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LETTERS

Tandem 1,3-dipolar cycloaddition of mesoionic 2,4-diphenyl-1,3-oxathiolium-5-olate with cycloocta-1,5-diene. A new synthesis of the tetracyclo[6.2.0.0^{4,10}.0^{5,9}]decane ring system

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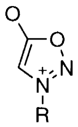
Abstract

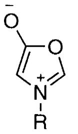
The mesoionic heterocycle 2,4-diphenyl-1,3-oxathiolium-5-olate (**5**) undergoes a tandem 1,3-dipolar cycloaddition reaction with cycloocta-1,5-diene (**6**) to give cycloadduct sulfide **7** in modest yield. Oxidation to sulfone **8** and photochemical extrusion of SO_2 affords 9,10-diphenyltetracyclo[6.2.0.0^{4,10}.0^{5,9}]decane (**9**) in high yield. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: 1,3-oxathiolium-5-olate; mesoionic; 1,3-dipolar cycloaddition; tetracyclo[6.2.0.0^{4,10}.0^{5,9}]decane.

1,3-Dipolar cycloaddition reactions of mesoionic heterocycles, such as sydnones **1** (1,2,3-oxadiazolium-5-olates), münchnones **2** (1,3-oxazolium-5-olates), isomünchnones **3** (1,3-oxazolium-4-olates), thioisomünchnones **4** (1,3-thiazolium-4-olates) and related conjugated heterocyclic mesomeric betaines,[1] have seen a resurgence of applications to synthesis.[2,3]



1



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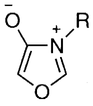

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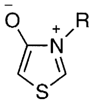

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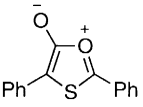

5

In continuation of our interest in 1,3-dipolar cycloaddition reactions of sydnones and münchnones with cyclic dienes[4] and nitro-substituted heterocycles,[5] we now report that 2,4-diphenyl-1,3-oxathiolium-5-olate (**5**), a mesoionic heterocycle that has been neglected since its original generation and trapping (with dimethyl acetylenedicarboxylate),[6] undergoes a tandem 1,3-dipolar cycloaddition reaction with cycloocta-1,5-diene (**6**) to afford 9,11-diphenyl-10-thiatetracyclo[6.3.0.0^{4,11}.0^{5,9}]undecane (**7**) in 32%

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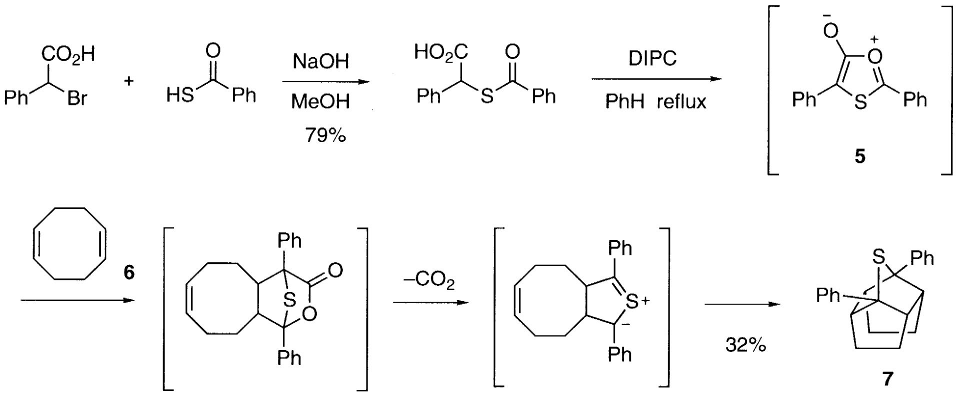
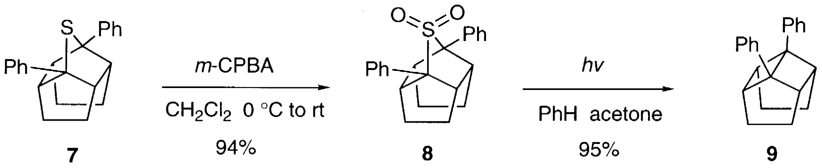
yield after column chromatography (Scheme 1). Mesoionic **5** was generated in situ from *S*-benzoyl-α-phenylthioglycolic acid[6] and diisopropylcarbodiimide (DIPC), conditions that we have used previously to generate münchnones.[4b,5] Cycloadduct **7** was fully characterized.[7,8]



Scheme 1.

The facile photochemical elimination of sulfur dioxide from benzylic sulfones[9] suggested to us that the sulfone **8** derived from **7** might undergo a similar extrusion of SO_2 to form 9,10-diphenyltetracyclo[6.2.0.0^{4,10}.0^{5,9}]decane (**9**). Indeed, as shown in Scheme 2 this sequence has been realized. Treatment of sulfide **7** with *m*-chloroperbenzoic acid (*m*-CPBA)[10] gave sulfone **8** in 94% yield.[11] After some experimentation[12] it was found that photolysis of sulfone **8** in 1:1 benzene–acetone (350 W Hanovia medium pressure lamp, pyrex filter, 2 h) gave the desired hydrocarbon **9** (mp 105–105.5°C) in 95% yield.[13] The identity of **9** was confirmed by comparison with a known sample, prepared by photolysis of **6** and diphenylacetylene to give **9** (mp 105–106°C) in 48% yield.[14] The two samples were identical by IR and ^1H and ^{13}C NMR spectroscopy.



Scheme 2.

Along the lines of our previous work involving the 1,3-dipolar cycloaddition reaction of münchnones with cyclooctatetraene (COT),[4b] we are currently examining the reaction of COT with 1,3-oxathiolium-5-olate **5** as a route to the pentaprismane ring system. Also, efforts to extend this chemistry to additional reactions of 1,3-oxathiolium-5-olates and other mesoionic heterocycles are in progress.

In conclusion, we have shown that the mesoionic heterocycle 2,4-diphenyl-1,3-oxathiolium-5-olate (**5**) undergoes a tandem 1,3-dipolar cycloaddition reaction with cycloocta-1,5-diene to form cycloadduct **7**. This sulfide is easily transformed by oxidation and photochemical extrusion of SO_2 to caged hydrocarbon **9** in high yield.

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7. Compound **7**: Mp 171–171.5°C; ^{1}H NMR (CD_2Cl_2) δ 7.6 (m, 4H), 7.35 (m, 4H), 7.25 (m, 2H), 3.0 (bs, 4H), 1.8–1.6 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 139.1, 128.5, 127.3, 127.1, 72.6, 52.3, 24.2; MS m/z 318 (M^+), 285, 249, 236, 182 (100%), 171, 141, 115, 91, 77; HRMS m/z calcd for $C_{22}H_{22}S$ (M^+) 318.1442, found 318.1436. Anal. calcd for $C_{22}H_{22}S$: C, 82.97; H, 6.96; S, 10.07. Found: C, 82.74; H, 7.02; S, 10.16.
8. Although an X-ray crystal structure determination indicated the correctness of **7**, the crystals were insidiously twinned and an R value that was acceptable for publication could not be obtained (unpublished results with Dr. Marianne P. Byrn).
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11. Compound **8**: Mp (under N_2) 329–330°C; IR (KBr) 1495, 1445, 1293, 1140, 761, 615, 579 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.64 (m, 4H), 7.45 (m, 6H), 3.40 (bs, 4H), 2.14 (bd, J=9.3 Hz, 4H), 1.67 (bd, J=10 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 129.3, 128.9, 128.7, 127.8, 72.2, 43.9, 22.9; uv (EtOH) λ_{max} (ε) 288 (15,000), 256 (530), 262 (590), 263 (510) nm; MS m/z 350, 286, 229, 215, 178, 165, 143 (100%), 128, 77; HRMS m/z calcd for $C_{22}H_{22}SO_2$ (M^+) 350.1341, found 350.1345. Anal. calcd for $C_{22}H_{22}O_2S$: C, 75.40; H, 6.33; S, 9.15. Found: C, 75.12; H, 6.28; S, 8.88.

12. For example, photolysis of **8** in neat benzene, neat acetone, or 4:1 benzene–acetone gave lower yields of **9**, or failed all together (benzene). Sensitizers with smaller triplet state energies than acetone (i.e., acridine, fluorenone, benzophenone, and xanthone) failed to extrude SO_2 from **8** when photolyzed in benzene solution.
13. Compound **9**: Mp 105–105.5°C (lit.[14] mp 105.5–106.5°C); ^{1}H NMR ($CDCl_3$) δ 7.22 (tt, J=1.5 and 7.6 Hz, 4H), 7.1 (tt, J=1.2 and 7.3 Hz, 2H), 7.02 (dt, J=1 and 7.6 Hz, 4H), 3.1 (bd, J=3 Hz, 4H), 2.1 (d, J=9 Hz, 4H), 1.8 (bd, J=9 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 142.7, 128.1, 126.7, 125.6, 61.3, 44.8, 27.3.
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