

REACTIONS OF A TETRASUBSTITUTED THIOCARBONYL YLIDE; NEW EVIDENCE
 FOR TWO-STEP CYCLOADDITIONS

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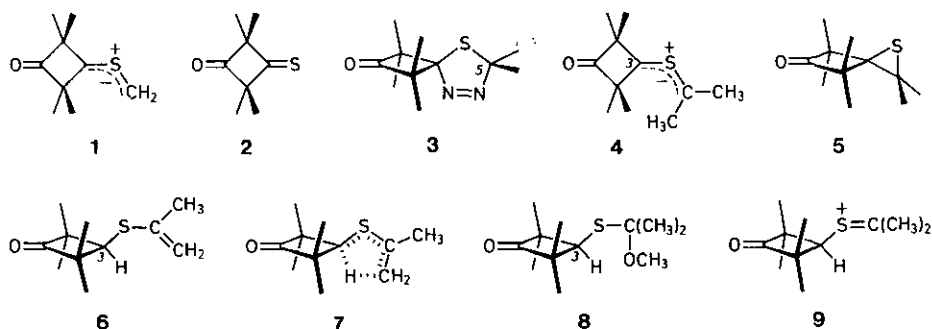
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Dedicated to the memory of Professor Tetsuji Kametani

Abstract - Zwitterionic intermediates from aliphatic thiocarbonyl ylides and tetrasubstituted acceptor olefins can close the 5-membered ring (thiolane) or the 7-membered ring (ketene imine), undergo rotation, and - shown here - furnish cyclopropane and thiirane in an intramolecular nucleophilic substitution.

The 1,3-cycloadditions of 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-methylide (**1**) to highly electron-deficient ethylenes served as models for the two-step mechanism; **1** adds nonstereospecifically to dimethyl 2,3-dicyanofumarate and 2,3-dicyanomaleate.^{2,3} Besides an extreme difference of π -MO energies of 1,3-dipole and dipolarophile, massive steric screening of *one* terminus of the 1,3-dipole was regarded as prerequisite for the two-step mechanism of cycloaddition. What would be the effect of steric hindrance at *both* termini of the 1,3-dipole?

Thione **2** and 2-diazopropane in pentane at 0°C furnished the 1,3,4-thiadiazoline **3** (84%, mp 54-55°C).⁴ With $t_{1/2} = 18$ min in toluene and 37 min in acetonitrile at 70°C, **3** extrudes N₂ slower than the thiadiazoline without the 5-methyl groups.⁵ According to ¹H nmr analysis with standard, the tetrasubstituted thiocarbonyl ylide **4** afforded 38% of thiirane **5** and 33% of the thioenol ether **6** in toluene, and 94% **5** + a trace of

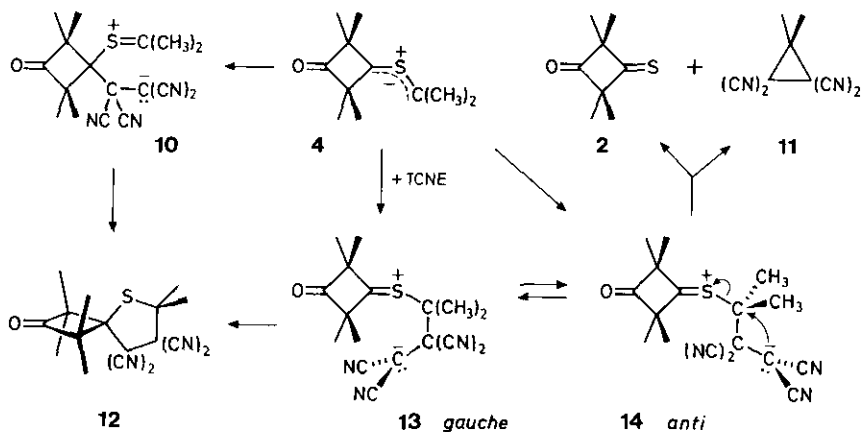


6 in acetonitrile at 70°C. The conrotatory electrocyclozation producing the thiirane 5 appears to pass a more polar transition state than the suprafacial 1,4-shift via 7, both being allowed by the Woodward-Hoffmann rules.

The generation of 4 from 3 in methanol (6 h, 60°C) provided 51% 6 and 37% of the *O,S*-acetal 8, but no thiirane 5. Our guess that the vinyl sulfide 6 is now the result of another pathway which exceeds the sigmatropic reaction via 7 in rate, found support in the behavior of 4 towards CH₃OD at 60°C. The 60:40 ratio of 6 and 8 was unchanged, and the D incorporation in 3-position of the ring amounted to 80% in 6 and 81% in 8; the 3-H compounds 6 and 8 were stable to CH₃OD at 60°C. The lack of an isotope effect in the product ratio suggests the sulfonium ion 9 as the *common intermediate* which either loses a proton or adds CH₃O⁻.

Thiocarbonyl ylides are bases; remarkably, the CH₂ group was the basic center in the thione *S*-methylide 1, and the addition of methanol took place in the *opposite* direction.⁵

The thiirane 5, mp 61-62.5°C, showed three ¹H singlets for three pairs of methyl groups. Separated by thick-layer chromatography, 6 and 8 were liquids. The t at δ_C 107.9 and s at 141.3 (CDCl₃) characterize the olefinic carbons of 6; the CH₃ of the unsaturated C-atom occurs at δ_H 1.97. Three ¹H singlets for 3 x 2 CH₃ groups in 8 leave no doubt, that CH₃O is located in the side chain and 3-H appears as s at δ 3.05.



The interaction of 4 with tetracyanoethylene (1.1 equiv, toluene, 6 h, 60°C) gave rise to 58% of thiolane 12 along with 40% of 3,3-dimethylcyclopropane-1,1,2,2-tetracarbonitrile (11) and 27% of thione 2; the expected equivalence of 11 and 2 was disturbed by the volatility of 2 during work-up. Three s at δ_H 1.42, 1.92, 1.97 for 6 methyl groups reveal the plane of symmetry in 12, mp 174-176°C. Cyclopropane

5% thiirane 5. The cis acceptor olefin 18b is sensitive to bases which establish a cis,trans equilibrium of 5:95.⁸ However, on reacting 3 with 1.1 equiv. of 18b for 1 h at 80°C, the unconsumed 18b did not contain 15b; thus, the formation of 94% cis-cyclopropane 19b and 5% of the trans isomer 16b denoted some nonstereospecificity.

One methyl s at δ_H 1.75 for 16b (mp 52-53°C) and two s at 1.69 and 1.82 for 19b (mp 81-82°C) were in accord with the structures. An ir absorption at 2035 cm^{-1} in the reaction solutions pointed to the ketene imine 21 which was not isolated; ¹⁹F nmr signals at -59.6 and -65.3 with $J_{FF} = 6.4$ Hz were tentatively assigned to 21. The 7-membered ketene imine 22 was the main product in the reactions of 1 with 15b or 18b;⁹ it results from a cyclization of the gauche zwitterion of type 13.

The intramolecular substitution furnishing cyclopropane + thione offers new evidence for the occurrence of zwitterionic intermediates; both this S_N2 type process and thiolane formation are irreversible. The loss of stereochemical integrity in the cycloadditions of 4 with 15 and 18 is smaller than observed for S-methylide 1. It is hard to predict the relative heights of rotational barriers in persubstituted zwitterions of type 13 and 14 in which steric hindrance plays such a dominant role. Stereoretention may be violated in two-step cycloadditions, *but not necessarily*.

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