

## Heterocycles by Cycloaddition. Part 5.<sup>1</sup> Preparation of 7,9-Diheteratricyclo[4.2.1.0<sup>2,5</sup>]non-3-en-8-one Derivatives from Mesoionic Compounds

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Cycloaddition of a mesoionic dithiolone or thiazolone (1) with dimethyl tricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene-7,8-dicarboxylate (2) occurred at the cyclobutene ring. Thermal fragmentation of the adducts (3) or the corresponding *S*-oxides (6) gave dimethyl phthalate and the title diheteratricyclononenone derivatives (4) or their *S*-oxides (7).

MESOIONIC compounds have found wide application in the synthesis of a variety of heterocyclic systems. Apart from their well-established use in the preparation of five-membered heterocycles by cycloaddition-extrusion reactions with olefins and acetylenes,<sup>2</sup> they serve as starting materials for the preparation of six-membered heterocycles by cycloaddition-extrusion-ring expansion reactions with small-ring olefins,<sup>3</sup> and we have recently reported a novel synthetic approach to both five- and six-membered aromatic heterocycles by cycloaddition-double fragmentation reactions of mesoionic compounds with suitable bicyclic olefins.<sup>1,4</sup> In this paper we describe the reactions of mesoionic compounds (1) with dimethyl tricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene-7,8-dicarboxylate (2), the adduct of cyclo-octa-tetraene and dimethyl acetylenedicarboxylate. This ring system has three potentially available double bonds for cycloaddition, and the cycloadducts, if formed, may undergo fragmentation in a variety of ways.

The reaction of the mesoionic 2,5-diphenyl-1,3-dithiol-4-one (1a) with the triene (2) slowly took place in refluxing benzene to give one 1 : 1 adduct in quantitative yield. The i.r., mass, and n.m.r. spectra combined with a decoupling experiment established that the addition occurred at the most strained cyclobutene ring to give the adduct (3a) (see later for configurational assignment). The reaction of the mesoionic 2,3,5-triphenylthiazol-4-one (1b) with (2) proceeded more sluggishly, but gave the corresponding adduct (3b) (43%). These results

should be compared with the reactions of (2) with nitrones,<sup>5</sup> nitrilimines,<sup>6</sup> and nitrile oxides,<sup>7</sup> which give adducts across both the cyclobutene and the cyclohexadiene double bonds. When the adducts (3a and b) were heated, fragmentation to phthalate (5) occurred in preference to extrusion of SCO or PhNCO to give 1,6-diphenyl-7,9-dithiatricyclo[4.2.1.0<sup>2,5</sup>]non-3-en-8-one (4a) (80%) and its 7-aza-analogue (4b) (56%), respectively.

The adducts (3a and b) were converted into the corresponding *S*-oxides (6a) (92%) and (6b) (93%) with *m*-chloroperbenzoic acid (MCPBA). We expected that these compounds would undergo fragmentation of the mesoionic part, because of the reports that SO is more readily extruded than SCO and PhNCO.<sup>4,8</sup> However, fragmentation to phthalate (5) still occurred to give the corresponding tricyclic *S*-oxides (7a) (79%) and (7b) (70%), identical with the *S*-oxides prepared by oxidation of (4a and b) with MCPBA.

The above results show that the triene (2) acts as a masked cyclobutadiene; reactions of this type afford an attractive synthetic route to tricyclic systems such as (4) and (7). Unsuccessful attempts to prepare heterocyclic systems analogous to (4) or its fragmentation product by the reaction of cyclobutadiene with a mesoionic oxazolone have been reported by Rees and his co-workers.<sup>9</sup> We expected that the tricyclic sulphides (4) and sulphoxides (7) could be converted further into the corresponding fully unsaturated seven-

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<sup>3</sup> H. Matsukubo and H. Kato, *J.C.S. Chem. Comm.*, 1974, 675; *J.C.S. Perkin I*, 1975, 632; *Chem. Letters*, 1975, 767; H. Matsukubo, M. Kojima, and H. Kato, *ibid.*, p. 1153; K. T. Potts and J. Baum, *J.C.S. Chem. Comm.*, 1973, 833; T. Eicher and V. Schäfer, *Tetrahedron*, 1974, **30**, 4025; H.-D. Martin and M. Hekman, *Angew. Chem. Internat. Edn.*, 1972, **11**, 926.

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<sup>5</sup> G. Bianchi, A. Gamba, and R. Gandolfi, *Tetrahedron*, 1972, **28**, 1601.

<sup>6</sup> G. Bianchi, R. Gandolfi, and P. Grünanger, *Tetrahedron*, 1973, **29**, 2405.

<sup>7</sup> G. Bianchi, R. Gandolfi, and P. Grünanger, *Tetrahedron*, 1970, **26**, 5113.

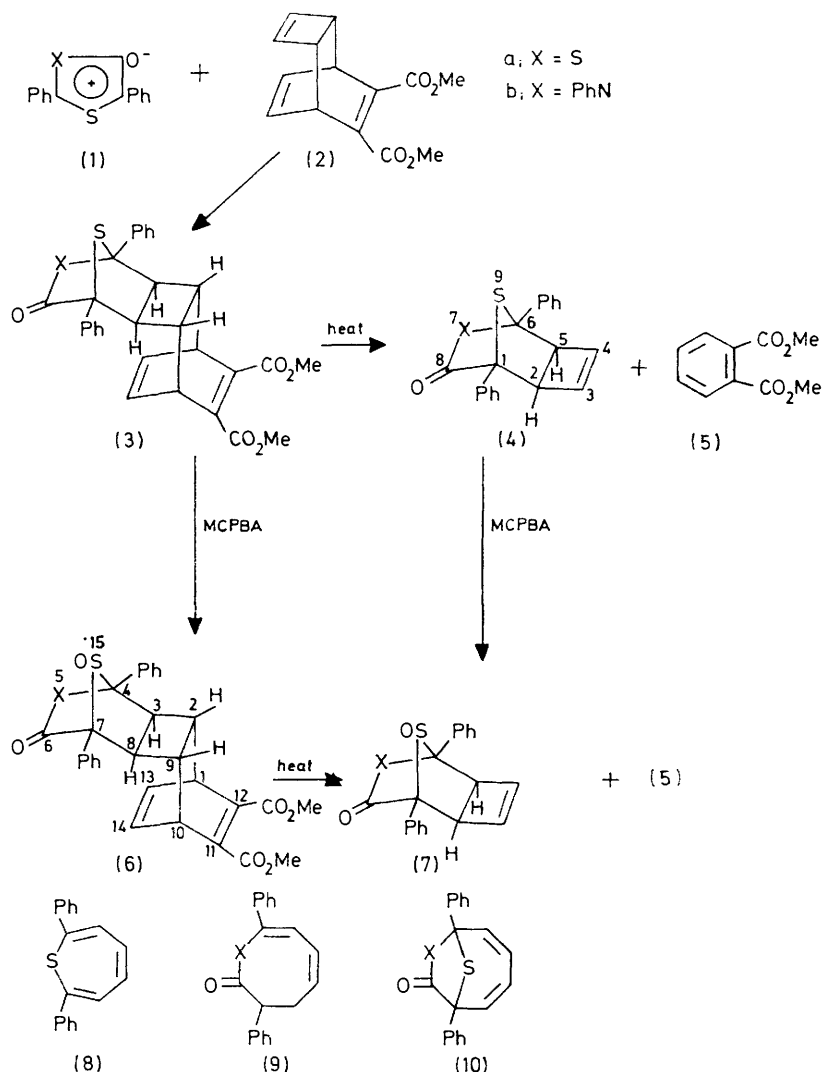
<sup>8</sup> H. Kato, S. Nakazawa, T. Kiyosawa, and K. Hirakawa, *J.C.S. Perkin I*, 1976, 672.

<sup>9</sup> T. L. Gilchrist, E. E. Nunn, and C. W. Rees, *J.C.S. Perkin I*, 1974, 1262.

or eight-membered heterocycles (8) or (9) by extrusion of XCO or SO with concomitant cleavage of the cyclobutene ring. However, compounds (4) and (7) were thermally very stable, and we have not been able to isolate such products after heating or irradiation.

The assignments of configurations to structures (3), (4), (6), and (7) are not very conclusive. The small coupling constants (*ca.* 3 Hz) between the two pairs of

the situation is reversed with the tricyclic sulphides (4a and b), both of which show a larger degree of magnetic non-equivalence of the 3- and 4-protons (0.22 and 0.47 p.p.m.) than of the 2- and 5-protons (0.12 and 0.16 p.p.m.). The sulphides (4) should retain the same configuration as the other products: it is unreasonable to expect inversion of configuration during fragmentation of (3), and the possibility of valence isomerisation



cyclobutane protons (H-2 and -3 and H-8 and -9) in (3) and (6) suggest that the approach of (1) to (2) occurred from 'above' the surface of the cyclobutene ring. That only the pair of protons at the 3- and 8-positions of (3) and (6) show magnetic non-equivalence to a considerable degree (0.29–0.51 p.p.m.) suggests that the XCO group is *exo* to the cyclobutane ring. The small effect of the sulphoxide oxygen with respect to the chemical shift values of (6) may be taken as evidence that the sulphoxide oxygen is also *exo* to the cyclobutane ring. The same consideration may be applied regarding the configuration of (7). However,

*via* the bridged diene (10) may be dismissed in view of an unsuccessful attempt to trap (10) with dienophiles and, above all, because the same *S*-oxides are formed by fragmentation of (6) and by oxidation of (4) with MCPBA. A similar but smaller magnetic non-equivalence of the olefinic protons is also observed with the corresponding *S*-oxides (0.14 and 0.11 p.p.m.), whereas protons at the corresponding positions (H-2 and -9) of (3) and (6) are all magnetically equivalent. The change in the torsion angle H-C-C-H with respect to the C-X-CO-C plane probably causes this anomalous result.

## EXPERIMENTAL

M.p.s were determined with a Yanagimoto hot-stage apparatus. U.v. and i.r. (KBr) spectra were recorded with Hitachi EPS-3T and EPI-SII spectrophotometers, and n.m.r. ( $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$  internal standard) and mass (70 eV; direct insertion) spectra were measured with JEOL JNM-4H-100 (100 MHz) and Hitachi RMU-6 spectrometers. All concentrations were carried out *in vacuo*, and compounds stated to be identical were so on the basis of m.p., mixed m.p., and i.r. spectral determinations.

*Dimethyl 6-Oxo-4,7-diphenyl-5,15-dithiapentacyclo[8.2.2.1.4.70.2.90<sup>3,8</sup>]pentadeca-11,13-diene-11,12-dicarboxylate* (3a).—A solution of the mesoionic 2,5-diphenyl-1,3-dithiol-4-one (1a)<sup>10</sup> (1 mmol) and dimethyl tricyclo[4.2.2.0<sup>2,5</sup>]deca-3,7,9-triene-7,8-dicarboxylate (2)<sup>11</sup> (80% purity; 1 mmol) in benzene (20 cm<sup>3</sup>) was refluxed for 50 h. The precipitate was collected and the solution was concentrated. The residue was triturated with methanol and the combined precipitate and residue were recrystallised (from benzene-n-hexane) to give the adduct (3a) as *prisms* (97%), m.p. 198–200 °C (Found: C, 67.25; H, 4.55.  $\text{C}_{29}\text{H}_{24}\text{O}_2\text{S}_2$  requires C, 67.4; H, 4.7%), u.v. (MeOH) end absorption;  $\nu_{\text{max}}$  1 728sh, 1 714, and 1 280 cm<sup>-1</sup>;  $\delta$  7.52–7.20 (10 H, m, ArH), 6.69 (2 H, dd, *J* 3.0 and 3.9 Hz, =CH), 4.15 (2 H, m, H-1 and -10), 3.67 (6 H, s, Me), 3.18 and 2.89 (each 1 H, dd, *J* 6.3 and 3 Hz, H-3 and -8), and 2.08 (2 H, m, H-2 and -9); irradiation at  $\delta$  6.67 caused the signal at  $\delta$  4.15 to collapse to d, *J* 3 Hz, and similarly irr. 4.15  $\rightarrow$  6.69, s; 2.08  $\rightarrow$  3.16, d, and 2.89, d, *J* 6.3 Hz; *m/e* 456 (6%, *M* – COS), 236 (50), 163 (100), 121 (34), and 77 (46).

*Dimethyl 6-Oxo-4,5,7-triphenyl-5-aza-15-thiapentacyclo[8.2.2.1.4.70.2.90<sup>3,8</sup>]pentadeca-11,13-diene-11,12-dicarboxylate* (3b).—A solution of the mesoionic 2,3,5-triphenylthiazol-4-one (1b)<sup>12</sup> (4.4 mmol) and the triene (2) (4.4 mmol) in benzene (150 cm<sup>3</sup>) was refluxed for 200 h. The solution was concentrated and the residue was chromatographed on silica (chloroform) to give the adduct (3b) as *prisms* (from benzene-n-hexane) (43%), m.p. 201–202 °C (Found: C, 72.9; H, 4.95; N, 2.35.  $\text{C}_{35}\text{H}_{29}\text{NO}_5\text{S}$  requires C, 73.0; H, 5.1; N, 2.45%), u.v. (MeOH) end absorption;  $\nu_{\text{max}}$  1 723sh, 1 714, and 1 276 cm<sup>-1</sup>;  $\delta$  7.44–7.22 (10 H, m, ArH), 7.10–6.95 (3 H, m, ArH), 6.82–6.72 (4 H, m, ArH and =CH), 4.31 and 4.18 (each 1 H, m, H-1 and -10), 3.72 (6 H, s, Me), 3.17 and 2.85 (each 1 H, dd, *J* 6 and 2 Hz, H-3 and -8), and 2.34br (2 H, s, H-2 and -9); *m/e* 381 [4%, *M* – (5)], 262 (15), 180 (13), 163 (100), 160 (13), and 77 (36).

*1,6-Diphenyl-7,9-dithiatricyclo[4.2.1.0<sup>2,5</sup>]non-3-en-8-one* (4a).—The adduct (3a) (0.97 mmol) in xylene (40 cm<sup>3</sup>) was heated under reflux for 92 h; the solution was concentrated and the residue was chromatographed on silica (benzene) to give *needles* (from petroleum) of (4a) (80%), m.p. 145.5–146 °C (Found: C, 70.85; H, 4.25.  $\text{C}_{19}\text{H}_{14}\text{OS}_2$  requires C, 70.8; H, 4.4%), u.v. (MeOH) end absorption;  $\nu_{\text{max}}$  1 703 cm<sup>-1</sup>;  $\delta$  7.70–7.25 (10 H, m, ArH), 6.43 and 6.21 (each 1 H, d, *J* 2.8 Hz, =CH), and 4.11 and 3.99 (each 1 H, d, *J* 3.5, H-2 and -5); *m/e* 262 (66%; *M* – COS), 236 (17), 229 (25), 173 (26), 160 (68), 121 (100), and 77 (28). A later eluate afforded dimethyl phthalate (5) (120%;

crude), which was converted<sup>13</sup> into phthalic anhydride (35%), identical with an authentic sample.

*1,6,7-Triphenyl-7-aza-9-thiatricyclo[4.2.1.0<sup>2,5</sup>]non-3-en-8-one* (4b).—A suspension of the adduct (3b) (0.26 mmol) in *o*-diethylbenzene (20 cm<sup>3</sup>) was heated under reflux for 11 h, and was similarly treated to give *prisms* (from *n*-hexane) of (4b) (56%), m.p. 152–153 °C (Found: C, 78.75; H, 4.9; N, 3.55.  $\text{C}_{25}\text{H}_{19}\text{NOS}$  requires C, 78.7; H, 5.0; N, 3.65%),  $\lambda_{\text{max}}$  (MeOH) 245sh nm (log  $\epsilon$  3.82);  $\nu_{\text{max}}$  1 699 cm<sup>-1</sup>;  $\delta$  7.78–6.92 (15 H, m, ArH), 6.67 and 6.22 (each 1 H, d, *J* 3 Hz, =CH), and 4.18 and 4.02 (each 1 H, d, *J* 3.5 Hz, H-2 and -5); *m/e* 381 (28%, *M*), 262 (100), 180 (88), 160 (88), 121 (78), and 77 (92).

*Dithiolone Adduct S-Oxide* (6a).—A solution of the adduct (3a) (0.85 mmol) and *m*-chloroperbenzoic acid (MCPBA) (80% purity; 0.88 mmol) in dichloromethane (30 cm<sup>3</sup>) was stirred at room temperature for 7 h. The solution was washed (aqueous sodium hydroxide; water), dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated, and the residue was recrystallised (from benzene-n-hexane) to give *prisms* of (6a) (98%), m.p. 207–208 °C (Found: C, 64.9; H, 4.45.  $\text{C}_{29}\text{H}_{24}\text{O}_6\text{S}_2$  requires C, 65.4; H, 4.55%),  $\lambda_{\text{max}}$  (MeOH) 217sh nm (log  $\epsilon$  4.46);  $\nu_{\text{max}}$  1 724sh, 1 714, 1 728, 1 095, and 1 066 cm<sup>-1</sup>;  $\delta$  7.67–7.25 (10 H, m, ArH), 6.74 (2 H, t, *J* 3.8 Hz, =CH), 4.31 (2 H, m, H-1 and -10), 3.69 (6 H, s, Me), 3.14 and 2.63 (each 1 H, dd, *J* 8.5 and 3.5 Hz, H-3 and -8), and 2.28br (2 H, s, H-2 and -9); *m/e* 290 [3%, (7a) – SO], 262 (10), 230 (7), 194 (9), 173 (12), 163 (100), 160 (21), 121 (25), and 77 (30).

*Thiazolone Adduct S-Oxide* (6b).—A solution of the adduct (3b) (0.43 mmol) and MCPBA (0.44 mmol) in dichloromethane (20 cm<sup>3</sup>) was stirred at room temperature for 6 h, and was worked up by a similar method to give (6b) (93%) as *prisms* (from chloroform-ether), m.p. 195–196 °C (Found: C, 70.8; H, 4.8; N, 2.3.  $\text{C}_{35}\text{H}_{29}\text{NO}_6\text{S}$  requires C, 71.05; H, 4.95; N, 2.35%),  $\lambda_{\text{max}}$  (MeOH) 227 nm (log  $\epsilon$  4.44);  $\nu_{\text{max}}$  1 723sh, 1 713, 1 277, and 1 066 cm<sup>-1</sup>;  $\delta$  7.75–6.95 (15 H, m, ArH), 6.83 (2 H, t, *J* 3 Hz, =CH), 4.45br (2 H, s, H-1 and -10), 3.78 (6 H, s, Me), 3.13 and 2.72 (each 1 H, *J* 9 and 3 Hz, H-3 and -8), and 2.46br (2 H, s, H-2 and -9); *m/e* 397 [2%, (7b)], 349 (13), 219 (15), 194 (14), 180 (18), 163 (100), and 77 (45).

*1,6-Diphenyl-7,9-dithiatricyclo[4.2.1.0<sup>2,5</sup>]non-3-en-8-one 9-Oxide* (7a).—(a) A suspension of the *S*-oxide (6a) (0.23 mmol) in xylene (15 cm<sup>3</sup>) was heated under reflux for 45 h. The solution was concentrated and the residue chromatographed on silica (benzene) to give *prisms* (from chloroform-ether) of (7a) (79%), m.p. 171.5–174 °C (Found: C, 67.35; H, 4.0.  $\text{C}_{19}\text{H}_{14}\text{O}_2\text{S}_2$  requires C, 67.45; H, 4.15%), u.v. (MeOH) end absorption;  $\nu_{\text{max}}$  1 708 and 1 083 cm<sup>-1</sup>;  $\delta$  7.70–7.23 (10 H, m, ArH), 6.46 and 6.32 (each 1 H, d, *J* 3 Hz, =CH), and 4.51 and 4.06 (each 1 H, d, *J* 4 Hz, H-2 and -5); *m/e* 338 (1%, *M*), 290 (11), 278 (9), 262 (45), 173 (46), 160 (87), and 121 (100). A later fraction afforded dimethyl phthalate (crude; 110%), which was converted into phthalic anhydride (90%), identical with an authentic specimen.

(b) A solution of (4a) (0.06 mmol) and MCPBA (0.06 mmol) in dichloromethane (2 cm<sup>3</sup>) was stirred for 5 h at room temperature, washed (aqueous sodium hydroxide; water), dried, and concentrated to give *prisms* (from

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<sup>11</sup> W. G. Dauben and L. N. Reitman, *J. Org. Chem.*, 1975, 40, 835.

<sup>12</sup> M. Ohta, H. Chosho, C. Shin, and K. Ichimura, *Nippon Kagaku Zasshi*, 1964, 85, 440.

<sup>13</sup> J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb, *J. Amer. Chem. Soc.*, 1963, 85, 2257.

chloroform-ether) of (7a) (37%), identical with the sample prepared by procedure (a).

**1,6,7-Triphenyl-7-aza-9-thiatricyclo[4.2.1.0<sup>2,5</sup>]non-3-en-8-one 9-Oxide (7b).**—(a) A suspension of (6b) (0.52 mmol) in xylene (20 cm<sup>3</sup>) was refluxed for 22 h. The crystals of (7b) which separated were collected; the solution was concentrated and the residue was washed (ether) to afford (7b). Chromatography on silica (chloroform) of the ether washings gave a further sample of (7b). The combined product was recrystallised (chloroform-ether) to give *prisms* of (7b) (total 70%), m.p. 243—244 °C (decomp.) (Found: C, 75.2; H, 4.6; N, 3.45. C<sub>25</sub>H<sub>19</sub>NO<sub>2</sub>S requires C, 75.55; H, 4.8; N, 3.5%),  $\lambda_{\max}$  (MeOH) 226 nm (log  $\epsilon$  4.36);  $\nu_{\max}$  1 714 and 1 069 cm<sup>-1</sup>;  $\delta$  7.78—6.95 (15 H, m, ArH), 6.48 and

6.37 (each 1 H, d,  $J$  2.6 Hz, =CH), and 4.57 and 4.13 (each 1 H, d,  $J$  4 Hz, H-2 and -5);  $m/e$  397 (7%,  $M$ ), 349 (60), 230 (40), 219 (95), 180 (100), and 77 (85).

(b) A solution of (4b) (0.13 mmol) and MCPBA (0.14 mmol) in dichloromethane (5 cm<sup>3</sup>) was stirred for 3 h at room temperature. Work-up similar to that in procedure (b) (above) gave *prisms* (chloroform-ether) of (7b) (67%), identical with the sample prepared by procedure (a).

We are indebted to Kyorin Chemical Laboratories for elemental analyses and mass spectra, and to Mr. Naomi Takagi for experimental assistance.

[6/1113 Received, 11th June, 1976]