Dipolar cycloadditions of several mesoionic compounds with *tert*-butylfulvene derivatives; versatile reactions, sterically controlled [4π + 6π] cycloadditions and a new route to heterocycles isoelectronic with azulene

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Several mesoionic compounds react with 2-*tert*-butylfulvene derivatives to form [4π + 2π] and [4π + 6π] cycloadducts, which under the reaction conditions, undergo further fragmentation, elimination, or isomerization giving a variety of products including several condensed heterocycles which are isoelectronic with azulene.

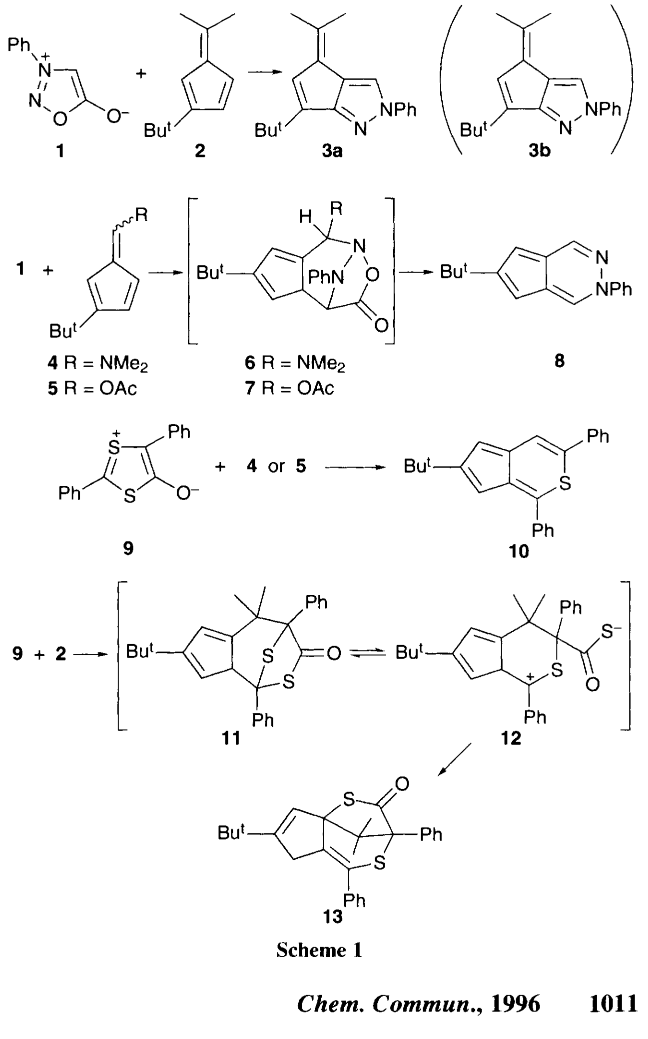
The cycloaddition reactions of mesoionic compounds have been extensively investigated.[1] We have recently reported the cycloaddition reactions of several mesoionic compounds with tropone,[2] the first time that [4π + 6π] cycloadditions of mesoionic compounds have been reported. It is known that mesoionic compounds react with fulvenes by a [4π + 2π] mode.[3] Here we report that this type of cycloaddition can be hindered effectively by the introduction of a bulky substituent on the fulvene ring and [4π + 6π] cycloadditions of mesoionic compounds with fulvenes can be realized. We also report that spontaneous extrusion and elimination reactions from suitably substituted [4π + 6π] cycloadducts afford a new short route to a variety of cyclopentaheterocycles which are isoelectronic with azulene. The formation of conventional [4π + 2π] cycloadducts and isomerizations of primary [4π + 6π] cycloadducts are also described.

The reaction of 3-phenylsydnone **1** with 2-*tert*-butyl-6,6-dimethylfulvene **2** gave the condensed pyrazole **3a** in 21% yield by extrusion of carbon dioxide from the [4π + 2π] cycloadduct and spontaneous dehydrogenation to the aromatic ring.† The possibility of the other regioisomer **3b** could be eliminated by NOE measurements (response between the isopropylidene methyls and 3- and 5-Hs, but no response between the *tert*-butyl and 3-H). The reaction of **1** with 6-dimethylamino- and 6-acetoxy-2-*tert*-butylfulvene **4** and **5** gave the cyclopenta[*d*]-pyridazine **8** in 31 and 47% yield respectively by extrusion of carbon dioxide and elimination of a molecule of dimethylamine or acetic acid from the [4π + 6π] adducts **6** and **7**. The product was not the [*c*]-condensed isomer because it did not show the ^1H NMR signal corresponding to two adjacent hydrogen atoms.

The mesoionic diphenyldithioliumolate **9** reacted similarly with the dimethylamino- and the acetoxy-fulvenes **4** and **5** to give the cyclopentathiapyrane **10** in 51 and 30% yield respectively *via* the [4π + 6π] adduct. When the dithioliumolate **9** and the dimethylfulvene **2** was heated under reflux in toluene, the bridged dithiepinone **13** (57%) was isolated. The structure of the rearrangement product **13** was established by single crystal X-ray analysis.‡ The formation of **13** is best rationalized by assuming rearrangement of the primary [4π + 6π] cycloadduct **11**. Owing to the absence of a good leaving substituent, **11** would undergo C–S bond cleavage to form a resonance-stabilized betaine intermediate **12**, whose recyclization at the 4a-position and hydrogen migration should give the bridged dithiepinone **13**.

A similar rearrangement of the plausible [4π + 6π] cycloadduct intermediate **15** was observed in the reaction of the mesoionic thiazolium-4-olate **14** *with the dimethylfulvene* **2**. The reaction occurred slowly, and the product isolated was the dihydrothiopyranecarbanilide **16** (17%).

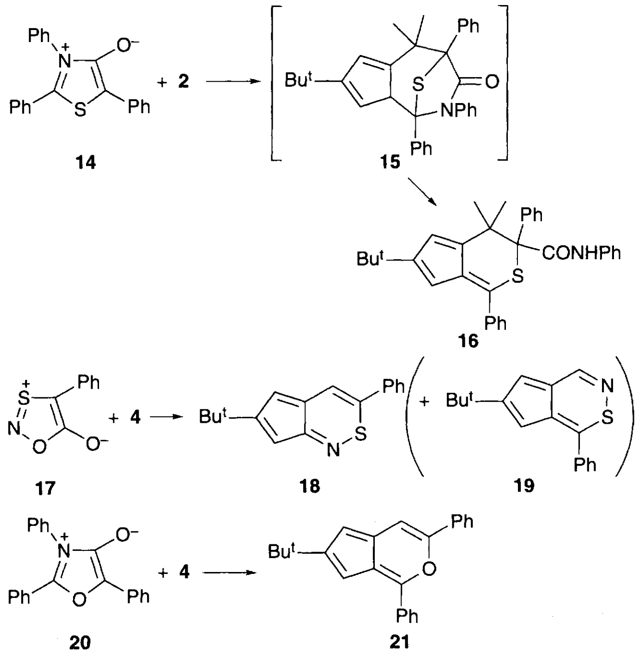
The reaction of the mesoionic 1,3,2-oxathiazolium-5-olate **17** with the dimethylaminofulvene **4** gave a [4π + 6π] cycloaddition–extrusion–elimination product in 29% yield, to which cyclopenta[*c*][1,2]thiazine structure **18** was assigned. This assignment is based mainly on NMR spectra which shows a quaternary carbon signal of the imino group (C-7a) at δ 170.1 and signals of C-4 and C-5 at δ 119.1 and 113.8, and a 7-H signal at δ 6.87. A further support for this assignment was provided by the isolation of a very small amount of an isomer (**19**; M^+ 267). Although good combustion analyses have not been obtained yet (C: −0.98%) due to its low yield, the C-4 and C-5 NMR signals of this minor isomer are shifted to lower magnetic field (δ 135.8 and 120.2) by the imino nitrogen atom, and 7-H is also deshielded (δ 7.44) by the nearby phenyl group. The mesoionic oxazolium-4-olate **20** reacted similarly with the



Scheme 1

dimethylaminofulvene **4** to give the cyclopentapyrane **21** (18%).

The preparation of the *tert*-butyl(dimethylamino)fulvene **4** has been reported.[4] We prepared this compound by treatment of sodium *tert*-butylcyclopentadienide with the *O*-methyl salt of dimethylformamide. The acetoxyfulvene **5** was prepared by treatment of the cyclopentadienide with ethyl formate and then with acetyl chloride.



Scheme 2

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Footnotes

† All new compounds gave satisfactory spectral (IR, ^{1}H and ^{13}C NMR, and low resolution MS) and combustion analytical data.

‡ *Crystal data* for **13**: $C_{27}H_{28}OS_2$, M_w = 432.6. Monoclinic, $P2_1/c$, a = 15.260(3), b = 9.051(3), c = 16.718(2) Å, β = 95.92(1)°, V = 2296.8(8) Å^3, T = 295 K, D_c = 1,251 g cm^{-3}, $F(000)$ = 920, R = 0.050, R_w = 0.083, GOOF = 2.54 for 3270 data [$F > 3\sigma(F)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/18.

References

1 K. T. Potts, in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley Interscience, New York, 1984, vol. 2, p. 1.
2 H. Kato, T. Kobayashi, T. Tokue and S. Shirasawa, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1617.
3 H. Kato, N. Aoki, Y. Kawarmura and K. Yoshino, *J. Chem. Soc., Perkin Trans. I*, 1985, 1245; W. Friedrichsen and W.-D. Schröer, *Liebigs Ann. Chem.*, 1981, 476; W. Friedrichsen, W.-D. Schröer and T. Debauerdemaeker, *Liebigs Ann Chem.*, 1981, 491; T. Debauerdemaeker, W.-D. Schröer and W. Friedrichsen, *Liebigs Ann. Chem.*, 1981, 502.
4 J. Abelt and H. D. Roth, *J. Am. Chem. Soc.*, 1985, **107**, 6814.

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