[3,2] Sigmatropic Rearrangements of Some Allylic Oxosulphonium Ylides. A Route to Trienes and Azatrienes, and Their Cyclic Isomers

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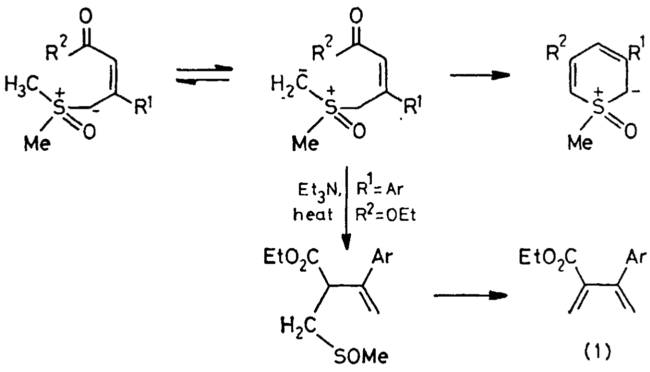
The imidoyl-substituted oxosulphonium ylides (2) reacted with dimethyl acetylenedicarboxylate and with dibenzoylacetylene by conjugate addition. The resulting allylic oxosulphonium ylides underwent [3,2] sigmatropic rearrangement at room temperature or below, to give the sulphoxides (3). These sulphoxides readily lost methanesulphinic acid when heated at 80 °C and gave the dihydropyridines (4). These reactions are presumed to go by way of intermediate azatrienes (6). The stabilised oxosulphonium ylides (7) reacted with dimethyl acetylenedicarboxylate by a similar sequence which gave the isolable trienones (9). These trienones underwent electrocyclic ring-closure when heated in xylene.

In an earlier paper [1] we described the preparation and properties of some imidoyl-substituted oxosulphonium ylides. As an extension of this work we have investigated the reactions of these and related ylides with electrophilic acetylenes, in order to provide a route to new, highly substituted oxosulphonium ylides.[2]

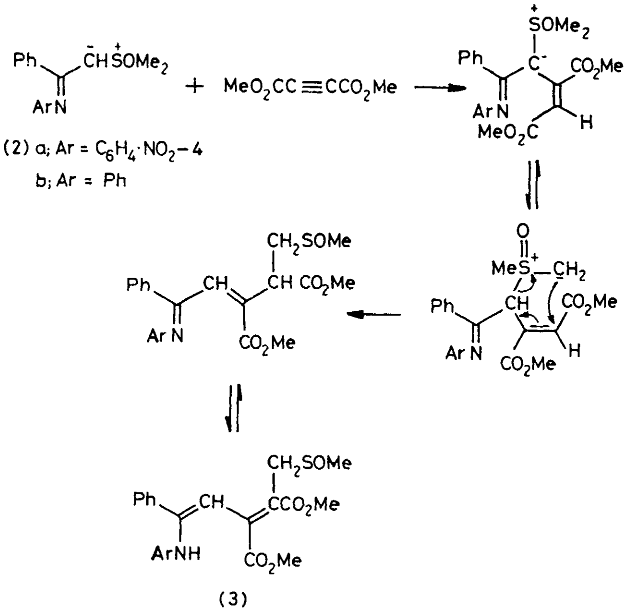
There have been several earlier reports of the reactions of dimethyloxosulphonium ylides with acetylenic ketones and esters.[3,4] In all cases the initial reaction is conjugate addition of the ylides to the triple bonds to give new, allylic ylides. These may then react further with acetylenes or may undergo a variety of intramolecular reactions. Several ylides of this type have been observed to undergo thermal or base-catalysed cyclisation to thiabenzene *S*-oxides (Scheme 1).[4,5] Furans have also been isolated from thermal or photochemical reactions of the ylides, these being formed by an internal displacement of dimethyl sulphoxide.[5,6] The adducts formed from dimethyloxosulphonium methylide and arylpropiolic esters were reported to undergo a base-catalysed rearrangement, followed by the elimination of methanesulphinic acid, to give the butadiene esters (1).[7] This last reaction is the only simple example of a [3,2] sigmatropic rearrangement of an allylic oxosulphonium ylide. In contrast, many such rearrangements of allylic sulphonium ylides are known, and the reaction is a useful method of forming carbon–carbon bonds.[8]



SCHEME 1

The ylide (2a) [1] reacted readily with an equimolar amount of dimethyl acetylenedicarboxylate in dichloromethane at room temperature, to give the sulphoxide (3a) as an unstable orange crystalline solid. The assignment of structure (3a) was based mainly on the ^{1}H n.m.r. spectrum, which showed the presence of only three methyl groups, and a methylene group as a singlet at δ 3.94. No molecular ion was detected in the mass spectrum, but an ion corresponding to the loss of methanesulphinic acid from the molecular ion was observed.

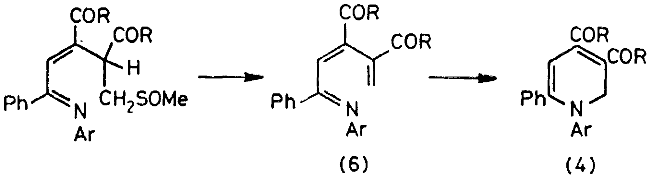
The formation of the sulphoxide (3a) is most easily rationalised by assuming that the conjugate addition of the imidoyl ylide to the acetylenic ester is followed by a sigmatropic rearrangement. In view of the ease with which the rearrangement evidently takes place, it seems surprising that similar reactions have not been observed in the earlier studies. The explanation may be related to the nature of the acetylene involved in the reactions: the rearrangement step (Scheme 2) may be facilitated by the presence of the second methoxycarbonyl group, which can provide additional activation to the terminal carbon



SCHEME 2

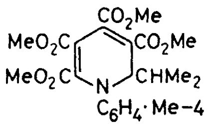
atom of the allyl system. Most of the allylic oxosulphonium ylides which have been prepared previously have lacked such a group. In accordance with this view we found that another doubly activated acetylene, dibenzoylacetylene, reacted in a similar way with the ylide (2a). On the other hand, ethyl propiolate failed to give any characterisable products although it reacted with the ylide (2a). Less activated acetylenes, such as ethyl phenylpropiolate, failed to react.

The sulphoxide (3a) readily lost methanesulphinic acid on heating in solution at 80 °C for 1 h and gave an orange product which was assigned the dihydropyridine structure (4a). The n.m.r. spectrum showed signals at δ 4.80 (2 H, s) and 6.17 (1 H, s) which were assigned to the hydrogen atoms at C-2 and C-5, respectively. Of the 1,2-dihydropyridines previously known, the closest analogous structure appears to be (5), which is a yellow compound with a signal in the n.m.r. spectrum at δ 4.64 for the hydrogen atom at C-2.[9] An alternative structure for the product of thermolysis of (3a), the azatriene (6a), was ruled out on the basis that the n.m.r. signal for the hydrogen atoms of the terminal methylene group of (6a) should be at lower field than that observed. Compound (6a) is, however, the primary product to be expected from cycloelimination of methanesulphinic acid from the sulphoxide (3a) (Scheme 3). It seems likely that this cycloelimination takes place but that the azatriene then undergoes rapid electrocyclic ring-closure to give the dihydropyridine (4a).



a; R = OMe, Ar = $C_6H_4 \cdot NO_2$-4
b; R = OMe, Ar = Ph
c; R = Ph, Ar = $C_6H_4 \cdot NO_2$-4
d; R = Ar = Ph

SCHEME 3



(5)

Three other dihydropyridines (4b—d) were prepared in a similar way from the ylides (2a and b) and dibenzoylacetylene or dimethyl acetylenedicarboxylate. No attempt was made to isolate and characterise the intermediate sulphoxides in these reactions. The overall yields of recrystallised products were in the range 54—59%.

In order to extend the reaction sequence to the preparation of all-carbon ring systems, the oxosulphonium ylides (7), derived from 3-chlorocyclohexenones, were chosen as starting materials. The ylide (7a) had been prepared earlier by Tamura and his co-workers,[10] and (7b) was available from other work.[11] The cyclic enone function of these ylides provides stabilisation (both are isolable solids) but formation of thiabenzene *S*-oxides in the manner shown in Scheme 1 is precluded for steric reasons. Both compounds (7a) and (7b) reacted readily with dimethyl acetylenedicarboxylate at room temperature. The adducts so formed were not isolated, but were heated in solution at 80 °C until no further changes in the composition of the reaction mixtures could be detected by t.l.c. Preparative t.l.c. was then used to separate the components. In each case the major product proved to be the trienone (9) derived from the ylides by conjugate addition, followed by [3,2] sigmatropic rearrangement of the products and loss of methanesulphinic acid. The trienones were then cyclised by heating in xylene.* Compound (9b) gave the bicyclic ketone (10) cleanly, but with compound (9a) a mixture of several bicyclic ketones was produced. Evidently the cyclisation product (11) was disproportionating under the reaction conditions. In the presence of sulphur as a dehydrogenating agent, the aromatic ketone (12) was isolated in moderate yield.

The preparative usefulness of this sequence was reduced by a significant side-reaction in the step leading to the trienones (9). Secondary products were isolated in each case, and these were assigned the structures (13) on the basis of analytical and spectroscopic data. Such compounds could be formed by the conjugate addition of the first-formed allylic ylides (14) to the trienones (9) (Scheme 4). Conjugate addition of stabilised ylides to enones normally results in the formation of cyclopropanes,[8] but cyclopropane structures were incompatible with the n.m.r. spectra of these compounds. It is possible that the sterically crowded ylides (14) cannot readily form the expected cyclopropanes.

The trienone (9b) did, however, react with a less crowded ylide, dimethyloxosulphonium methylide, to form a cyclopropane (15) at the terminal double bond. The structure was established from the ^{1}H n.m.r. spectrum in which two of the vinylic hydrogen signals of the trienone (9b) were replaced by two high-field coupled multiplets, each due to two hydrogen atoms. These were assigned to the hydrogens of the three-membered ring. The other signals present in the spectrum of the trienone also appeared, with little change, in that of the cyclopropane.

The formation of the adducts (13) requires the simultaneous presence in the reaction mixtures of the trienones (9) and the ylides (14). We attempted to minimise this side-reaction in a number of ways, the most successful of which was to prepare the ylides (14) at room temperature and then to add solutions containing the ylides very slowly to boiling xylene, so bringing about the rearrange-

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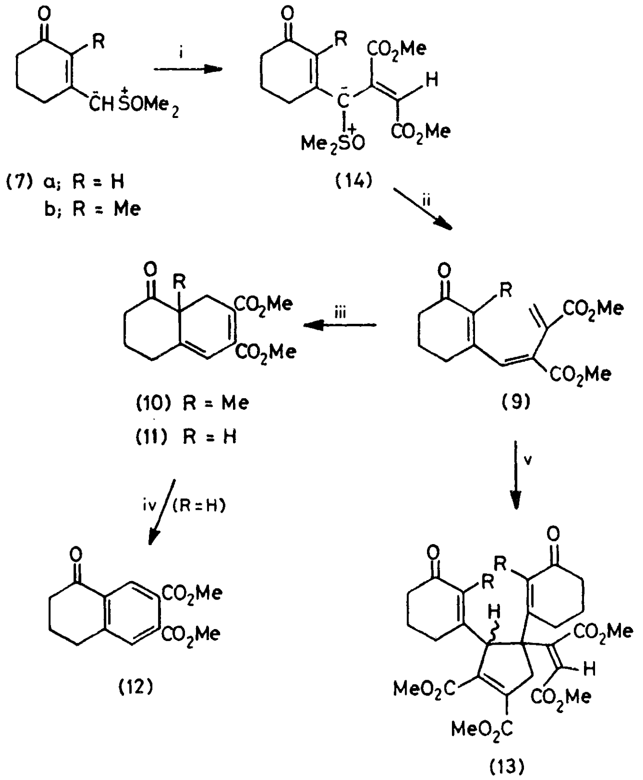
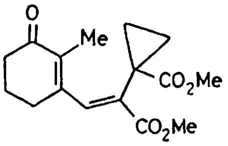
* The stereochemistry of compounds (9) was not established but it is assumed that they can isomerise to the configuration necessary for cyclisation on heating.

ment, elimination, and cyclisation in a 'one-pot' sequence. In this way the ketone (10) was obtained from the ylide (7b) in a yield of 63% and the formation of the side-product (13b) was greatly reduced.



SCHEME 4 *Reagents:* i, $MeO_2CC{\equiv}CCO_2Me$, 20 °C; ii, 80 °C; iii, 138 °C; iv, sulphur, 138 °C; v, (14)

On the basis of this work we conclude that this method of formation of six-membered rings is viable, but probably only for a very limited range of structures. It seems likely that only acetylenes bearing two activating groups can be used in order that the [3,2] shift should go readily, and that, with the all-carbon systems, ylides stabilised by cyclic enone or similar groups will be required, to preclude the formation of thiabenzene *S*-oxides. The method does, however, provide cyclised products, such as (10) and (12), with a pattern of substituents which is not readily available by existing procedures.



(15)

EXPERIMENTAL

I.r. spectra were recorded for liquids as thin films on a Pye Unicam SP 200 instrument, and for solids as KBr discs on a Perkin-Elmer 125 spectrometer, except where indicated otherwise. ^{1}H N.m.r. spectra were obtained for solutions in $CDCl_3$ on a Perkin-Elmer R34B instrument (operating at 220 MHz). U.v. spectra were recorded using a Pye Unicam SP 800 spectrometer and were calibrated against holmium glass. Mass spectra were measured using an A.E.I. MS12 spectrometer with a direct-insertion probe, at 70 eV. Kieselgel PF254 (Merck) or aluminium oxide PF254 (Merck) were used for preparative t.l.c. All preparations were carried out under dry nitrogen, except where indicated otherwise.

2,3-*Bismethoxycarbonyl*-5-(4-*nitrophenylamino*)-5-*phenyl-penta*-2,4-*dienyl Methyl Sulphoxide* (3a).—Dimethyloxosulphonium 2-(4-nitrophenylamino)-2-phenylethylide (2a)[1] (0.100 g, 0.32 mmol) in dry dichloromethane (10 cm^3) was added dropwise during 0.25 h to a stirred solution of dimethyl acetylenedicarboxylate (0.053 g, 0.37 mmol) in dichloromethane (5 cm^3). After a further 1 h the solvent was removed. The residue was purified by precipitation from dry benzene solution by addition of hexane, followed by crystallisation to give the *sulphoxide* (3a) (0.100 g, 68%), m.p. 80 °C (decomp.) (from chloroform–hexane) (Found: C, 57.5; H, 5.05; N, 5.9. $C_{22}H_{22}N_2O_7S$ requires C, 57.6; H, 4.8; N, 6.1%); $\nu_{max.}$ ($CHCl_3$) 3 400 (NH), 1 700 (C=O), 1 590, and 1 320 cm^{-1}; $\lambda_{max.}$ (EtOH) 228 (ε 10 300), 330 (8 700), and 405 nm (17 400); δ 2.64 (3 H), 3.50 (3 H), 3.77 (3 H), 3.94 (2 H), 6.31 (1 H), 6.51 (2 H, d, *J* 9 Hz), 7.16—7.56 (5 H, m), and 7.97 (2 H, d, *J* 9 Hz); *m/e* 394 (M^+ – MeSOH), 335, and 276.

Dimethyl 1,2-*Dihydro*-1-(4-*nitrophenylamino*)-6-*phenyl-pyridine*-3,4-*dicarboxylate* (4a).—The sulphoxide (3a) (0.830 g, 1.81 mmol) was heated under reflux in dry benzene (125 cm^3) for 1 h. Removal of the solvent followed by preparative t.l.c. on silica [chloroform–ethyl acetate (9 : 1 v/v)] and slow crystallisation at 0 °C gave the *dihydropyridine* (4a) (0.390 g, 55%), m.p. 110—112 °C (from ether) (Found: C, 64.2; H, 4.6; N, 7.3. $C_{21}H_{18}N_2O_6$ requires C, 63.95; H, 4.6; N, 7.1%); $\nu_{max.}$ 1 732 and 1 706 cm^{-1} (C=O); δ 3.75 (3 H), 3.90 (3 H), 4.80 (2 H), 6.17 (1 H), 6.94 (2 H, d, *J* 9 Hz), 7.22—7.40 (5 H, m), and 8.00 (2 H, d, *J* 9 Hz); *m/e* 394 (M^+).

Preparation of Other Dihydropyridines. General Procedure.—The *N*-arylbenzimidoyloxosulphonium ylide (2)[1] (1.0 mmol) in dry dichloromethane (45 cm^3) was added dropwise during 0.25 h to the appropriate acetylene (1.1 mmol) in dichloromethane (15 cm^3) and the mixture was kept at room temperature for 1 h. The solution was then evaporated and the residue was heated in dry benzene (75 cm^3) under reflux for 1 h (3 h in the case of dibenzoylacetylene adducts). The product was isolated by preparative t.l.c. on silica [chloroform–ethyl acetate (19 : 1 v/v)]. The following dihydropyridines were prepared in this way: *dimethyl* 1,2-*dihydro*-1,6-*diphenylpyridine*-3,4-*dicarboxylate* (4b) (54%), m.p. 108—110 °C (from ether) (Found: C, 72.4; H, 5.6; N, 4.2. $C_{21}H_{19}NO_4$ requires C, 72.2; H, 5.5; N, 4.0%); $\nu_{max.}$ 1 722 and 1 692 cm^{-1} (C=O); δ 3.71 (3 H), 3.90 (3 H), 4.81 (2 H), 5.91 (1 H), and 6.90—7.42 (10 H, m); *m/e* 349 (M^+); 3,4-*dibenzoyl*-1,2-*dihydro*-1-(4-*nitrophenyl*)-6-*phenylpyridine* (4c) (57%), m.p. 147—149 °C (decomp.) (from ether) (Found: C, 76.5; H, 4.5; N, 5.8. $C_{31}H_{22}N_2O_4$ requires C, 76.5; H, 4.6; N, 5.8%); $\nu_{max.}$ 1 658 cm^{-1} (C=O); δ 5.03 (2 H), 6.51 (1 H), 7.07 (2 H, d, *J* 9 Hz), 7.13—7.57 (15 H, m), and 8.08 (2 H, d, *J* 9 Hz); *m/e* 486 (M^+); and 3,4-*dibenzoyl*-1,2-*dihydro*-1,6-*diphenylpyridine* (4d) (59%), m.p. 105—106 °C (decomp.) (from benzene–hexane) (Found: C, 84.55; H, 5.5; N, 3.0. $C_{31}H_{23}NO_2$ requires C, 84.3; H, 5.3; N, 3.2%); $\nu_{max.}$ 1 652 cm^{-1}

(C=O); δ 4.99 (2 H), 6.27 (1 H), and 7.02—7.67 (20 H, m); *m/e* 441 (M^+).

Reaction of Dimethyloxosulphonium-3-oxocyclohex-1-enylmethylides with Dimethyl Acetylenedicarboxylate and Solution Pyrolysis of the Resulting 1 : 1 *Adducts*.—(a) *Dimethyloxosuphonium-3-oxocyclohex-1-enylmethylide* (7a).[10] The ylide (7a) (0.500 g, 2.69 mmol) in dry dichloromethane (15 cm^3) was added dropwise during 0.25 h to a solution of dimethyl acetylenedicarboxylate (0.420 g, 29.6 mmol) in dichloromethane (25 cm^3). After 1 h the solvent was removed and the residue was heated in benzene (60 cm^3) under reflux for 3 h. Preparative t.l.c. on silica [chloroform–ethyl acetate (9 : 1 v/v)] gave, as the less mobile component, 1-(3-*oxocyclohex*-1-*enyl*)-2,3-*bismethoxycarbonylbuta*-1,3-*diene* (9a), an oil (0.290 g, 41%); $\nu_{max.}$ 1 715 and 1 665 cm^{-1} (C=O); δ 1.93—2.11 (2 H, m), 2.30—2.50 (4 H, m), 3.79 (3 H), 3.80 (3 H), 5.74 (1 H), 6.10 (1 H), 6.50 (1 H), and 7.38 (1 H); 264 (M^+). A faster-running band gave *dimethyl* 4-(1,2-*bismethoxycarbonylvinyl*)-3,4-*bis*-(3-*oxocyclohex*-1-*enyl*)*cyclopentene*-1,2-*dicarboxylate* (13a) (0.035 g, 5%), m.p. 181—183 °C (from dichloromethane–hexane) (Found: C, 63.1; H, 5.8. $C_{27}H_{30}O_{10}$ requires C, 63.0; H, 5.9%); $\nu_{max.}$ 1 728 and 1 662 cm^{-1} (C=O); δ 1.99—2.52 (13 H, m), 2.73 (1 H, d, *J* 17.5 Hz), 3.71 (3 H), 3.73 (3 H), 3.75 (3 H), 3.79 (3 H), 4.27 (1 H), 5.82 (1 H), 5.85 (1 H), and 6.40 (1 H).

The trienone (9a) was thermolysed under the following conditions. (i) The trienone (0.095 g, 0.36 mmol) and sulphur (0.028 g) were heated in dry xylene (4 cm^3) under reflux for 24 h. The major component was separated by preparative t.l.c. on silica [chloroform–ethyl acetate (4 : 1 v/v)] and gave *dimethyl* 1-*oxo*-1,2,3,4-*tetrahydronaphthalene* 6,7-*dicarboxylate* (12) as an oil (0.041 g 44%); $\nu_{max.}$ 1 720 and 1 685 cm^{-1} (C=O); δ 2.15—2.30 (2 H, m), 2.74 (2 H, t, *J* 7 Hz), 3.07 (2 H, t, *J* 7 Hz), 3.94 (3 H), 3.96 (3 H), 7.58 (1 H), and 8.49 (1 H); *m/e* 262 (M^+). The 2,4-*dinitrophenylhydrazone* of (12) had m.p. 250—251 °C (from acetonitrile) (Found: C, 54.6; H, 4.4; N, 14.4. $C_{20}H_{18}N_4O_8$·MeCN requires C, 54.7; H, 4.4; N, 14.5%). (ii) The trienone (9a) (0.245 g, 0.93 mmol) was heated in xylene (4 cm^3) under nitrogen for 24 h. Preparative t.l.c. gave, as the most mobile component, the ketone (12) (0.050 g, 21%). Two further bands were removed but the components were unstable in air and gave a mixture which was again subjected to preparative t.l.c. This gave three major components, one of which was not identified. The others were characterised as the ketone (12) (9 mg, 4%) and *dimethyl* 1-*oxo*-1,2,3,4,5,6,7,8-*octahydronaphthalene*-6,7-*dicarboxylate*, an oil (0.020 g, 8%); δ 1.85—2.07 (2 H, m), 2.23—2.62 (6 H, m), 2.70—2.90 (2 H, m), 2.92—3.05 (1 H, m), 3.10—3.20 (1 H, m), 3.67 (3 H), and 3.69 (3 H); characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 161—162 °C (from ether) (Found: C, 53.9; H, 5.0; N, 12.4. $C_{20}H_{22}N_4O_8$ requires C, 53.8; H, 5.0; N, 12.55%); *m/e* 446 (M^+).

(b) *Dimethyloxosulphonium* 2-*methyl*-3-*oxocyclohex*-1-*enylmethylide* (7b).[11] (i) A solution of the ylide (7b) (0.400 g, 2.00 mmol) in dichloromethane (10 cm^3) was added dropwise during 0.25 h to a stirred solution of dimethyl acetylenedicarboxylate (0.310 g, 2.18 mmol) in dichloromethane (30 cm^3). After a further 1 h the solvent was removed and the residue was heated in dry benzene (60 cm^3) for 3 h. Preparative t.l.c. on silica [chloroform–ethyl acetate (9 : 1 v/v)] gave, as the less mobile component, 1-(2-*methyl*-3-*oxocyclohex*-1-*enyl*)-2,3-*bismethoxycarbonylbuta*-1,3-*diene* (9b), an oil (0.260 g, 47%); δ 1.79 (3 H), 1.84—2.02 (2 H, m), 2.32—2.52 (4 H, m), 3.79 (6 H), 5.65 (1 H), 6.42 (1 H), and 7.60 (1 H). A second fraction from the plate gave *dimethyl* 4-(1,2-*bismethoxycarbonylvinyl*)-3,4-*bis*-(2-*methyl*-3-*oxocyclohex*-1-*enyl*)*cyclopentene*-1,2-*dicarboxylate* (13b) as a gum (0.200 g, 37%); δ 1.63 (3 H), 1.84 (3 H), 1.90—2.09 (4 H, m), 2.25—2.55 (8 H, m), 3.51 (3 H), 3.65 (3 H), 3.70 (3 H), 3.74 (3 H), 4.46 (1 H), and 6.71 (1 H); characterised as its *bis*-2,4-*dinitrophenylhydrazone*, m.p. 165—168 °C (decomp.) (Found: C, 55.2; H, 5.0; N, 12.4. $C_{41}H_{42}N_8O_{16}$ requires C, 54.50; H, 4.7; N, 12.4%); and its *mono*-2,4-*dinitrophenylhydrazone*, m.p. 198—199 °C (from ether–hexane) (after separation from the bis-hydrazone by preparative t.l.c. on alumina) (Found: C, 58.6; H, 5.3. $C_{35}H_{38}N_4O_{13}$ requires C, 58.2; H, 5.3%).

The trienone (9b) (0.140 g, 0.50 mmol) was cyclised by heating in xylene (4 cm^3) under reflux for 24 h. This gave, after preparative t.l.c. on silica [chloroform–ethyl acetate (2 : 1 v/v)] *dimethyl* 1-*oxo*-1,2,3,4,8,8a-*hexahydro*-8a-*methylnaphthalene*-6,7-*dicarboxylate* (10) (0.090 g, 64%) as an oil; $\nu_{max.}$ 1 730, 1 710, and 1 660 cm^{-1} (C=O); δ 1.28 (3 H), 2.00—2.15 (2 H, m), 2.40—2.56 (4 H, m), 2.61 (1 H, d, *J* 18 Hz), 2.90 (1 H, d, *J* 18 Hz), 3.70 (3 H), 3.79 (3 H), and 7.00 (1 H); characterised as its 2,4-*dinitrophenylhydrazone* m.p. 271—272 °C (from dichloromethane–hexane) (Found: C, 55.1; H, 4.9; N, 12.4. $C_{21}H_{22}N_4O_8$ requires C, 55.0; H, 4.8; N, 12.2%); *m/e* 458 (M^+).

(ii) A solution of the ylide (7b) (0.200 g, 1.00 mmol) in dry dichloromethane (15 cm^3) was added during 0.25 h to a solution of dimethyl acetylenedicarboxylate (0.160 g, 1.13 mmol) in dichloromethane (5 cm^3). After a further 1 h the solvent was removed and the residue was dissolved in xylene (10 cm^3). This solution was then added dropwise during 5 h to xylene (20 cm^3) which was being heated under reflux. After a further 16 h at reflux the products were separated by preparative t.l.c. on silica [chloroform–ethyl acetate (2 : 1 v/v)] which gave the cyclopentene (13b) (0.016 g, 6%) and the naphthalenone (10) (0.176 g, 63%).

Addition of Dimethyloxosulphonium Methylide to the Trienone (9b).—Dimethyloxosulphonium methylide (1.0 cm^3 of a 0.59M-solution in tetrahydrofuran[12]) was added dropwise to a stirred solution of the trienone (9b) (0.136 g, 0.49 mmol) in tetrahydrofuran (15 cm^3) at 20 °C and the resulting deep red solution was stirred at room temperature for 0.5 h then at reflux for 0.5 h. The solvent was removed; preparative t.l.c. on silica [chloroform–ethyl acetate 19 : 1 (v/v)] gave the *cyclopropane* (15) as an oil (0.080 g, 56%); $\nu_{max.}$ 1 715 and 1 660 cm^{-1} (C=O); δ 1.10—1.18 (2 H, m), 1.50—1.62 (2 H, m), 1.67 (3 H), 1.95—2.10 (2 H, m), 2.34—2.50 (4 H, m), 3.67 (3 H), 3.72 (3 H), and 6.61 (1 H); characterised as its 2,4-*dinitrophenylhydrazone*, m.p. 149—153 °C (from dichloromethane–hexane) (Found: C, 55.7; H, 5.15; N, 12.1. $C_{22}H_{24}N_4O_8$ requires C, 55.9; H, 5.1; N, 11.9%); *m/e* 472 (M^+).

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