formation of axial product, suggested a stereoelectronic requirement for the rearrangement.[9,10] Only in example d was a product arising from a [1,2] shift detected.[11]

We envisage extension of the above methodology by utilization of the metalated *N*-cyanoalkyl function as an acyl carbanion equivalent[12] and work is in progress; *e.g.*, example d simply carried out in DMSO-d_6 afforded α-[^{2}H]tolualdehyde [deuterium enrichment >95%; ν_{max} 2050, 1675 cm^{-1} (-C^{2}H=O)].[13]

Preparation of Pyrrolidinium Salts.—(a) Allylic bromide (10^{-3} mol) was added dropwise to a stirred solution of *N*-cyanomethylpyrrolidine (1.07×10^{-3} mol) in DMSO (3 ml) at ambient temperature under an atmosphere of nitrogen. Completion of salt formation (from 1.0 hr at 20° to 18 hr at 45°) was monitored by nmr spectroscopy. (b) Allylic amine (10^{-3} mol) in DMSO (3 ml) was treated with chloracetonitrile (1.01×10^{-3} mol) under a nitrogen atmosphere and the mixture stirred at 45° for 18 hr.

Ylide Formation and Rearrangement.—A solution of the salt (10^{-3} mol) in DMSO (3 ml) was diluted with dry THF (15 ml) cooled to −10° and treated with solid KO-*t*-Bu (1.25×10^{-3} mol). The reaction mixture was stirred for 3 hr, diluted with hexane (40 ml), washed with brine and water, and dried (Na_2SO_4). Removal of solvent gave rearranged amine.

Hydrolysis of α-Pyrrolidinonitriles.—The nitrile (10^{-3} mol) in THF (8 ml) was treated with a warm solution of oxalic acid (30% w:v, 8 ml); the two-phase mixture was heated under reflux for 0.25 hr, cooled, and extracted with hexane (40 ml). The hexane solution was washed with brine and water, dried (Na_2SO_4), and reduced to dryness to afford a mixture of aldehydes.

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[9] The Claisen rearrangement of 4-*tert*-butyl-1-cyclohexenylmethyl vinyl ether affords only the axial product: Professor R. E. Ireland, personal communication. Presumably, the transition state for the Claisen rearrangement, with its higher activation energy, is structured more like product; *cf.* R. F. Church, R. E. Ireland, and J. A. Marshall, *J. Org. Chem.*, **27**, 1118 (1962).

[10] S. Mageswaran, W. D. Ollis, I. O. Sutherland, and Y. Thebtaranonth, *Chem. Commun.*, 1494 (1971).

[11] S. H. Pine, *Org. React.*, **18**, 403 (1970).

[12] (a) D. Seebach, *Angew. Chem, Int. Ed. Engl.*, **8**, 639 (1969); (b) G. Stork and L. Maldonado, *J. Amer. Chem. Soc.*, **93**, 5286 (1971).

[13] D. J. Bennett, G. W. Kirby, and V. A. Moss, *Chem. Commun.*, 218 (1967).

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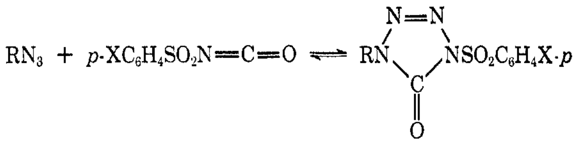
1,3-Dipolar Cycloadditions of Alkyl Azides with Sulfonyl Isothiocyanates. A Synthetic Method for 1,2,3,4-Thiatriazolines

Summary: 4-Alkyl-5-sulfonylimino-Δ^2-1,2,3,4-thiatriazolines (**2**) are readily prepared from alkyl azides and sulfonyl isothiocyanates. Upon thermolysis, they give rise to a novel type of external stabilized 1,3 dipole (**6**) which undergoes cycloaddition with enamines and ynamines.

Sir: We recently reported[1] that alkyl azides and aryl azides reacted with sulfonyl isocyanates to give 1-alkyl- (or aryl-) 4-sulfonyl-Δ^2-tetrazolin-5-ones (**1**).



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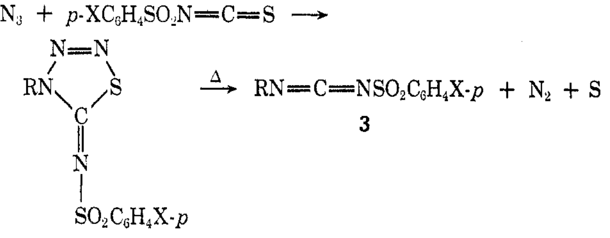
These compounds underwent cycloreversion on thermolysis. Extension of this study to isothiocyanates has led to the observation of a different behavior which we report briefly at this time. *n*-Butyl azide or benzyl azide reacted readily with equimolar amounts of sulfonyl isothiocyanates[2] at room temperature to yield 1:1 adducts in 50–75% yield which were characterized as 4-alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines (**2**).

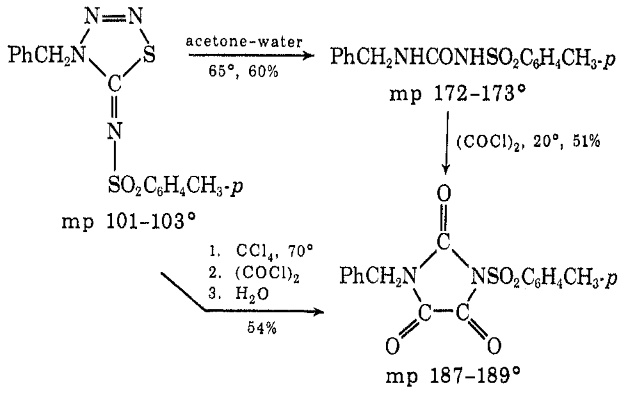


2

R = *n*-Bu, PhCH$_2$; X = H, CH$_3$, Cl

The structures **2** are consistent with analysis, nmr, ir (C=N at 1510–1535 cm^{-1}),[3] mass spectra (M·$^+$, M·$^+$ − N$_2$, M·$^+$ − N$_2$ − S), and degradation experiments. Thus, thermal decomposition of **2** at a moderate temperature (45–80°) furnished the carbodiimides **3** which exhibited a characteristic ir absorption band[4] at 2160 cm^{-1}. The latter were also trapped by typical reagents[5] as illustrated in Scheme I. That the isolated products **2** could not be formulated as the C=N adducts (*i.e.*, **5**) is clear from this chemical evidence. Indeed, the isomeric compounds **5**, prepared in 50–80% yield by sulfonation of 1-benzyl- (or butyl-)

SCHEME I



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[1] J.-M. Vandensavel, G. Smets, and G. L'abbé, *J. Org. Chem.*, **38**, 675 (1973).

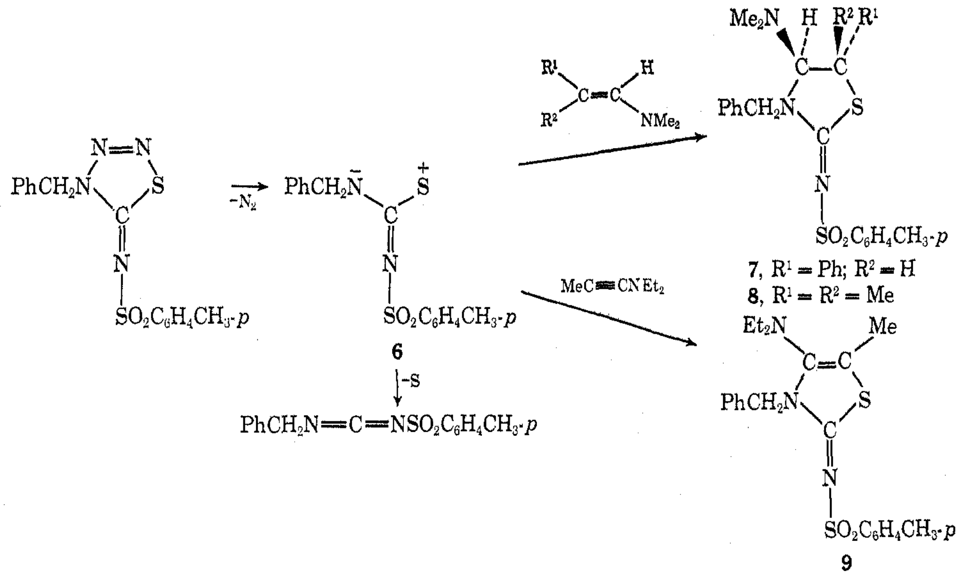
[2] K. Hartke, *Arch. Pharm. (Weinheim)*, **299**, 174 (1966).

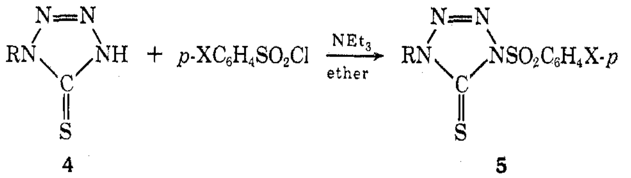
[3] J. Goerdeler and U. Krone, *Chem. Ber.*, **102**, 2273 (1969).

[4] R. Neidlein and E. Heukelbach, *Arch. Pharm. (Weinheim)*, **299**, 944 (1966); H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Tetrahedron*, **22**, 1565 (1966).

[5] H. G. Khorana, *Chem. Rev.*, **53**, 145 (1953); F. Kurzer and K. D. Zadeh, *ibid.*, **67**, 107 (1967).

SCHEME II





R = n-Bu or $PhCH_2$; X = H, CH_3 or Cl

Δ^2-tetrazoline-5-thiones (4),[6] showed different physical and spectroscopic characteristics and a much higher thermal stability.

It is reasonable to assume that an external stabilized 1,3 dipole (*e.g.*, **6**) is the intermediate in the thermal conversion of **2** to **3**. This has been confirmed by carrying out the decomposition of 4-benzyl-5-tosylimino-Δ^2-1,2,3,4-thiatriazoline in the presence of electron-rich dipolarophiles.[7] Thus, thiazolidine **7** (mp 161–162°) was obtained in 73% yield when **2** (R = $PhCH_2$, X = CH_3) was decomposed in the presence of an equimolar amount of β-*trans*-*N*,*N*-dimethylaminostyrene in CCl_4 at 60°. The structure of **7** was deduced from microanalysis, ir (1530 cm^{-1}),[8] nmr [ring protons at τ 5.55 and 5.68 (J = 2.5 Hz), two nonequivalent benzyl protons at τ 4.72 and 5.81 (J = 14.5 Hz)], and mass spectra ($M\cdot^+$ at m/e 465, $M\cdot^+$ − $HNMe_2$ at m/e 420, and $\text{Ph}\overline{\text{CHC(NMe}_2\text{)HS}}\cdot^+$ at m/e 179). Similarly, when **2** (R = $PhCH_2$, X = CH_3) was heated with an equimolar amount of *N*,*N*-dimethylaminoisobutene in benzene for 3 hr, a 1:1 adduct (mp 132–133°) was obtained in 55% yield, corresponding to structure **8** on the basis of ir (1530 cm^{-1}), nmr [ring proton at τ 6.12, ring methyls at τ 8.66 and 8.77, two nonequivalent benzyl protons at τ 4.55 and 6.08 (J = 14.5 Hz)], and mass spectra ($M\cdot^+$ at m/e 4.17, $M\cdot^+$ − NMe_2, $\text{Me}_2\overline{\text{CC(NMe}_2\text{)HS}}\cdot^+$ at m/e 131). The stereochemistry of **7** was deduced from the C-4–C-5 hydrogen coupling constant (J = 2.5 Hz), whereas the indicated regiochemistry rests upon the observed chemical shift values of the *C*-N and *C*-S absorptions in the ^{13}C nmr spectra of **7** and **8**. (See Scheme II.)

Ynamines also proved to be suitable dipolarophiles for **6**. For instance, when **2** (R = $PhCH_2$, X = CH_3) was heated with 1 equiv of *N*,*N*-diethylaminopropyne in benzene for 4 hr, thiazoline **9** (mp, 118–119°) was obtained (50–60% by nmr, 21% isolated). The adduct exhibited ir (C=N at 1500 cm^{-1}), nmr [benzyl protons at τ 4.90 (s), ring methyl at τ 7.85], and mass spectra ($M\cdot^+$ at 429, $M\cdot^+$ − $PhCH_2$ at m/e 338, $M\cdot^+$ − Tos at m/e 274) consistent with the structure.

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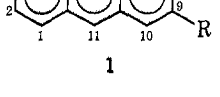
(6) E. Lieber and J. Ramachandran, *Can. J. Chem.*, **37**, 101 (1959).

(7) Preliminary experiments indicate that electron-poor olefins are not suitable dipolarophiles for **6**.

Correlation between Proton Magnetic Resonance Chemical Shift and Rate of Polar Cycloaddition

Summary: A significant correlation has been found between the chemical shifts of the proton at position 6 of 9-substituted acridizinium perchlorates and the log of the ratio of rate constants (k/k^0) for the cycloaddition of 9-substituted acridizinium salts with styrene; the chemical shift data likewise give a significant correlation with Hammett substituent constants.

Sir: It was shown earlier that the rate of cycloaddition of the 9-substituted acridizinium cation (1) with



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