New 7,8-Dithiabicyclo[4.2.1]non-3-en-9-ones *via* Novel Thermal 1,3-Dipolar [4 + 3] Cycloaddition Reactions of Mesoionic 1,2-Dithiol-4-ones

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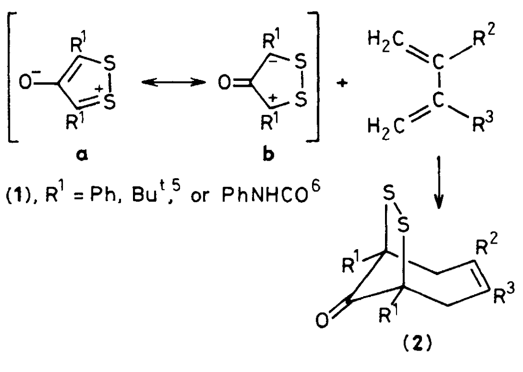
1,2-Dithiolylium-4-olates combine with 1,3-dienes to produce new 7,8-dithiabicyclo[4.2.1]non-3-en-9-one derivatives as a result of a 1,3-dipolar [4 + 3] cycloaddition reaction, whereas the reaction of 3,5-bis(methylthio)-1,2-dithiolylium-4-olate with 2,3-dimethylbuta-1,3-diene affords two isomeric 1 : 2 adducts.

Whereas [3 + 2] cycloaddition reactions of mesoionic 1,3-dithiol-4-ones[1] (type A mesoionic compounds)[2] with multiple bond systems offer synthetically valuable entries to thiophenes[3] or 2,7-dithiabicyclo[2.2.1]heptan-3-one derivatives,[4] there has been no report of cycloaddition reactions of the isomeric mesoionic 1,2-dithiol-4-ones (type B) at the 3,5-position.[2] Herein we report the first 1,3-dipolar [4 + 3] cycloaddition reactions of 1,2-dithiolylium-4-olates (**1**) to 1,3-dienes.

As the limiting formula (**1b**) symbolizes, (**1**) contains in 3,4,5-positions a masked 1,3-dipole which formally corresponds to an allyl cation with additional external negative charge stabilization. Since the signs of the frontier molecular orbital coefficients at the reaction centres of (**1**) and 1,3-dienes match correctly, (**1**) should be capable of 1,3-dipolar [4 + 3] cycloaddition to 1,3-dienes according to a $[_{\pi}4_s + {}_{\pi}2_s]$ process.

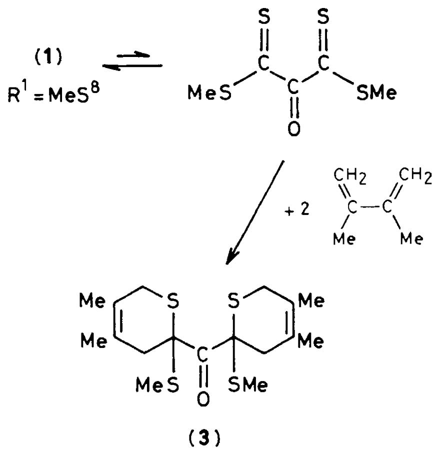


Scheme 1

Table 1. 7,8-Dithiabicyclo[4.2.1]non-3-en-9-ones (**2**) from (**1**) and 1,3-dienes.

(2)	R^1	R^2	R^3	% Yield	M.p. (t/°C)
a	Ph	Me	Me	71	118—120
b	Ph	Me	H	34	80—83
c	Ph	$-[CH_2]_4-$		66	120—121
d	Bu^t	Me	Me	72	90—92
e	Bu^t	Ph	H	47	107—108
f	Bu^t	$-[CH_2]_4-$		81	91—92
g	PhNHCO	Me	Me	76	162—165
h	PhNHCO	$-[CH_2]_4-$		80	162—170[a]

[a] Decomp.



Scheme 2

When 3,5-diphenyl-1,2-dithiolylium-4-olate (**1**, R^1 = Ph)[7] was heated in toluene (110 °C) with 2,3-dimethylbuta-1,3-diene until the violet colour of (**1**) disappeared, crystallization from ether afforded a 71% yield of the pale yellow 7,8-dithiabicyclo[4.2.1]non-3-en-9-one derivative (**2a**): i.r. ν(C=O) 1720, ν(C=C) 1680 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 8.46—7.27 (10 H, m), 3.57 and 3.15 (4 H, 2 d, *J* 15.0 Hz), and 1.88 (6 H, s); *m/z* 352 (M^+). In a similar manner, the new 7,8-dithiabicyclo[4.2.1]nonenones (**2b**—**h**) (Table 1) were synthesized and their constitutions established by elemental analyses and spectroscopic data.

However, the reaction of the bismethylthio compound (**1**, R^1 = MeS)[8] with 2,3-dimethylbuta-1,3-diene did not lead to the expected [4 + 3] cycloadduct, but surprisingly proceeded with formation of a mixture of the stereoisomeric 1 : 2 adducts (**3**), m.p. 129—130 °C, yield 35%: i.r. ν(C=O) 1640 cm^{-1}; ^1H n.m.r. (C_6H_6) δ 3.77—2.42 (8 H, m), 1.80 (6 H, s), 1.56 and 1.46 (12 H, 2 s); *m/z* 374 (M^+); and m.p. 96—98 °C, yield 31%: i.r. ν(C=O) 1645 cm^{-1}; ^1H n.m.r. (C_6H_6) δ 3.83—2.32 (8 H, m), 1.90 (6 H, s), 1.56, and 1.46 (12 H, 2 s); *m/z* 374.† This result may be explained by [4 + 2] cycloadditions of the diene to a valence tautomer of (**1**), as outlined in Scheme 2.

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† Both isomers gave satisfactory microanalytical data.

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