 were also carried out at different temperatures giving the following activation parameters: E_a = 16.3 kcal/mol and $\Delta S^{\neq}$ = -32 e.u.

Since the dipole moment of 2 is smaller than that of 3 (3.6 and 5.0 D for 2b and 3b respectively, determined in benzene), for the concerted mechanism we may expect a small increase in rate constant as the polarity of the solvent increases. This, however, was not found when benzene was substituted for acetonitrile or dimethyl sulfoxide. The rate acceleration observed in chloroform does not fit the general trend but is indeed reproducible. If, on the contrary, the isomerization proceeds in a stepwise manner via decomposition of 5 in the rate-determining step, we may

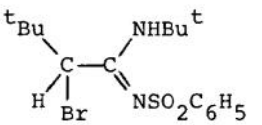
Table 1. Kinetics for the isomerization 2a → 3a

Solvent[a]	Temp, °C	10^5 k_1 (sec^{-1})
C_6D_6	55	2.88
	61	4.25
	69	8.21
	74.5	11.7
$CDCl_3$	60	11
CD_3CN	60	4.95
DMSO-d_6	60	1.45

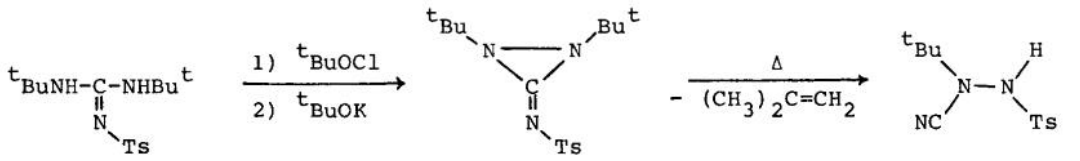
[a] The solvents were treated with alumina in order to avoid acid-catalyzed isomerization

expect a similar kinetic behaviour to that reported by Quast (autocatalytic reaction!).[3] This was not found to be the case so that no definite conclusion can be drawn on the mechanism at the present time.

Attempts to synthesize the desired sulfonyl substituted aziridinimines (e.g. 5) were unsuccessful. For instance, 6 proved to be unreactive towards ^{t}BuOK or lithium 2,2,6,6-tetramethylpiperidide.[4] This contrasts sharply with the isolation of the tosyl substituted diaziridinimine 8 (mp 80-81°) in 85% yield from the guanidine 7[5] as shown below.



6



7 8 9

Compound 8 possesses an IR spectrum (KBr) with absorptions at 1750 (broad s, C=N), 1320 and 1160 cm^{-1} (SO_2), while the ^{1}H NMR spectrum ($CDCl_3$) indicates the presence of one broad tert-butyl signal at δ 1.25 ppm.[6] The presence of two identical tert-butyl substituents is also apparent from the ^{13}C NMR spectrum (resonances at

δ 26.8 and 62.1 ppm). The ring carbon atom is found at δ 157.9 ppm. The mass spectrum of 8 features peaks at m/e 323 (2%, $M^{\cdot+}$), 267 (20%, $M^{\cdot+}$ - $Me_2C{=}CH_2$), 211 (6%, $M^{\cdot+}$ - 2 $Me_2C{=}CH_2$), 168 (60%), 155 (34%, Ts^+) and 91 (90%, $CH_3C_6H_4^+$). Thermolysis of 8 in boiling toluene for 5 h yielded the hydrazine 9 as white needles (mp 176-177°) in 58% yield. The formation of this compound is interpreted in terms of fragmentation[7] of 8 into $^tBuN{=}NH$ and TsNC with elimination of isobutene. The tosyl isonitrile[8] then rearranges to the more stable nitrile and adds to the azo compound, yielding 9.

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2. The starting materials 1a-c were prepared from the corresponding N-sulfonyl substituted α-bromoamides by treatment with PCl_5 and then with primary amines, analogous to the procedures described by J. v. Braun and W. Rudolph, Ber., 67, 1762 (1934).
3. H. Quast and P. Schäfer, Tetrahedron Lett., 1057 (1977).
4. R. A. Olofson and C. M. Dougherty, J. Am. Chem. Soc., 95, 581 (1973).
5. W. V. Farrar, J. Chem. Soc., 856 (1965).
6. At lower temp. (-6°) the tert-butyl groups become magnetically non-equivalent and give rise to two singlets. This is due to restricted isomerization at the C=N double bond, see also ref. 7.
7. H. Quast and E. Schmitt, Angew. Chem., 81, 428 (1969); Angew. Chem. Int. Ed. Engl., 8, 448 (1969).
8. Sulfonyl isonitriles are unknown but N-acyl and N-imidoyl substituted isonitriles have recently been prepared, see G. Höfle and B. Lange, Angew. Chem., 89, 272 and 742 (1977); Angew. Chem. Int. Ed. Engl., 16, 262 and 727 (1977).

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