Heterocycles by Cycloaddition. Part 10.[1] Cycloaddition–Extrusion–Ring Expansion of Mesoionic Compounds with Benzocyclobutene. Approaches to Seven- and Eight-Membered Fully Conjugated Systems

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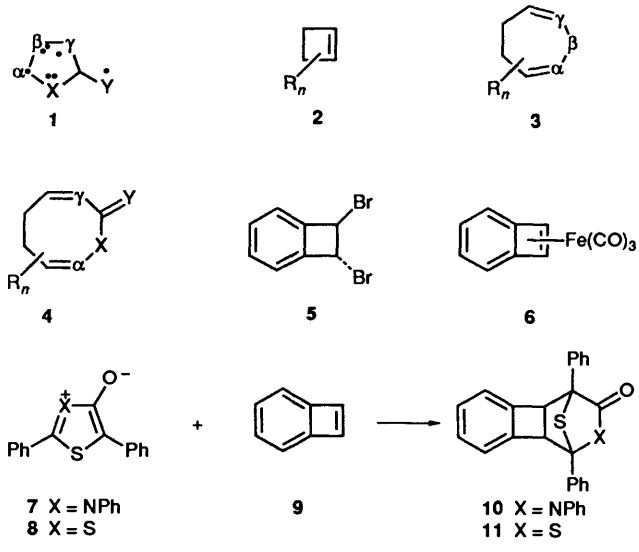
Several mesoionic compounds undergo dipolar cycloaddition with benzocyclobutene. The sydnone **12** directly gave the 2,3-benzodiazepine **14** by cycloaddition–extrusion–ring expansion, while primary cycloadducts **10**, **11** and **16** could be isolated from the thiazolium-4-olate **7**, 1,3-dithiolium-4-olate **8**, and thiazolium-5-olate **15**. The 2-Methylthiothiazolium-5-olate **20** gave secondary products **21**, **22** and **23**. Pyrolysis of the thiazolium-5-olate adduct **16** gave the 3-benzazepine **17** by extrusion of SCO. The benzazocinone **35** was formed by oxidation of the sulfoxide **32** or the sulfenate **36**, which were derived from the thiazolium-4-olate adduct **10**.

The dipolar cycloaddition–extrusion reactions of mesoionic compounds represented by general formula **1** provide valuable routes for the preparation of five-membered heterocycles.[2] When the reactions of this type are applied to small-membered cyclic olefins, six-,[3] nine- and ten-membered[1] fully conjugated heterocycles are formed by ring expansion. If mesoionic compounds react similarly with cyclobutenes **2**, these reactions should give seven- and possibly eight-membered heterocycles **3** and **4**. It has indeed been known for mesoionic oxazolium-5-olates to react with electron-deficient cyclobutenes[4] and 2-phenylbenzazete[5] to give dihydroazepines and 1,3-benzodiazepines respectively, and sydnones react with a cyclobutenone to give diazepinones.[6] However, it has been also reported that a mesoionic oxazolium-5-olate was recovered on attempted cycloaddition with cyclobutadiene, generated by oxidation of its iron carbonyl complex.[7] We report here that a closely related compound, benzocyclobutene, reacts with several mesoionic compounds to give cycloadducts, some of which can be converted into fully conjugated seven- and eight-membered heterocycles.



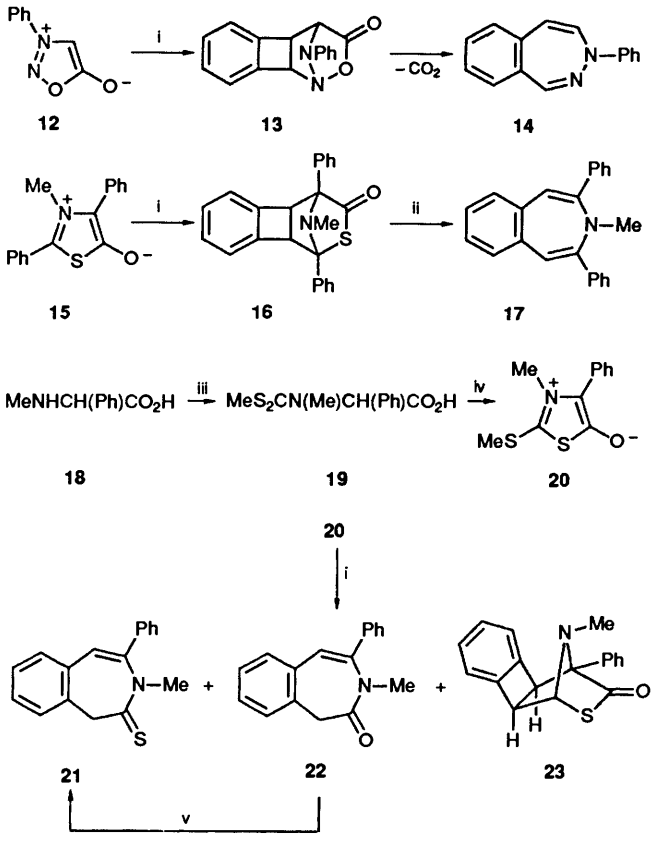
Results and Discussion

When the mesoionic thiazolium-4-olate **7** was treated in dimethylformamide (DMF) with benzocyclobutene **9**, generated by treatment of the dibromide **5** with zinc powder, the corresponding cycloadduct **10** was formed in 70% yield. The presence of a strained amide carbonyl group (1720 cm^{-1}), two adjacent sp^3 CH groups (δ 4.66 and 4.88; J 3.8 Hz), and four sp^3 carbon atoms established the structure of the adduct. It is worthy of note that when benzocyclobutene was generated by oxidation [$FeCl_3$, $(NH_4)_2Ce(NO_2)_6$, or $Pb(OAc)_4$] of its iron carbonyl complex **6**, a complex product mixture resulted and only a trace amount, if any, of the adduct **10** could be detected. Accordingly, benzocyclobutene was generated from the dibromide **5** in the reactions described below. A similar reaction of the mesoionic 1,3-dithiolium-4-olate **8** with benzocyclobutene also gave the corresponding cycloadduct **11** (63%). The stereochemistry of these cycloadducts will be discussed later in this paper.

It has been reported that sydnones do not react with 2-phenylbenzazete,[8] but it was found that 3-phenylsydnone **12** reacted with benzocyclobutene to give 3-phenyl-3*H*-2,3-benzodiazepine **14** (30%), by consecutive dipolar cycloaddition and concomitant extrusion of carbon dioxide and ring expansion of the primary cycloadduct **13** under the reaction conditions (Scheme 1). The structure of the benzodiazepine **14** was based, *inter alia*, on the absence of any ^{13}C NMR signal assignable to sp^3 carbon atom(s), and on ^1H NMR data (doublets at δ 5.66 and 5.93, J 8.2 Hz and a singlet at δ 7.41), which are similar to the NMR data of known 3*H*-2,3-benzodiazepines[9a,c] and monocyclic 1*H*-1,2-diazepines.[10] However, attempted preparation of benzodiazepine derivatives from 3-methyl- and 3-methyl-4-phenylsydnone were unsuccessful.

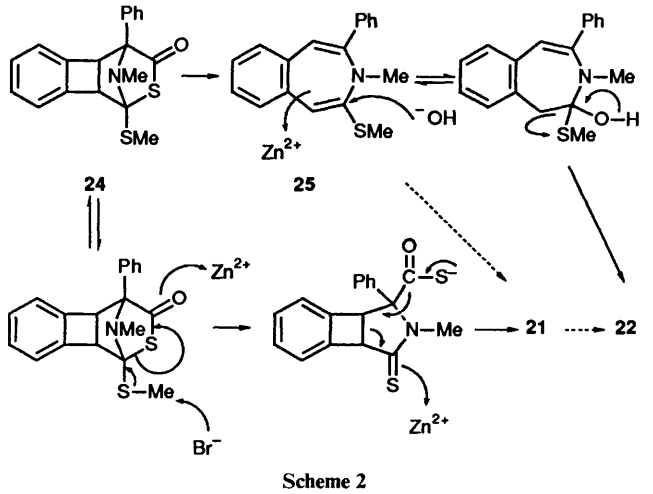
The reaction with the mesoionic 3-methyl-2,4-diphenylthiazolium-5-olate **15** under similar conditions in DMF (100 °C) likewise gave 3-methyl-2,4-diphenyl-3*H*-3-benzazepine **17** (16%). On the other hand, when the same reaction was performed in ethanol under reflux, the primary cycloadduct **16** was isolated (33%). The adduct **16** was converted into the benzazepine **17** (87%) when heated in benzene. Fully unsaturated 3*H*-2,3-diazepines[9] and 3*H*-3-benzazepines[9c,11] are relatively rare, and all those systems prepared so far are substituted with electron-withdrawing group(s).

The 2-methylthiothiazolium-5-olate **20** was prepared from *N*-methyl-*C*-phenylglycine **18** as shown in Scheme 1, and was allowed to react with benzocyclobutene. This reaction gave complex products, from which the expected cycloadduct or the extrusion–ring expansion product was not isolated. The products actually isolated were the benzazepinethione **21** (5%), the benzazepinone **22** (19%), and the cycloadduct **23** (1%) which



Scheme 1 *Reagents and conditions:* i, **5** and Zn; ii, heat; iii, KOH and CS_2, then MeI; iv, Ac_2O, or Ac_2O and Et_3N; v, Lawesson's reagent

is devoid of the methylthio substituent. The product ratio varied considerably with slight variation of reaction conditions. The benzazepinone **22** showed an amide absorption at 1655 cm^{-1} and NMR signals (δ_H 3.64, 2 H; δ_C 43.0, t) assignable to a methylene group, and it was converted into the thione **21** on treatment with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide (Lawesson's reagent). The structure assignment of the adduct **23** was based mainly on the IR band at 1700 cm^{-1} (strained thiol lactone), and NMR signals (δ_H 5.28, d; 4.24, dd; and 3.84, d; δ_C 53.2, d; 53.8; and 79.5, d) supporting the presence of three adjacent sp^3 CH units. It appears likely that the product **23** was formed by reductive elimination of the methylthio substituent of the primary cycloadduct **24** by the zinc metal. As shown in Scheme 2, the dihydrobenzazepines **21** and **22** were probably formed by zinc bromide-assisted

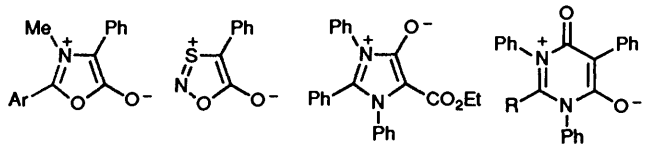


Scheme 2

hydrolysis of the methylthiobenzazepine **25** or fragmentation of the primary cycloadduct **24**.

The small value of the coupling constant (0.8 Hz) of the bridgehead proton of the adduct **23** shows that this adduct has the *exo* configuration. It appears plausible that other cycloadducts of mesoionic compounds with benzocyclobutene, *i.e.* compounds **10**, **11**, and **16**, also have the *exo* configurations because the coupling constants between the two methine protons (3.6–3.8 Hz) of these compounds are close to that of **23** (3.8 Hz). Therefore, the cycloaddition takes a transition state in which the 4π-ylide portion of the mesoionic ring overlaps the benzene ring of benzocyclobutene.

Benzocyclobutene either did not react or gave complex products with the following compounds: oxazolium-5-olates **26** and **27**, 1,3,2-oxathiazolium-5-olate **28**, imidazolium-4-olate **29**, and 6-oxopyrimidinium-4-olates **30** and **31**.



26 Ar = Ph
27 Ar = *p*-$NO_2C_6H_4$

28

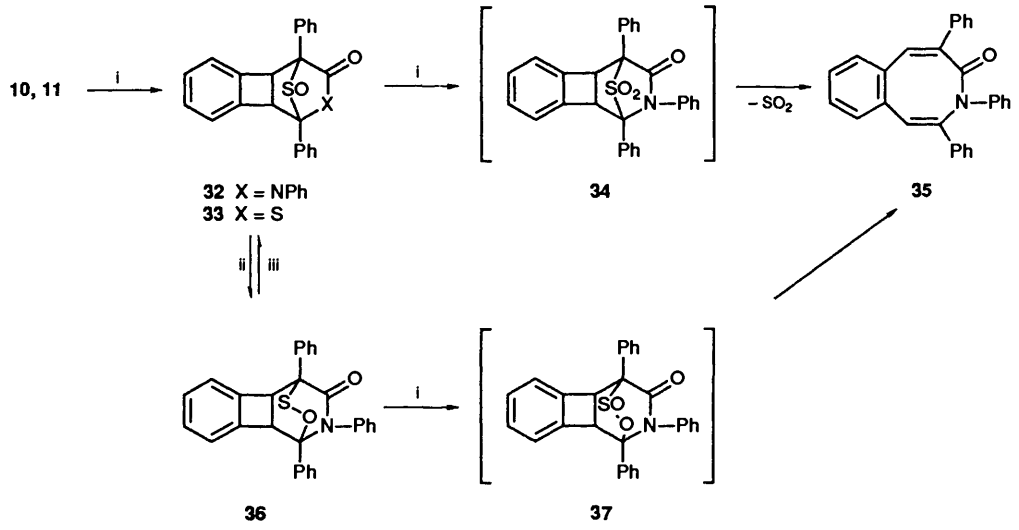
29

30 R = Ph
31 R = Me

The mass spectrum of the thiazolium-4-olate adduct **10** showed a base peak at *m/z* 312 corresponding to $(M - PhNCO)^+$, suggesting a ready extrusion of phenyl isocyanate. However, the adduct is thermally stable, complex products resulted upon thermolysis (reflux in *m*- and *p*-diethylbenzene mixture), and it was recovered unchanged on attempted photolysis (high-pressure mercury lamp; Pyrex filter; benzene). Equally unsuccessful were attempts at preparation of the benzazocinone **35** by desulfurisation of the sulfur bridge of the adduct **10** with tributylphosphine, trimethylsilyl iodide, low-valent titanium, or iron pentacarbonyl: in every case, the adduct was recovered unchanged (Scheme 3).

The thiazolium-4-olate adduct **10** was converted into the sulfoxide **32** (90%) with *m*-chloroperbenzoic acid (MCPBA). Conversion of the sulfur bridge into an *S*-oxide did not facilitate the extrusion–ring expansion: pyrolysis (reflux in diphenyl ether) of the sulfoxide **32** gave complex products. Attempted removal of the sulfoxide bridge from compound **32** by oxidation with sodium periodate resulted in recovery of the sulfoxide **32**. However, when the sulfoxide **32** was treated further with MCPBA, the benzazocinone **35** was formed (31%) probably by extrusion of sulfur dioxide from the sulfone intermediate **34**. The crude azocinone **35** was also formed in low yield by treatment of the sulfoxide **32** with dimethyldioxirane, but it was contaminated by other by-products which could be separated only with difficulty. The structure of the azocinone **35** was supported by the presence of an amide carbonyl group (1670 cm^{-1}), and the absence of NMR signals attributable to sp^3 carbons or protons attached to them. The benzazocinone **35** is a stable compound, and it was recovered unchanged on treatment with methylamine, potassium hydroxide, or hydrochloric acid in ethanol.

When a benzene solution of the sulfoxide **32** was irradiated, an isomer was isolated. The isomer no longer showed IR bands assignable to a sulfoxide group, and the two methine proton NMR signals were shifted upfield relative to those of the sulfoxide **32**. One of the two bridgehead sp^3 carbon singlet signals of compound **32** shifted upfield (δ_C 60.5), while the other shifted downfield to as far as δ_C 96.4. These spectral changes suggest an unusual sulfenate-bridged structure **36** for the isomer.[12] This isomer was converted back into the sulfoxide **32** on treatment with trifluoroacetic acid (TFA). This isomerisation proceeded cleanly, and UV monitoring of this reaction showed



Scheme 3 *Reagents:* i, MCPBA; ii, *hν*; iii, TFA

an isosbestic point at 309 nm. When the isomer **36** was treated with MCPBA, the benzazocinone **35** was formed (52%), probably by extrusion of sulfur dioxide *via* the sulfinate intermediate **37**. There are precedents concerning the ready fragmentation of 3,6-dihydro-1,2-oxathiine 2-oxides by extrusion of sulfur dioxide.[13] However, the possibility of an initial acid-catalysed isomerisation to the sulfoxide **32** and its further oxidation cannot be ruled out.

The dithioliumolate adduct **11** is also stable, and it was not possible to remove the SCO bridge by pyrolysis. This thermal stability of the dithioliumolate adduct **11** is remarkable, because the thiazoliumolate adduct **16**, which also has the SCO bridge and similar substituents, readily undergoes thermal fragmentation to give the benzazepine **17**. In the hope of removing the sulfur bridge, the adduct was converted into the sulfoxide **33** (81%) by treatment with MCPBA. The mass spectrum of the sulfoxide **33** did not show the molecular ion peak, suggesting its ready fragmentation by pyrolysis. However, attempts at converting it into a benzothiecinone by pyrolysis or photolysis were not successful. The sulfoxide **33** was treated further with MCPBA in order to convert it into the sulfone and thence to the benzothiecinone. This treatment resulted in only complex products.

In conclusion, the results presented above show that several mesoionic ring systems can undergo cycloadditions across the strained double bond of benzocyclobutene which is not activated by electron-withdrawing groups, and that some of these cycloadducts can be converted into fully conjugated seven- and eight-membered heterocycles by extrusion–ring expansion. Therefore, mesoionic compounds can now be regarded as attractive building blocks, which provide short-step approaches to fully conjugated heterocycles with every ring size ranging from five to ten.

Experimental

M.p.s (uncorrected) were determined on a Yanagimoto hot-stage apparatus. UV and IR (KBr) spectra were recorded with a Shimadzu UV-260 and a Hitachi 345 spectrophotometer respectively. Unless otherwise stated, ^{1}H (90 MHz) and ^{13}C (22.5 MHz) NMR spectra were recorded with a JEOL JNM-FX-90Q spectrometer on solutions in deuteriochloroform (tetramethylsilane internal standard). *J*-Values are given in Hz. Mass spectra (electron impact) were measured with a JEOL JMS-01SG-2 or a Shimadzu GCMS-QP1000EX spectrometer. Chromatographic separations were performed with Merck Kieselgel 60 or Merck Kieselgel 60 PF_{254}. Yields are based on isolated products with sufficient purity.

1,10,11-*Triphenyl*-13-*thia*-11-*azatetracyclo*[8.2.1.0^{2,9}.0^{3,8}]-*trideca*-3,5,7-*trien*-12-*one* **10**.—A solution of dibromodihydrobenzocyclobutene[14] **5** (5.24 g, 20 mmol) in DMF (10 cm^3) was added dropwise at 95 °C to a stirred mixture of the thiazolium-4-olate[15] **7** (3.29 g, 10 mmol), activated (dil. HCl) zinc powder (1.99 g, 30 mmol) and DMF (100 cm^3). After 10 min, when the dibromide had disappeared (TLC), the mixture was poured into water and extracted with dichloromethane. The extracts were washed with water, dried (Na_2SO_4), and concentrated to give the *cycloadduct* **10** (3.03 g, 70%) as needles, m.p. 229–231 °C (from benzene–hexane) (Found: C, 80.9; H, 4.9; N, 3.35. $C_{29}H_{21}NOS$ requires C, 80.7; H, 4.9; N, 3.25%); ν_{max}/cm^{-1} 1720 (C=O); δ_H 4.66 and 4.88 (each 1 H, d, *J* 3.8, 2- and 9-H) and 6.93–7.59 (19 H, m, ArH); δ_C 52.8 (d, C-2), 57.6 (d, C-9), 69.0 (s, C-1), 83.8 (s, C-10) and 174.2 (s, C=O); *m/z* 431 (M$^+$, 3%), 312 (M – PhNCO, 100), 280 (M – PhNCO – S, 5), 180 (PhCNPh$^+$, 13) and 121 (PhCS$^+$, 74).

1,10-*Diphenyl*-11,13-*dithiatetracyclo*[8.2.1.0^{2,9}.0^{3,8}]*trideca*-3,5,7-*trien*-12-*one* **11**.—A solution of the dibromide **5** (1.45 g, 5.5 mmol) in DMF (10 cm^3) was added dropwise over a period of 10 min to a stirred mixture of the dithioliumolate[16] **8** (1.0 g, 3.7 mmol) in DMF (50 cm^3) at 95 °C, and the mixture was stirred at this temperature for 10 min. The mixture was filtered, water (100 cm^3) was added, and the resulting mixture was extracted with dichloromethane. The organic phase was washed with water, dried (Na_2SO_4), and concentrated to give the *adduct* **11** (870 mg, 63%) as needles, m.p. 201 °C (from benzene–hexane) (Found: C, 73.9; H, 4.45. $C_{23}H_{16}OS_2$ requires C, 74.2; H, 4.3%); ν_{max}/cm^{-1} 1710 (C=O); δ_H 4.68 and 4.84 (each 1 H, d, *J* 3.6, 2- and 9-H), 6.75–6.90 (2 H, m, ArH), 7.14–7.24 (2 H, m, ArH), 7.35–7.52 (8 H, ArH) and 7.61–7.67 (2 H, m, ArH); δ_C 52.7 (d, C-2), 61.8 (d, C-9), 73.5 (s, C-1), 78.9 (s, C-10) and 203.0 (s, C=O); *m/z* 344 (M – CO, 3%), 312 (M – SCO, 100), 280 (M – SCO – S, 25), 265 (**8**$^+$, 4), 223 (M – CO – PhCS, 30) and 121 (PhCS$^+$, 74).

3-*Phenyl*-3H-2,3-*benzodiazepine* **14**.—The sydnone[17] **12** (974 mg, 6 mmol) was treated similarly as described above. The crude residue was extracted repeatedly with hexane and chromatographed (silica; benzene–hexane) to give, besides the recovered sydnone **12** (26%), the *benzodiazepine* **14** (404 mg, 30%) as orange needles, m.p. 96–97.5 °C (from methanol)

(Found: C, 81.5; H, 6.0; N, 12.5. $C_{15}H_{12}N_2$ requires C, 81.4; H, 5.9; N, 12.7%); ν_{max}/cm^{-1} 1605, 1485, 1290, 795 and 760; δ_H 5.66 and 5.93 (each 1 H, d, *J* 8.2, 5- and 4-H), 6.02–7.29 (9 H, m, Ar) and 7.41 (1 H, s, 1-H); δ_C 114.6–153.2 (13 peaks); *m/z* 220 (M^+, 100%), 117 (M − PhNC, 61) and 104 ($PhNCH^+$, 39).

13-*Methyl*-1,10-*diphenyl*-11-*thia*-13-*azatetracyclo*-[8.2.1.0^{2,9}.0^{3,8}]*trideca*-3,5,7-*trien*-12-*one* **16**.—A solution of the dibromide **5** (472 mg, 1.8 mmol) in ethanol (10 cm^3) was added dropwise over a period of 30 min to a stirred, refluxing mixture of the thiazolium-5-olate[18] **15** (400 mg, 1.5 mmol), zinc powder (353 mg, 5.4 mmol), and ethanol (20 cm^3). The mixture was filtered and concentrated, and the residual oil was extracted with dichloromethane. The extracts were washed with water, dried (Na_2SO_4), and concentrated, and the residue was triturated with hexane to give the *cycloadduct* **16** (182 mg, 33%) as yellow prisms, m.p. 123–124 °C (decomp.) (from benzene–hexane) (Found: C, 77.75; H, 5.3; N, 3.6. $C_{24}H_{19}NOS$ requires C, 78.0; H, 5.2; N, 3.8%); λ_{max}(EtOH)/nm 240 (log ε 4.61), 254 (4.35), 259 (4.39), 267 (4.41), 274 (4.33) and 303 (2.96); ν_{max}/cm^{-1} 1720 (C=O); δ_H 2.18 (3 H, s, NMe), 3.91 and 4.39 (each 1 H, d, *J* 3.8, 2- and 9-H), 6.35 (1 H, m, ArH), 6.67 (1 H, m, ArH) and 7.12–7.72 (12 H, m, ArH); δ_C 31.6 (q, NMe), 52.6 (d, C-2), 61.2 (d, C-9), 83.0 (s, C-1), 94.1 (s, C-10) and 207.4 (s, C=O); *m/z* 309 (M − SCO, 14%) and 118 ($PhCNMe^+$, 100).

3-*Methyl*-2,4-*diphenyl*-3H-3-*benzazepine* **17**.—(*a*) When the thiazolium-5-olate **15** (200 mg, 0.75 mmol) was treated in DMF (5 cm^3) at 100 °C under otherwise similar conditions to those described above, the *benzazepine* **17** (36 mg, 16%) was isolated as red needles, m.p. 137–138 °C (from ethanol) (Found: C, 89.0; H, 6.0; N, 4.25. $C_{23}H_{19}N$ requires C, 89.3; H, 6.2; N, 4.5%); λ_{max}(EtOH)/nm 206 (log ε 4.61), 272 (4.58), 304 (3.98) and 344 (3.57); ν_{max}/cm^{-1} 1650 and 1600; δ_H 2.53 (3 H, s, NMe), 5.83 (2 H, s, 1- and 5-H), 6.74–7.02 (4 H, m, ArH) and 7.19–7.62 (10 H, m, ArH); δ_C 39.8 (q, NMe), 119.7 (d, C-1), 127.0 (d), 127.6 (d), 128.1 (d), 128.4 (d), 129.7 (d), 137.5 (s), 140.8 (s) and 152.6 (s); *m/z* 309 (M^+, 22%) and 118 ($PhCNMe^+$, 100).

(*b*) A solution of the adduct **16** (730 mg, 2.0 mmol) in benzene (25 cm^3) was refluxed for 3 h. The solution was concentrated, and washed with methanol to give the benzazepine **17** (540 mg, 87%), identical with the sample described above.

N-*Methyl*-N-[(*methylthio*)*thiocarbonyl*]-C-*phenylglycine* **19**.—Carbon disulfide (4.5 cm^3, 75 mmol) was added to a stirred solution of *N*-methyl-*C*-phenylglycine **18** hydrochloride (10 g, 50 mmol) and 3 mol dm^{-3} aq. potassium hydroxide (50 cm^3, 150 mmol) in water (100 cm^3). After 1 h, iodomethane (4.7 cm^3, 75 mmol) was added and the resulting mixture was stirred for 6 h at room temperature. The mixture was washed with dichloromethane and acidified, and the precipitate was collected to give the *dithioester* **19** (11.4 g, 94%) as needles, m.p. 161–162 °C (from benzene) (Found: C, 52.0; H, 5.0; N, 5.7. $C_{11}H_{13}NO_2S_2$ requires C, 51.7; H, 5.1; N, 5.5%); ν_{max}/cm^{-1} 3300–2400br (OH) and 1705 (C=O); δ_H 2.71 (3 H, s, SMe), 3.13 (3 H, s, NMe), 7.39 (5 H, br s, Ph) 7.99 (1 H, br s, CH) and 8.32 (1 H, br s, OH; replaceable with D_2O); δ_C[$(CD_3)_2SO$] 20.0 (q, SMe), 36.3 (q, NMe), 67.9 (d, CH), 169 (s, C=O) and 200.3 (s, C=S); *m/z* 255 (M^+, 19%), 207 (M − MeSH, 29), 164 (M − CSSMe, 23) and 118 ($PhCNMe^+$, 100).

3-*Methyl*-2-*methylthio*-4-*phenylthiazolium*-5-*olate* **20**.—(*a*) A solution of the acid **19** (3.67 g, 14 mmol) in acetic anhydride (60 cm^3) was kept for 3.5 h at room temperature, then was concentrated under reduced pressure, and the residue was washed with diethyl ether and recrystallised (benzene–diethyl ether) to give *compound* **20** as yellow plates (1.72 g, 52%), m.p. 102–103 °C (Found: C, 55.8; H, 4.55; N, 5.7. $C_{11}H_{11}NOS_2$ requires C, 55.7; H, 4.7; N, 5.9%); ν_{max}/cm^{-1} 1590 (C=O); δ_H 2.55 (3 H, s, SMe), 3.70 (3 H, s, NMe) and 7.33–7.40 (5 H, m, Ph); δ_C 19.9 (SMe), 38.3 (NMe) and 171.6 (C=O); *m/z* 237 (M^+, 57%), 209 (M − CO, 22) and 118 ($PhCNMe^+$, 100).

(*b*) This compound could also be prepared in comparable yields by treatment of the acid **19** with a mixture of five-times its weight of a mixture of acetic anhydride and triethylamine (1:1) and collection by filtration of the precipitate of the product **20**.

Reaction of 3-*Methyl*-2-*methylthio*-4-*phenylthiazolium*-5-*olate* **20** *with Benzocyclobutene*.—A solution of dibromodihydrobenzocyclobutene **5** (2.48 g, 9.5 mmol) in DMF (20 cm^3) was added over a period of 30 min at 100 °C to a stirred mixture of the thiazoliumolate **20** (1.5 g, 6.3 mmol) and zinc powder (1.85 g, 28.3 mmol) in DMF (30 cm^3). The mixture was filtered and concentrated, and the residue was extracted with dichloromethane, the extract was washed with water, and the product was separated chromatographically on silica gel with benzene–ethyl acetate (2:1) to give 1,3-*dihydro*-3-*methyl*-4-*phenyl*-2H-3-*benzazepin*-2-*one* **22** (300 mg, 19%) as yellow needles, m.p. 138–139 °C (from benzene–hexane) (Found: C, 82.2; H, 5.95; N, 5.8. $C_{17}H_{15}NO$ requires C, 81.9; H, 6.1; N, 5.6%); ν_{max}/cm^{-1} 1655 (C=O); δ_H 2.85 (3 H, s, NMe), 3.64 (2 H, br s, CH_2), 6.79 (1 H, s, 5-H) and 7.33–7.45 (9 H, m, ArH); δ_C 35.0 (q, NMe), 43.0 (t, CH_2), 120.1 (d, C-5) and 169.6 (s, C=O); *m/z* 249 (M^+, 76%), 221 (M − CO, 6), 220 (M − NMe, 26), 192 (M − MeNCO, 10) and 118 ($PhCNMe^+$, 100).

Other fractions were further separated by chromatography (silica; benzene) to give 1,3-*dihydro*-3-*methyl*-4-*phenyl*-2H-3-*benzazepine*-2-*thione* **21** (90 mg, 5%) as yellow needles, m.p. 119–120 °C (from benzene–hexane) (Found: C, 76.7; H, 5.7; N, 5.2. $C_{17}H_{15}NS$ requires C, 76.9; H, 5.7; N, 5.3%); ν_{max}/cm^{-1} 1480 and 1460; δ_H 3.25 (3 H, s, NMe), 3.90 and 4.48 (each 1 H, d, *J* 11.8, CH_2), 6.98 (1 H, s, 5-H) and 7.32–7.45 (9 H, m, ArH); δ_C 43.3 (q, NMe), 52.5 (t, CH_2), 123.3 (d, C-5) and 200.2 (C=S); *m/z* 265 (M^+, 47%), 192 (M − MeNCS, 8) and 118 ($PhCNMe^+$, 100), and 13-*methyl*-1-*phenyl*-11-*thia*-13-*azatetracyclo*-[8.2.1.0^{2,9}.0^{3,8}]*trideca*-3,5,7-*trien*-12-*one* **23** (20 mg, 1%) as pale yellow prisms, m.p. 152–153 °C (decomp.) (from benzene–hexane) (Found: C, 73.6; H, 5.3; N, 4.8. $C_{18}H_{15}NOS$ requires C, 73.7; H, 5.15; N, 4.8%); ν_{max}/cm^{-1} 1700 (C=O); δ_H 2.37 (3 H, s, Me), 3.84 (1 H, d, *J* 3.8, 2-H), 4.24 (1 H, dd, *J* 3.8 and 0.8, 9-H), 5.28 (1 H, d, *J* 0.8, 10-H), 6.26–6.35 (1 H, m, ArH) and 7.10–7.61 (8 H, m, ArH); δ_C 34.1 (q, Me), 53.2 (d, C-2 or -9), 53.8 (d, C-9 or -2), 79.3 (s, C-1 or -10), 79.5 (d, C-10 or -1) and 207.1 (s, C=O); *m/z* 265 (M − CO, 18%), 233 (M − COS, 50), 191 (M − C_8H_6, 10) and 118 ($PhCNMe^+$, 100); CI-MS (isobutane) *m/z* 294 (M^+ + H, 73%).

3-*Methyl*-4-*phenyl*-2H-3-*benzazepine*-2-*thione* **21** *from the Benzazepinone* **22**.—Lawesson's reagent (80 mg, 0.2 mmol) was added to a benzene solution (10 cm^3) of the benzazepinone **22** (80 mg, 0.32 mmol), and the stirred mixture was heated under reflux for 30 min. The product was purified by chromatography (silica; benzene) to give the thione **21** (70 mg, 80%), which was identical with the specimen described above.

1,10,11-*Triphenyl*-13-*thia*-11-*azatetracyclo*[8.2.1.0^{2,9}.0^{3,8}]-*trideca*-3,5,7-*trien*-12-*one* 13-*Oxide* **32**.—A solution of the thiazoliumolate adduct **10** (1.71 g, 4 mmol) and MCPBA (85% purity; 0.86 g, 4 mmol) in dichloromethane (70 cm^3) was stirred for 10 min. The solution was washed with aq. sodium hydroxide, dried (Na_2SO_4), and concentrated, and the residue was triturated with hexane to give the *sulfoxide* **32** (1.59 g, 90%) as needles, m.p. 208–209 °C (from benzene–hexane) (Found: C, 78.0; H, 4.8; N, 3.2. $C_{29}H_{21}NO_2S$ requires C, 77.8; H, 4.7; N,

3.1%); ν_{max}/cm^{-1} 1720 (C=O) and 1090 (S=O); δ_H 4.69 and 5.13 (each 1 H, d, *J* 5.0, 2- and 9-H) and 7.10–7.89 (19 H, m, ArH); δ_C 45.9 (d, C-2), 50.6 (d, C-9), 76.4 (s, C-1), 83.7 (s, C-10) and 170.7 (s, C=O); *m/z* 447 (M^+, 4%), 399 (M − SO, 27), 280 (M − PhNCO − SO, 7) and 180 ($PhCNPh^+$, 100).

1,10-*Diphenyl*-11,13-*dithiatetracyclo*[8.2.1.0^{2,9}.0^{3,8}]*trideca*-3,5,7-*trien*-12-*one* 13-*Oxide* **33**.—Similar treatment of the dithioliumolate adduct **11** (170 mg, 0.46 mmol) with MCPBA (85% purity; 108 mg, 0.51 mmol) gave the *sulfoxide* **33** (144 mg, 81%) as needles, m.p. 207–208 °C (from benzene–hexane) (Found: C, 73.9; H, 4.45. $C_{23}H_{16}OS_2$ requires C, 74.2; H, 4.3%); ν_{max}/cm^{-1} 1700 (C=O) and 1090 (S=O); δ_H 4.61 and 5.09 (each 1 H, d, *J* 4.6, 2- and 9-H) and 6.85–7.83 (14 H, m, ArH); δ_C 45.5 (d, C-2), 51.5 (d, C-9), 76.7 (s, C-1), 85.6 (s, C-10) and 198.0 (s, C=O); *m/z* 340 (M − SO, 18%), 312 (M − SO − CO, 33%), 280 ($Ph_2C_{10}H_6^+$, 33), 265 (**8**$^+$, 3), 223 (M − SO − PhCCO, 68), 121 ($PhCS^+$, 100) and 105 ($PhCO^+$, 27).

1,10,13-*Triphenyl*-12-*oxa*-11-*thia*-13-*azatetracyclo*-[8.2.2.0^{2,9}.0^{3,8}]*tetradeca*-3,5,7-*trien*-14-*one* **36**.—A deaerated solution of the sulfoxide **32** (500 mg) in benzene (250 cm^3) was irradiated internally with a high-pressure mercury lamp (100 W) through a Pyrex filter for 16 h below 10 °C. The product was chromatographed twice (silica; dichloromethane, then silica; benzene) to give the unchanged sulfoxide **32** (167 mg recovery) and the *isomer* **36** (87 mg, 17%) as yellow prisms, m.p. 212–213 °C (from ethanol) (Found: C, 78.1; H, 4.8; N, 3.0. $C_{29}H_{21}NO_2S$ requires C, 77.8; H, 4.7; N, 3.1%); λ_{max}(EtOH)/nm 203 (log ε 4.69), 259 (3.43), 266 (3.44), 272 (3.27) and 329 (2.39); ν_{max}/cm^{-1} 1700 (C=O) and 1342; δ_H 4.49 and 4.92 (each 1 H, d, *J* 6.4, 2- and 9-H) and 6.62–7.69 (19 H, m, ArH); δ_C 46.2 (d, C-9), 53.6 (d, C-2), 60.5 (s, C-10), 96.4 (s, C-1) and 170.3 (s, C=O); *m/z* 447 (M^+, 13%), 399 (M − SO, 50), 223 (M − PhNCO − PhCO, 29), 180 ($PhCNPh^+$, 100) and 119 ($PhNCO^+$, 17).

Acid Treatment of the Photo Isomer **36**.—A solution of the photo isomer (30 mg) and TFA (30 mm^3) in dichloromethane (10 cm^3) was kept until the substrate had disappeared (1 day; TLC). Concentration of the solution afforded the sulfoxide **32** (20 mg, 67%), identical with an authentic specimen.

2,3,5-*Triphenyl*-3-*benzazocin*-4(3H)-*one* **35**.—(*a*) A solution of the sulfoxide **32** (500 mg, 1.12 mmol) and MCPBA (85% purity; 460 mg, 2.27 mmol) in dichloromethane (50 cm^3) was stirred at room temperature. Further portions of MCPBA (227 and 455 mg each) were added after 9 and 18 h respectively. After a total of 25 h, the solution was washed with aq. sodium hydroxide, dried (Na_2SO_4), and concentrated, and the residue was chromatographed (silica; dichloromethane) to give yellow microcrystals of the *benzazocinone* **35** (138 mg, 31%), m.p. 235–236 °C (from benzene) (Found: C, 86.9; H, 5.3; N, 3.7. $C_{29}H_{21}NO$ requires C, 87.2; H, 5.3; N, 3.5%); λ_{max}(EtOH)/nm 204 (log ε 4.62) and 256 (4.52); ν_{max}/cm^{-1} 1670 (C=O); δ_H 7.09–7.82 (m); δ_C 125.0–143.6 and 168.6 (s, C=O); *m/z* 399 (M^+, 69%), 280 ($Ph_2C_{10}H_6^+$, 24), 180 ($PhCNPh^+$, 100) and 119 ($PhNCO^+$, 5).

(*b*) Treatment of the sulfenate **36** (30 mg) with MCPBA (29 mg) in dichloromethane (5 cm^3) for 21 h, and similar work-up as described above, afforded the benzazocinone **35** (14 mg, 52%).

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