Pergamon

Tetrahedron Letters 44 (2003) 6709–6711

TETRAHEDRON
LETTERS

Cycloadditions of N=S functions to cyclopentadienones

Hadjila Chabane,[a] Otto Meth-Cohn,[a,*] Charles W. Rees,[b,*] Andrew J. P. White[b] and
David J. Williams[b]

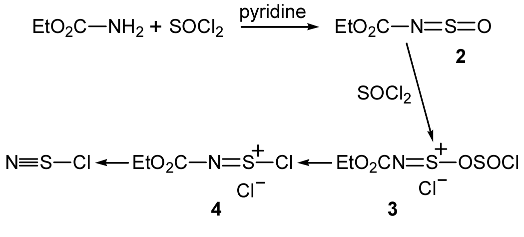
[a]*Chemistry Department, University of Sunderland, Sunderland SR1 3SD, UK*
[b]*Chemistry Department, Imperial College London, London SW7 2AZ, UK*

Received 2 June 2003; revised 20 June 2003; accepted 27 June 2003

Abstract—Cyclopentadienones react with $EtO_2CN{=}S{=}O$ and related N=S reagents to provide ready syntheses of 1,2,5-thiadiazolidines (**8**, **12**, **17**), diaminosulfanes (**11**, **13**), an aminocyclopentenone (**10**) and the first unoxidised 1,2,3-oxathiazolidine (**16**), all in a mechanistically rational manner.

Tetracyclone **1** is the classic reagent for the interception of transient dienophiles, and cyclopentadienones are widely used 4π components in Diels–Alder reactions.[1] However, almost nothing is known of their reactions with N=S containing dienophiles which are known to react effectively with enes and dienes.[2] Tetracyclone is converted into tetraphenylpyrid-2-one **7** by warming with trithiazyl trichloride $(NSCl)_3$, which dissociates into the monomeric thiazyl chloride, NSCl, a highly reactive dienophile;[3] this transformation is achieved quantitatively and much more conveniently[4] if the NSCl is generated in situ from urethane, thionyl chloride and pyridine—the highly effective Katz reagent.[5,6]

We now report a diverse range of reactions of some representative cyclopentadienones **1**, **9** and **15** with Katz reagent, which involves the intermediates **2**, **3** and **4** (Scheme 1), and with preformed EtO_2CNSO **2** and the closely related *N*,*N*′-bis(ethoxycarbonyl) sulfur diimide, $EtO_2C{-}N{=}S{=}N{-}CO_2Et$ (**5**).



Scheme 1.

With Katz reagent in boiling benzene (12 h) tetracyclone **1** gave the pyrid-2-yl carbonate **6** (31%) and thence the pyridone **7** (37%) but in boiling toluene (12 h) it gave **7** quantitatively. However, if the urethane was replaced by EtO_2CNSO **2**, **1** was rapidly converted into **7** (86%) in 3 h at room temperature (rt). There was no reaction with **2** in the absence of thionyl chloride and pyridine even on prolonged heating in toluene, but on addition of pyridine (which catalyses the conversion of **2** into the sulfur diimide **5**[7]) the pyridone **7** is again formed together with a low yield of the formal [3+2] cycloadduct **8** of **1** and **5**. A much higher yield of **8** (81%) was formed directly from **5** in boiling toluene (12 h) and its structure was confirmed by X-ray crystallography.[8] Tetracyclone **1** is thus converted into the pyridone under acidic conditions ($SOCl_2$), and into the cycloadduct **8** under neutral conditions, both in high yield (Scheme 2).

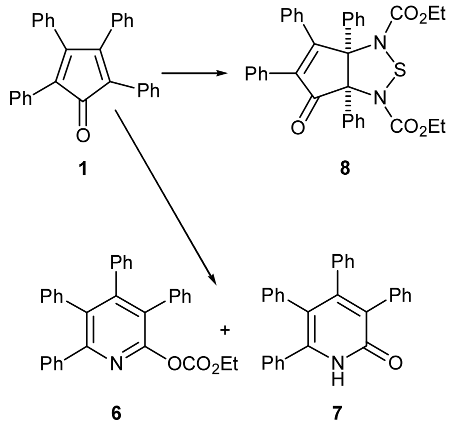
None of the analogous pyridones were formed from the dimethyldiphenyl-cyclopentadienones **9** and **15**. The 3,4-dimethyl compound **9** (Scheme 3) reacted slowly with Katz reagent at rt to give a product shown (Fig. 1) by X-ray crystallography[8,9] to be the primary amine **10** (17%); this yield was increased to 54% by slowly adding $SOCl_2$ to a mixture of all the other reactants. An extra equivalent of urethane was added to the Katz mixture in the hope of generating the sulfur diimide **5** in situ, and this mixture reacted with **9** at rt to give a minor red oil **11** and a major colourless oil **12**.

The cyclopentadienone structure of **11** was confirmed by X-ray crystallography[8] of **13** (Fig. 2), its Diels–Alder adduct with DMAD (Scheme 3). The pattern of bond-

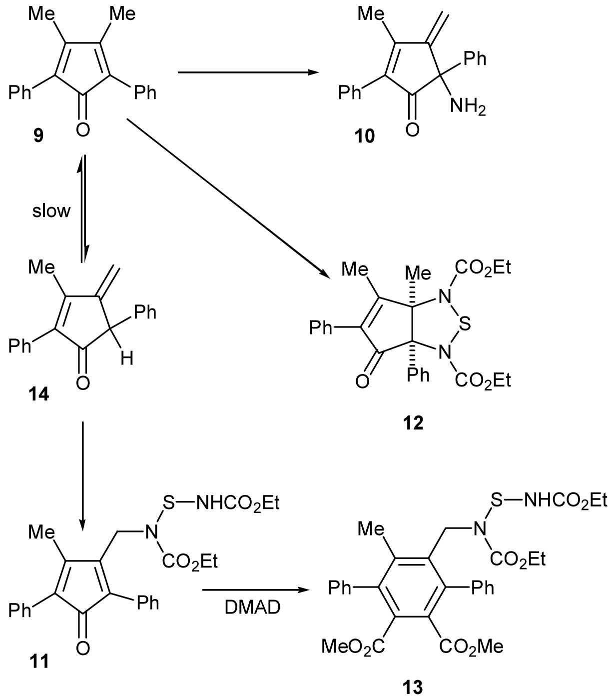
---

* Corresponding authors.

0040-4039/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0040-4039(03)01646-0



Scheme 2.



Scheme 3.

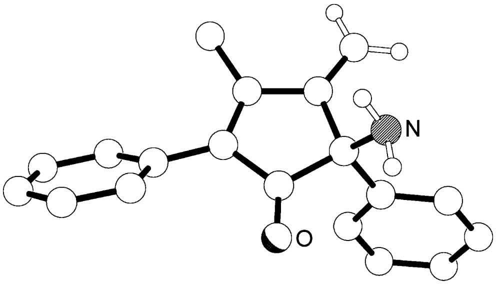


Figure 1. The molecular structure of **10**.

ing within the –$CH_2N(CO_2R)SN(CO_2R)$-fragment is very similar to that observed in the only other structurally characterised example of a molecule containing this unusual fragment, dimethyl *N*,*N'*-(thio-bis-(methyliminocarbonyloxy))-bis(ethanimidothiolate).[10]

Product **12** is a formal [3+2] adduct of **9** and **5**, and the minor product was traced to the acid-catalysed conversion of **9** into the small amount of the non-antiaromatic isomer **14** with an exocyclic methylene group. Pure **14** gave the new cyclopentadienone **11** as the sole product in up to 34% with all three N=S reagents. Preformed sulfur diimide **5** converted **9** into the cycloadduct **12** in high yield (79%) at rt in toluene; only a trace of **11** was found since there was very little tautomerism of **9** under these neutral conditions.

The 2,5-dimethyl analogue **15** exists as its Diels–Alder dimer at rt and does not react with N=S reagents until heated. The Katz mixture gave the formal [3+2] adduct **16** of **15** with EtO_2CNSO **2** at 70°C (35%) and the same product was formed in higher yield (74%) by brief (15 min) heating of neat **15** and **2** at 130°C. The sulfur diimide **5**, from Katz reagent with extra urethane, gave the corresponding adduct **17** (65%) (Scheme 4).

We now suggest a rational and unifying mechanistic scheme which accounts for these diverse products. Following Weinreb and Kresze's detailed studies of simpler dienes with N=S reagents,[2] we propose that the reactions all start by [4+2] cycloaddition of the 4π donor cyclopentadienones with $EtO_2C–N=S^+–X$ where $X=O^-$, OSOCl, Cl and EtO_2CN^-; electrophilic catalysts are represented by protons. The fate of the [4+2] adduct **18** (Scheme 5) depends critically upon its substituents and

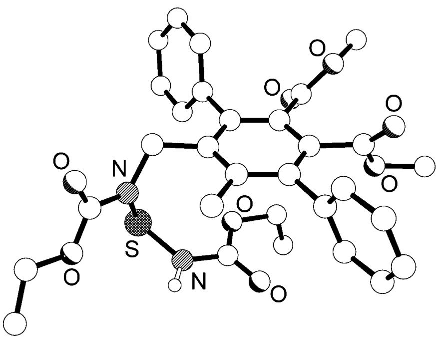
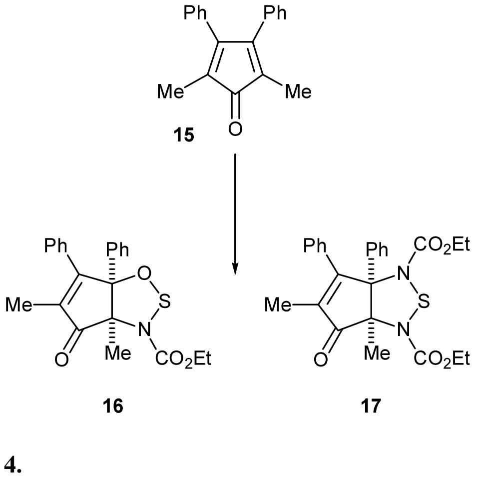
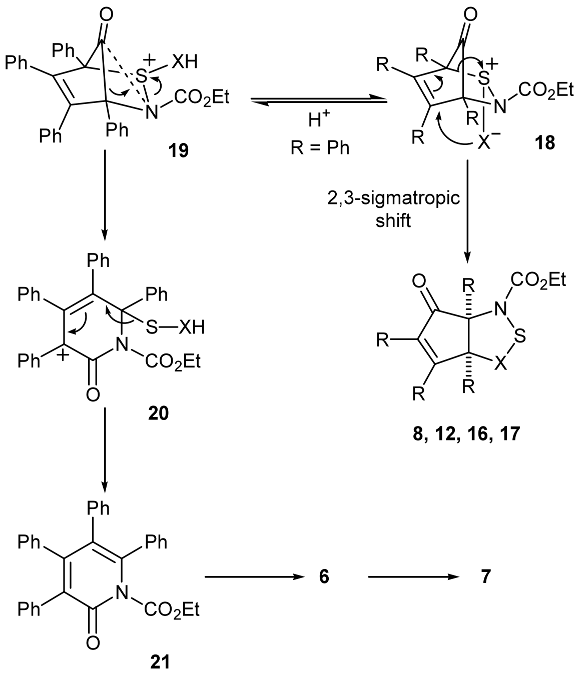


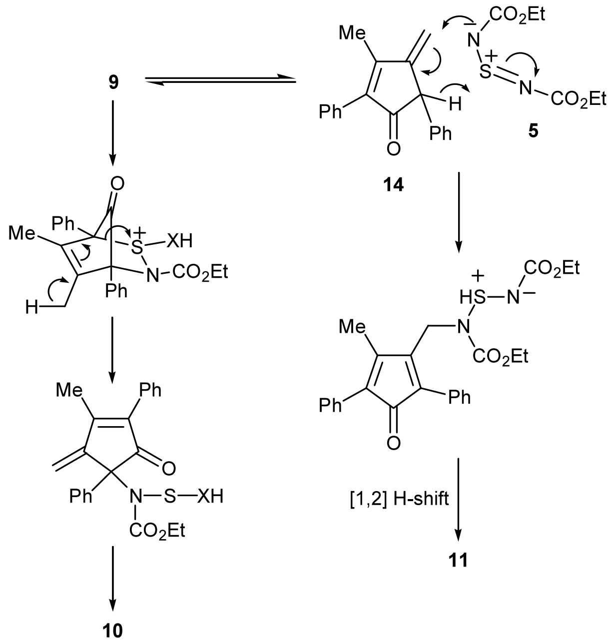
Figure 2. The molecular structure of **13**.



Scheme 4.



Scheme 5.



Scheme 6.

on the electrophilicity of the dienophile and the medium.

In the absence of electrophiles such as thionyl chloride the initial adducts undergo a thermal 2,3-sigmatropic rearrangement (arrows in **18**) to give the formal [3+2] adducts **8**, **12**, **16** and **17**. With tetracyclone **1** in the presence of $SOCl_2$ and pyridine, the adduct **18** can undergo a faster acid-catalysed rearrangement (**19**→**20**) via a stabilised 1,3-diphenylallylic carbonium ion **20**, to give *N*-ethoxcarbonylpyridone **21** which rearranges to **6**[11] and finally gives pyridone **7**. In contrast, the two dimethylcyclopentadienones **9** and **15** gave no pyridones, possibly because of reduced stability of the key carbonium ions analogous to **20**; furthermore the presence of a methyl group provides a lower energy pathway for the conversion of **9** into the amine **10** (Scheme 6). The methylene isomer **14** of **9** is well set up to undergo an ene reaction to give the bisaminosulfane **11** (Scheme 6). The [4+2] cycloaddition—2,3-sigmatropic rearrangement sequence (Scheme 5) in the reaction of the 2,5-dimethyl analogue **15** with **2** and **5** leads to the observed adducts **16** and **17** (Scheme 4).

Thus we have shown that the readily available cyclopentadienones react with some N=S reagents, also readily available, to provide useful syntheses of some new and rare structures. These are 1,2,5-thiadiazolidines and imidazolones derived therefrom, pyridones, diaminosulfanes, an aminocyclopentenone, and the first unoxidised 1,2,3-oxathiazolidine **16**,[12] and a mechanistic framework is proposed to account for their formation.

References

1. Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261–367.
2. (a) Garigipati, R. S.; Freyer, A. J.; Whittle, R. R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1984**, *106*, 7861–7867; (b) Natsugari, H.; Whittle, R. R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1984**, *106*, 7867–7872; (c) Bussas, R.; Kresze, G. *Liebigs Ann. Chem.* **1982**, 545–563.
3. Duan, X.-L.; Perrins, R.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1617–1622.
4. Laaman, S. M.; Meth-Cohn, O.; Rees, C. W. *Arkivoc* **2002**, *ii*, 90–94.
5. Shi, S.; Katz, T. J.; Young, B. V.; Liu, L. *J. Org. Chem.* **1995**, *60*, 1285–1297.
6. Laaman, S. M.; Meth-Cohn, O.; Rees, C. W. *Synthesis* **1999**, 757–759.
7. Smyth, T. P.; O'Donnell, M. E.; O'Connor, M. J.; St. Ledger, J. O. *J. Org. Chem.* **1998**, *63*, 7600–7618.
8. Crystallographic data (excluding structure factors) for the structures in this paper, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 198788 to 198790. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).
9. Compound **10** exhibits spontaneous resolution upon crystallisation, though the absolute chirality of the molecules in the crystal studied could not be determined from the X-ray data.
10. Ammon, H. L.; Seymour, R. J.; Huffman, W. M.; D'Silva, T. D. J. *Acta Crystallogr., Sect. C* **1995**, *51*, 1619–1621.
11. (a) McKillop, A.; Zelesko, M. J.; Taylor, E. C. *Tetrahedron Lett.* **1968**, 4945–4948; (b) Afarinkia, K.; Mahmood, F. *Tetrahedron Lett.* **1998**, *39*, 493–496.
12. Examples of the *S*-oxides and -dioxides are known, e.g.: Posakony, J. J.; Grierson, J. R.; Tewson, T. J. *J. Org. Chem.* **2002**, *67*, 5164–5169.