

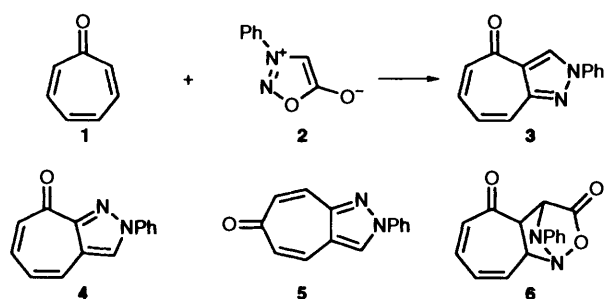
Heterocycles by Cycloaddition. Part 11.¹ Dipolar Cycloadditions of Mesoionic Compounds with Tropone: *peri*-Selective $[4\pi + 2\pi]$ and $[4\pi + 6\pi]$ Cycloadditions

Hiroshi Kato,* Tomoshige Kobayashi, Kazuhiko Tokue and Sonoko Shirasawa
Department of Chemistry, Faculty of Science, Shinshu University, Asahi, Matsumoto 390, Japan

The cycloaddition of 3-phenylsydnone **2** with tropone proceeded through a $[4\pi + 2\pi]$ mode, and gave the diazaazulenone **3** by subsequent extrusion of carbon dioxide and dehydrogenation. On the other hand, in the reactions of the mesoionic dithioliumolate **7** and oxazolium-4-olate **10** with tropone, $[4\pi + 6\pi]$ dipolar cycloadditions of mesoionic compounds were observed for the first time to give the tricyclic adducts **8** and **11**. Copper(II) acetate was found to show a slight catalytic effect in some of these reactions. Rather than undergoing extrusion reactions which are common with cycloadducts of mesoionic compounds, the tricyclic adducts **8** and **11** underwent thermal cycloreversion relatively readily.

A variety of fully conjugated heterocycles ranging from five- to ten-membered rings have been prepared by cycloaddition-extrusion reactions of mesoionic compounds with many unsaturated systems.¹⁻⁴ It is rather surprising to find that all the cycloadditions of mesoionic compounds known so far are of the $[4\pi + 2\pi]$ type, although there are several examples of $[4\pi + 6\pi]$ dipolar cycloadditions of diazomethane,⁵ an azomethanimine,⁶ nitrones,⁶ a nitrile ylide,⁷ a nitrile oxide,⁸ a nitrilimine,⁹⁻¹¹ a thiocarbonyl ylide,¹² and pyridinium-3-olates.¹³ Attempts to realise cycloadditions of the $[4\pi + 6\pi]$ mode by the reactions of mesoionic compounds with fulvenes gave instead the corresponding $[4\pi + 2\pi]$ adduct.¹⁴ The only reactions of mesoionic compounds which may be formally classified, if desired, as $[4\pi + 6\pi]$ are those with benzocyclopropene (trinorcaratriene) leading to nine- and ten-membered heterocycles.⁴

We report here reactions of mesoionic compounds with tropone **1**. These reactions were found to undergo either the first examples of $[4\pi + 6\pi]$ or the customary $[4\pi + 2\pi]$ cycloadditions selectively, depending on the structure of the starting mesoionic compounds.



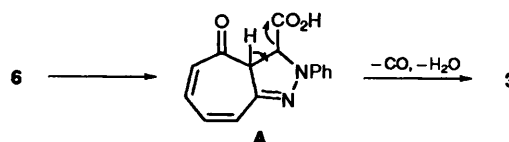
Scheme 1

Results and Discussion

The reaction of 3-phenylsydnone **2** with tropone **1** in xylene (commercial mixture of isomers) under reflux gave the diazaazulenone **3** though only in 10% yield. The IR absorption at 1605 cm^{-1} showed that this product is a fully conjugated tropone-like ketone. The selection of the correct structure **3** from the candidates **3**, **4**, and **5** rests mainly on NMR spectral data. The ¹H NMR signal corresponding to the four protons on the tropone skeleton appeared as a complex multiplet, while a pair of quasi-AB signals would be expected for structure **5**. That the product is the 4-one **3** rather than the 8-one **4** could be derived from measurements of its ¹H NMR spectrum with tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)-

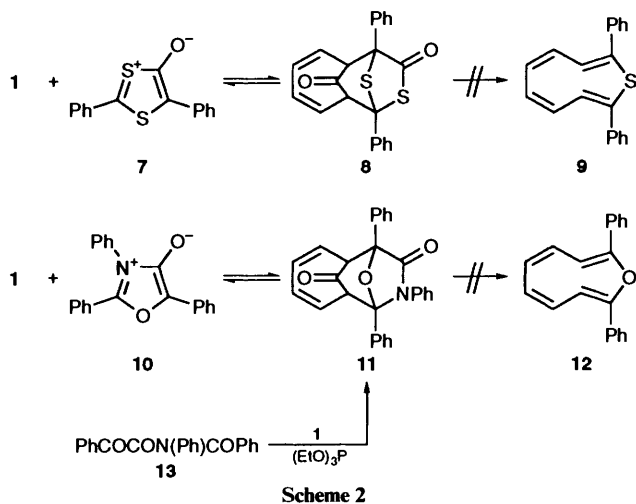
europium [Eu(fod)₃] and tris-(2,2,6,6-tetramethylheptane-3,5-dionato)praseodymium (Pr-DPM). In both cases, the doublet signal of the pyrazole proton shifted down- and up-field, respectively, to the largest degree next to the shift of the signal of the proton on the carbon atom which is adjacent to the carbonyl carbon. This shows that this product has the structure **3** and that the pyrazole proton couples probably with the 8-H (*J* 0.7 Hz) through five bonds. In addition, the measurement with Pr-DPM allowed a complete assignment of the H-H couplings of compound **3** (see Experimental section). The results presented above show that the cycloaddition of 3-phenylsydnone **2** proceeded *peri*- and regio-selectively in a $[4\pi + 2\pi]$ mode to give the adduct **6**, followed by extrusion of carbon dioxide and dehydrogenation.† A careful literature search revealed a very brief statement by Houk and collaborators¹¹ to the effect that 'electron-deficient (nitrile oxide, nitrile imine and sydnone) dipoles prefer $[4\pi + 2\pi]$ cycloadditions' (to tropone). However, the structure of the product(s) was not shown, and experimental details are no longer known, even to Professor Houk himself.¹⁷

Efforts to improve the yield of the diazaazulenone **3** were not very successful. The yield rose to 32% upon performing the reaction with an excess of tropone in bromobenzene under reflux in the presence of anhydrous copper(II) acetate. Crystalline 3-phenylsydnone **2** decomposes above its m.p. ($137\text{ }^\circ\text{C}$). However, a control experiment showed that, in solution, it decomposed only slightly under the experimental conditions described above. The yield of the diazaazulenone **3** could not be improved by use of dehydrogenating agents (Pd-C/PhNO₂, chloranil, or SeO₂), a Lewis acid (BF₃·OEt₂), or a soluble copper chelate [Cu(acac)₂].



† A referee has commented that a far more satisfactory explanation of the genesis of compound **3** would be elimination of CO and water from the intermediate **A**. We thank the referee for pointing out this possibility. Such ring openings of primary cycloadducts to carboxylic acids have been observed occasionally in reactions of mesoionic oxazolium-5-olates.¹⁵ However, it should be noted that a derivative of 3-benzoyl-2,3-dihydropyrrole-2-carboxylic acid, when heated, gives a 2,3-dihydropyrrole by decarboxylation,¹⁵ and the reactions of acyl-alkenes and alkenylcarboxylic esters with mesoionic compounds such as sydrones and oxazolium-5-olates give dihydroazoles by decarboxylation.^{2,16}

An entirely different mode of cycloaddition was observed in the reaction of the mesoionic dithioliumolate **7** with tropone **1**. In this case, the reaction proceeded in a $[4\pi + 6\pi]$ mode when these two components were heated in xylene (commercial mixture) under reflux, and the primary cycloadduct **8** could be isolated though the yield was only 7% (Scheme 2). The yield of

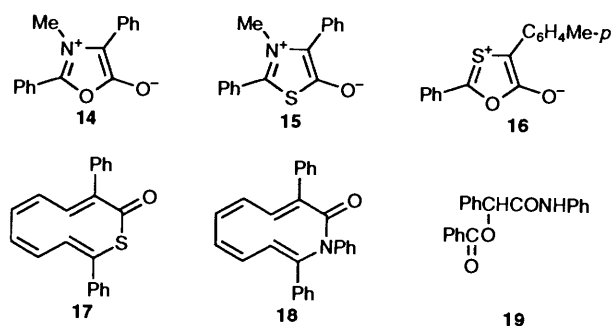


this cycloadduct was improved somewhat to 19%, again by addition of anhydrous copper(II) acetate in toluene. The addition of Lewis acids [$\text{BF}_3 \cdot \text{OEt}_2$, AlCl_3 , ZnI_2 , and $\text{Cu}(\text{acac})_2$] reduced the yield of compound **8**. The IR signal of the isolated bridged carbonyl group of adduct **8** is superimposed with the carbonyl signal of the strained thiolactone (1715 cm^{-1}). This structure is also supported by the presence of four sp^3 ^{13}C NMR signals at δ_{C} 60.9 (d), 66.3 (d), 68.1 (s) and 79.9 (s), and the ^1H NMR signals of the methine protons at δ_{H} 4.23 (dd) and 4.32 (dd) and a pair of multiplets for the olefinic protons at δ_{H} 5.26–5.34 and 5.98–6.10 each corresponding to two protons, as well as H–H and H–C COSY NMR spectra. The mass spectral peaks of this adduct at m/z 288 and 134 corresponding to diphenylthionine **9** and didehydrothionine, respectively, would lend further support to this structural assignment. Two configurations are possible for this cycloadduct depending on the mode of approach of the two components. However, the stereochemistry of this cycloadduct could not be elucidated from the available spectral data.

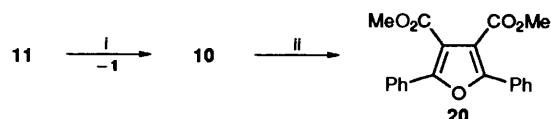
The reaction of the mesoionic oxazolium-4-olate **10** with tropone proceeded even at room temperature, and the $[4\pi + 6\pi]$ cycloadduct **11** with an unknown configuration was isolated in 34% yield. The oxazoliumolate **10** is unstable, both in the isolated form and especially in solution. Therefore, a better yield (49%) of the adduct **11** could be attained when tropone and *N*-benzoylphenylglyoxylanilide **13** were heated together with triethyl phosphite,¹⁸ so that the oxazoliumolate **10**, as it is formed, would react with tropone. The structure of the adduct is based on spectral properties, *inter alia* IR signals at 1725 and 1720 cm^{-1} , the methine ^{13}C NMR signals at δ_{C} 57.5 (d), 60.4 (d), 86.3 (s) and 97.6 (s), ^1H NMR signals of the methine protons at δ_{H} 4.00 (dd) and 4.25 (dd), and a pair of multiplets for the olefinic protons at δ_{H} 5.28–5.39 and 5.91–6.04, each corresponding to two protons. To the best of our knowledge, this reaction is the first example of $[4\pi + 6\pi]$ cycloaddition not only of a mesoionic compound but also of a carbonyl ylide.

To our regret, the reactions of tropone with mesoionic ring systems generally did not take place cleanly, and complex products resulted from reactions with the mesoionic oxazolium-5-olate **14**, thiazolium-5-olate **15**, and oxathiazolium-5-olate **16**.

At the outset of the present studies, it was hoped that once these cycloadditions would be made to follow the $[4\pi + 6\pi]$ mode, then elimination of carbon monoxide and the readily



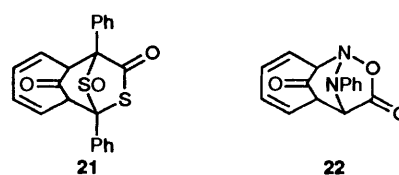
extrudable atom or group of atoms, originating from the mesoionic ring, from the primary cycloadducts would take place to give fully conjugated nine- or ten-membered heterocycles, such as the thionine **9**, and the oxonine **12**, the thiecinone **17**, and the azecinone **18**. Analysis of the electron-impact mass spectrum of the dithioliumolate adduct **8** would appear to support this expectation because it does not show any molecular ion peak but instead the peak with the highest mass corresponds to diphenylthionine **9**. Contrary to this expectation, when the dithioliumolate adduct **8** was heated in dichlorobenzene, it underwent cycloreversion to regenerate the dithioliumolate **7** (46%) and tropone. Similarly, when the oxazoliumolate adduct **11** was heated in bromobenzene under reflux, *O*-benzoylmandelanilide **19** was isolated (69%). This compound has been reported as the hydrolysis product of the mesoionic oxazolium-4-olate **10**.¹⁸ As reflected in the mass spectrum of the cycloadduct **11**, which shows the base peak corresponding to oxazoliumolate **10**, this cycloreversion occurs relatively readily. When the cycloadduct **11** was boiled in toluene for 6 days in the presence of dimethyl acetylenedicarboxylate (DMAD), the oxazoliumolate **10** formed by cycloreversion was intercepted by DMAD to give the furandicarboxylate **20** (17%), while 55% of the cycloadduct was recovered unchanged (Scheme 3). It has been known that furans are formed by



Scheme 3 Reagents and conditions: i, heat; ii, DMAD

cycloaddition–extrusion reactions of a mesoionic oxazolium-4-olate and DMAD,¹⁹ and the reaction of the oxazoliumolate **10** with DMAD indeed gave the furan **20**. Based on the colour change of the cycloadduct of the oxazoliumolate **10** and *N*-phenylmaleimide above its melting point, Haddadin *et al.* have suggested the regeneration of the oxazoliumolate **10** at this temperature.¹⁸ Attempted photolysis (Pyrex filter; benzene) of the dithioliumolate adducts **8** resulted in recovery, and similar irradiation of the oxazoliumolate adduct **11** in dichloromethane gave complex products. Equally unsuccessful was attempted desulfurisation of the sulfur atom leading to the thiecinone **17** by treatment of the dithioliumolate adduct **8** with tributylphosphine: the adduct was recovered unchanged.

The dithioliumolate adduct **8** was converted into the *S*-oxide **21** (74%). The *S*-oxide was also stable, and attempted thermal extrusion of sulfur monoxide from compound **21** could not be realised. Photolysis (Pyrex filter, benzene) of the *S*-oxide gave complex products.



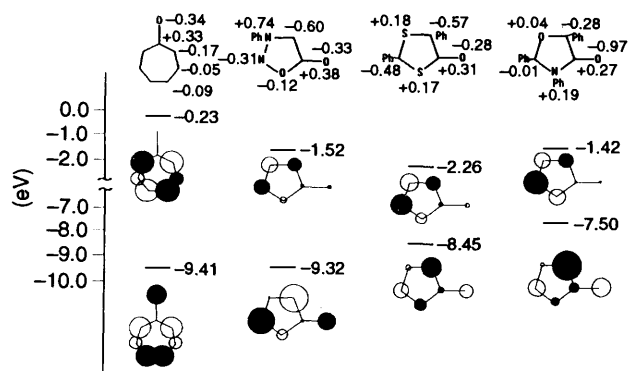


Fig. 1 PM3 Calculations of charge densities and HOMO-LUMO energies and coefficients of tropone 1 and mesoionic compounds 2, 7, and 10.²⁰ Compounds 1, 2, and 7 were calculated with the precise option, and compound 10 with the NOMM option. A planar geometry was assumed for tropone 1.

Hoping to gain insight into the different *peri*-selectivities of mesoionic compounds toward tropone, we performed PM3-MO calculations on tropone 1 and the mesoionic compounds 2, 7, and 10, and the results are shown in Fig. 1. This diagram shows that, for every mesoionic compound used in this study, each one of the conceivable modes of cycloaddition is symmetry-allowed to proceed in a concerted fashion. It does not appear likely that the charge distribution on the molecule would control the mode of approach of these molecules. It may be possible that steric factors control this selectivity. In the reaction with the sydnone 2, the phenyl substituent on the central atom (N) of the 1,3-dipole which is twisted considerably from the plane of the sydnone ring²¹ may hinder approach of the two components in the $[4\pi + 6\pi]$ mode. The other two mesoionic compounds 7 and 10 have no substituent on the central atom (S and O) of the three atoms which constitute the 1,3-dipole of the mesoionic ring, and this may allow cycloadditions to occur in the $[4\pi + 6\pi]$ mode. Considering that the diazaazulenone 3 could be isolated only in low yield, it may also be possible that the $[4\pi + 6\pi]$ cycloaddition of the sydnone actually occurred to a certain extent but that the primary cycloadduct 22 by this mode would readily lose carbon dioxide and would decompose further under the reaction conditions to leave compound 3 derived from the $[4\pi + 2\pi]$ cycloadduct 6 as the only isolable compound. Finally, the possibility cannot be excluded rigorously that the sydnone 2 might also give the $[4\pi + 6\pi]$ cycloadduct 22 with tropone, and that the primary cycloadduct would undergo thermal isomerisation to the isomer 6 by 1,5 sigmatropic shift involving the C-N bond. Although similar isomerisation involving the C-C bond of the $[4\pi + 6\pi]$ cycloadducts of both a nitrilimine^{10,11} and a nitrile oxide¹⁰ with tropone have been reported, such a situation appears unlikely in the present case because the cycloadducts of sydnones with unsaturated systems generally lose carbon dioxide quite readily.^{2,16}

As to the catalytic effect of copper(II) acetate, we presume that the metal would be coordinated to the exocyclic oxygen atom of either tropone or the mesoionic compound and would facilitate the cycloaddition. However, at present, we can offer no reasonable explanation as to why the soluble copper chelate $[\text{Cu}(\text{acac})_2]$ and several Lewis acids showed no effect.

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, ¹H (90 MHz) and ¹³C

(22.5 MHz) NMR spectra were recorded with a JEOL JNM-FX-90Q spectrometer on solutions in deuteriochloroform (tetramethylsilane internal standard). 300 MHz ¹H and 75 MHz ¹³C NMR spectra were measured on a General Electric QE300 spectrometer. *J* Values are given in Hz. Mass spectra were measured with a Shimadzu GCMS-QP1000EX spectrometer. GLC Analyses were performed on a Shimadzu GC-12A apparatus (10% Carbowax column). Chromatographic separations were performed with Merck Kieselgel 60 or Merck Kieselgel 60 PF₂₅₄. Yields are based on isolated products with sufficient purity.

2-Phenylcyclohepta[c]pyrazol-4(2H)-one 3.—A stirred mixture of tropone 1 (637 mg, 6.0 mmol), 3-phenylsydnone 2²² (324 mg, 2.0 mmol), and anhydrous copper(II) acetate (95% purity; 1.91 g, 10.0 mmol) in bromobenzene (20 cm³) was heated under reflux for 29 h. The solvent was removed under reduced pressure, and the residue was extracted with benzene and chromatographed [alumina; AcOEt-hexane (1 : 10)] to give the pyrazole 3 (142 mg, 32%), m.p. 132–134 °C (light tan needles from ethanol) (Found: C, 75.4; H, 4.4; N, 12.7. C₁₄H₁₀N₂O requires C, 75.7; H, 4.5; N, 12.6%); $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$ 207 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.40), 229 (4.46), 243 (4.41) and 349 (4.07); $\nu_{\text{max}}/\text{cm}^{-1}$ 1605 (C=O); δ_{H} 6.62–7.27 (4 H, m, *J*_{5,6} 12.6, *J*_{6,7} 8.2, *J*_{7,8} 10.8, 5-, 6-, 7- and 8-H) (these coupling constants are for Pro-coordinated 3), 7.33–7.90 (5 H, m, Ph) and 8.80 (1 H, d, *J* 0.7, 3-H); δ_{C} 119.8, 126.8, 127.9, 128.1, 129.4, 130.0, 130.7, 135.3, 135.7, 138.7, 149.0 and 182.8 (s, C=O); *m/z* 222 (M⁺, 64%), 194 (M – CO, 100), 117 (M – CO – Ph, 10), 103 (PhN=C, 7), 91 (PhN, 33) and 77 (Ph⁺, 100).

2,5-Diphenyl-3,12-dithiatricyclo[4.4.1.1^{2,5}]dodeca-7,9-diene-4,11-dione 8.—A stirred mixture of tropone 1 (636 mg, 6.0 mmol), the dithioliumolate 7²³ (812 mg, 3.0 mmol), and finely powdered anhydrous copper(II) acetate (1.15 g, 6.0 mmol) in toluene (20 cm³) was heated under reflux for 7 h. The mixture was filtered, the filtrate was concentrated, and the residue was triturated with methanol to give the adduct 8 (213 mg, 19%), m.p. 149–151 °C (decomp.) (light orange needles from ethanol) (Found: C, 70.5; H, 4.3. C₂₂H₁₆O₂S₂ requires C, 70.2; H, 4.3%); $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$ 211 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.37), 260sh (3.56) and 302 (3.09); $\nu_{\text{max}}/\text{cm}^{-1}$ 1715 (C=O); δ_{H} (300 MHz) 4.23 (1 H, dd, *J* 8.5 and 2.2, 1- or 6-H), 4.32 (1 H, dd, *J* 8.2 and 2.4, 6- or 1-H), 5.26–5.34 (2 H, m, 7- and 10-H), 5.98–6.10 (2 H, m, 8- and 9-H) and 7.37–7.60 (10 H, m, Ph); δ_{C} (75 MHz) 60.9 (d, C-1), 66.3 (d, C-6), 68.1 (s, C-2), 79.9 (s, C-5), 199.9 (C=O) and 202.9 (C=O); *m/z* (Cl/isobutane) 377 (M⁺ + H, 2%), 271 (7 + H, 79) and 107 (1 + H, 100); (EI) 288 (9, 7%), 270 (7, 49), 178 (PhCCPh, 25), 134 (9 – 2 Ph, 63), 121 (PhCS, 100), 102 (9 – 2 Ph – S, 49), 106 (1, 17), 78 (PhH, 99) and 77 (Ph, 98).

2,3,5-Triphenyl-12-oxa-3-azatricyclo[4.4.1.1^{2,5}]dodeca-7,9-diene-4,11-dione 11.—(a) A stirred mixture of *N*-benzoylphenylglyoxyylanilide 13³ (2.8 g, 8.5 mmol), tropone 1 (1.84 g, 17 mmol), and triethyl phosphite (8.5 cm³, 50 mmol) in benzene (60 cm³) was heated under reflux for 3 h under argon. The mixture was concentrated under reduced pressure, methanol was added to the residue, and the solid which separated out was collected to give the adduct 11 (1.76 g, 49%), m.p. 209–211 °C (needles from ethanol) (Found: C, 80.4; H, 5.0; N, 3.4. C₂₈H₂₁NO₃ requires C, 80.2; H, 5.05; N, 3.3%); $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$ 203 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.67), 250 (3.90), 259 (3.97), 270 (3.86), 315 (2.66) and 335 (2.00); $\nu_{\text{max}}/\text{cm}^{-1}$ 1725 and 1720 (C=O); δ_{H} 4.00 (1 H, dd, *J* 7.4 and 2.4, 1- or 6-H), 4.25 (1 H, dd, *J* 7.5 and 2.5, 6- or 1-H), 5.28–5.39 (2 H, m, 7- and 10-H), 5.91–6.04 (2 H, m, 8- and 9-H), 6.58–6.69 (2 H, m, Ph), 7.11–7.23 (3 H, m, Ph), 7.37–7.52 (8 H, m, Ph) and 7.78–7.89 (2 H, m, Ph); δ_{C} 57.5 (d, C-1), 60.4 (d, C-6), 86.3 (s, C-5), 97.6 (s, C-2), 169.1 (s, NC=O) and 202.6 (s, C=O); *m/z*

(Cl/isobutane) 420 ($M^+ + H$, 15%), 314 ($10 + H$, 100), 180 ($PhC=NPh$, 12) and 107 ($1 + H$, 63).

(b) A solution of the oxazoliumolate **10**¹⁸ (2.33 g, 7.4 mmol) and tropone **1** (1.15 g, 10.8 mmol) in toluene (50 cm³) was stirred for 18 h at room temperature. Similar work-up gave the adduct **11** (1.06 g, 34%).

Thermal Cycloreversion of the Dithioliumolate Adduct 8.—A solution of the adduct **8** (101 mg, 0.27 mmol) in *o*-dichlorobenzene (10 cm³) was heated under reflux for 3 h. The solution was concentrated and the residue was separated on TLC (silica; chloroform) to give the dithioliumolate **7** (33 mg, 46%), identical with an authentic specimen. Another oily fraction (13 mg) showed a GLC retention time identical with that of tropone. This component was identified by conversion into tropone picrate (trace, m.p. 96–97 °C), which was identical with an authentic specimen.

Thermal Cycloreversion of the Oxazoliumolate Adduct 11.—A solution of the adduct **11** (0.4 g, 0.95 mmol) in bromobenzene (20 cm³) was heated under reflux for 28 h. The solution was concentrated under reduced pressure, and the precipitate which separated out on addition of ethanol was collected and purified on TLC (silica; dichloromethane) to give *O*-benzoylmandelanilide **19** (217 mg, 69%), m.p. and mixed m.p.¹⁸ 183–184 °C.

Thermal Cycloreversion of the Oxazoliumolate Adduct 11 in the Presence of DMAD.—A solution of the adduct **11** (290 mg, 0.7 mmol) and DMAD (98 mg, 0.7 mmol) in toluene (10 cm³) was boiled for 6 days. The mixture was concentrated, and separated on TLC (silica; dichloromethane) to afford the recovered adduct **11** (160 mg, 55%), dimethyl 2,5-diphenylfuran-3,4-dicarboxylate **20** (40 mg, 17%), identical with the specimen prepared as described below, and a fraction (20 mg) showing the same GLC retention time as that of tropone

Dimethyl 2,5-Diphenylfuran-3,4-dicarboxylate 20 from the Oxazoliumolate 10.—DMAD (230 mg, 1.6 mmol) was added to a refluxing solution of the oxazoliumolate **10** (468 mg, 1.6 mmol) in toluene (20 ml). The colour of the oxazoliumolate disappeared as soon as the addition was complete. The solution was concentrated, methanol was added, and the crystals which separated out were collected to give the furandicarboxylate **20** (272 mg, 54%), m.p. 82 °C (lit.,²⁴ 80–81 °C); ν_{max}/cm^{-1} 1715 and 1710; δ_H 3.87 (6 H, s, Me), 7.40–7.50 (6 H, m, Ph) and 7.81–7.91 (4 H, m, Ph).

2,5-Diphenyl-3,12-dithiatricyclo[4.4.1.1^{2,5}]dodeca-7,9-diene-4,11-dione 12-Oxide 21.—A solution of the adduct **8** (156 mg, 0.42 mmol) and *m*-chloroperbenzoic acid (85% purity; 111 mg, 0.55 mmol) in dichloromethane (50 cm³) was stirred at room temperature for 4 h. The solution was washed with aq. sodium hydroxide, dried and concentrated to give the *S*-oxide **21** (120 mg, 74%), m.p. 214–215 °C (from benzene–hexane) (Found: C, 67.5; H, 4.1. $C_{22}H_{16}O_3S_2$ requires C, 67.3; H, 4.1%); ν_{max}/cm^{-1} 1730 (C=O), 1700 (C=O) and 1090 (S=O); δ_H 4.08 (1 H, dd, *J* 8.1 and 4.0, 1-H), 4.26 (1 H, dd, *J* 8.1 and 4.0, 6-H), 5.08–5.75 (2 H, m, 7- and 10-H), 5.93–6.30 (2 H, m, 8- and 9-H) and 7.25–7.82 (10 H, m, Ph); δ_C 62.4 (C-1), 66.8 (C-6), 80.8 (C-2), 91.6 (C-5),

196.5 (C=O) and 199.3 (C=O); m/z 392 (M^+ , 4%), 344 ($M - SO$, 64), 121 ($PhCS$, 100) and 77 (Ph , 38).

Acknowledgements

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