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STRAINED CYCLIC ACETYLENES, VII [1] ADDITION OF SULFUR AND PYRIDINE-N-OXIDE TO SEVEN MEMBERED CYCLOALKYNES [2]

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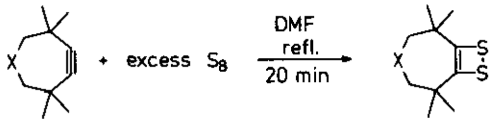
Abstract - The first isolable dialkyl dithietes, 3 and 4, which are not stabilized by strongly electron withdrawing substituents, have been prepared from sulfur and the seven membered cycloalkynes, 1 and 2, respectively. The first 2H-azepine, 9, has been synthesized by reaction of 1 with pyridine-N-oxide, and its structure has been determined by an X-ray analysis. It rearranges on heating to the pyridine derivative 11.

Seven membered cycloalkynes, such as 1 or 2, show an enhanced reactivity in addition reactions of 1,3-dienes, carbon disulfide, phenylazide, isocyanides and nitrones to the strained triple bond compared to open-chain analogs [3-5]. In this paper we report the reactions of 1 and 2 with elemental sulfur, and of 1 with pyridine-N-oxide.

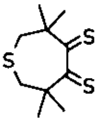
On heating 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne (1) [3] with an excess of elemental sulfur in refluxing dimethylformamide for 20 min 3',3',6',6'-tetramethyl-1'-thiacyclohepteno [4,5-c] dithiete (3) (m.p. 91-91.5°C) was obtained in 77 % yield. From 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne-1,1-dioxide (2) [5] the corresponding dithiete 4 (m.p. 190-190.5 °C, 51 %) can be prepared in an analogous manner.



1 X = S
2 X = SO_2

3 X = S
4 X = SO_2

Evidence for the structures 3 and 4 rests on the elementary analyses, the mass spectra, osmometric molecular weight determinations and particularly on the ^{13}C nmr spectra with peaks at $\delta = 139.3$ (3) and $\delta = 137.7$ ppm (4) for the sp^2 hybridized carbons. This eliminates the dithione structure 5, since the signals for C=S-carbons appear near $\delta = 230$ ppm. The uv spectrum of 3 (isooctane) with maxima at $\lambda (\lg \varepsilon) = 224 (3.88), 273 (2.34)$ and 351 nm (1.75) is also in accord with the spectrum observed for 6[7].



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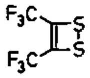

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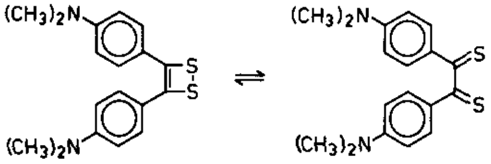
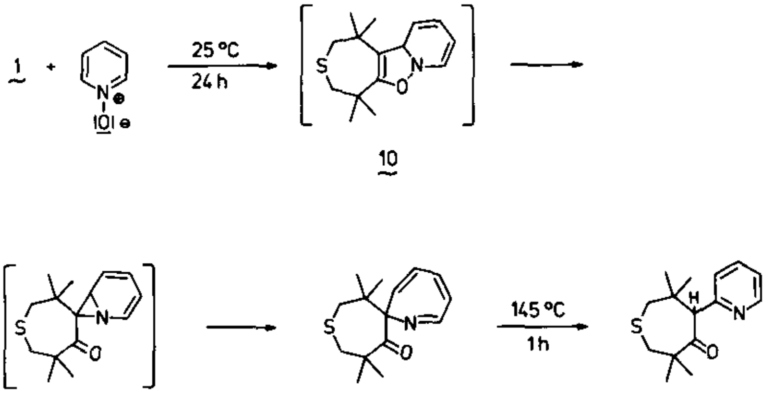


7 8

3 and 4 represent the first examples of isolable alkyl substituted dithietes, which are not stabilized by strongly electron withdrawing groups. Up to now, apart from a benzoannellated system[6], only bis(perfluoroalkyl)dithietes, such as 6, have been isolated[7] and an aryl substituted dithiete 7, has been detected by spectroscopic means in equilibrium with the corresponding dithione 8[8]. Attempts at the isolation of other alkyl substituted dithietes have failed, but two alkyl dithietes have been generated photochemically and observed at 77 K in an organic matrix[9]. According to HMO calculations the substituents $CF_3 \sim CN > CH_3 > N(CH_3)_2$ stabilize the dithiete relative to the corresponding dithione in that order[10]. While dithiooxamide exists only in the dithione form, in 6 only the dithiete form is observed. It is interesting to note that in the alkyl substituted derivatives 3 and 4 only the dithiete form is found; at present it is not known whether the stability of 3 and 4 relative to the corresponding dithiones is due to electronic or steric substituent effects. The facile syntheses of 3 and 4 are another good example to illustrate the exceptional reactivity of these seven membered cycloalkynes and the ability of bulky groups to prevent dimerization.

Pyridine-N-oxide reacts with 1 (25 °C, 24 h, $CHCl_3$ solution) to give the 1:1-adduct 9 (m.p. 145-146 °C, 54 %). The expected 4-isoxazoline structure 10 is excluded by the appearance of a strong carbonyl band in the ir spectrum near

1685 cm^{-1}, and the ^{13}C nmr spectrum with five signals in the olefinic region. Based on the known *rearrangement of 4-isoxazolines to 2-acylaziridines* [11] and a newly observed thermal rearrangement of 9 (145 °C, 1 h) to the pyridine *derivative 11 (m.p. 137 °C, 70 %) the 2H-azepine structure 9 was proposed for* the isolated addition product; indeed, this structure has been confirmed by an *X-ray analysis* [12]. *To the best of our knowledge* 9 is the first 2H-azepine reported in the literature.



10

12 9 11

The formation of 9 can be rationalized by a 1,3 dipolar addition of pyridine-N-oxide to give 10; analogous 4-isoxazolines were isolated in the reactions of 1 with various nitrones [3]. However, an isoxazoline system 10 does not seem to be stable under the reaction conditions and rearranges to 9, possibly via the azanorcaradiene 12. Here the valence isomer 9 is apparently more stable than 12 as is the case with most cycloheptatrienes in comparison with the corresponding norcaradienes [13]. A thermal azepine-pyridine rearrangement has not been reported, but azepine-aniline [14] and cycloheptatriene-benzene [13] rearrangements are known.

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    Crystal data: $C_{15}H_{21}NOS$, space group $P\bar{1}$, $a = 16.114(5)$, $b = 8.720(5)$, $c = 6.271(5)$ Å, $\alpha = 97.73(5)$, $\beta = 108.24(5)$, $\gamma = 114.80(5)^{\circ}$
    $V = 722.7$ Å^3, $Z = 2$, $D_x = 1.210$ gcm^{-3}, refined to $R = 0.070$ for 1064 counter reflections.
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