Syntheses of 1-substituted furan-fused 3-sulfolenes and their Diels–Alder reactions

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The preparation of 1-substituted 4*H*,6*H*-dihydrothieno[3,4-*c*]furan 5,5-dioxides and their intermolecular Diels–Alder reactions with typical dienophiles are described. 1-Acetyl-1d and 1-nitro-furansulfolene 1e were prepared by simple new methods. Acetyl and nitro substituents in the furan moiety did little to diminish its Diels–Alder reactivity relative to the corresponding furans. Furthermore, on reaction with dimethyl fumarate, 1-acetylfuransulfolene 1d acted like the corresponding 3,4-dimethylenefuran.

Introduction

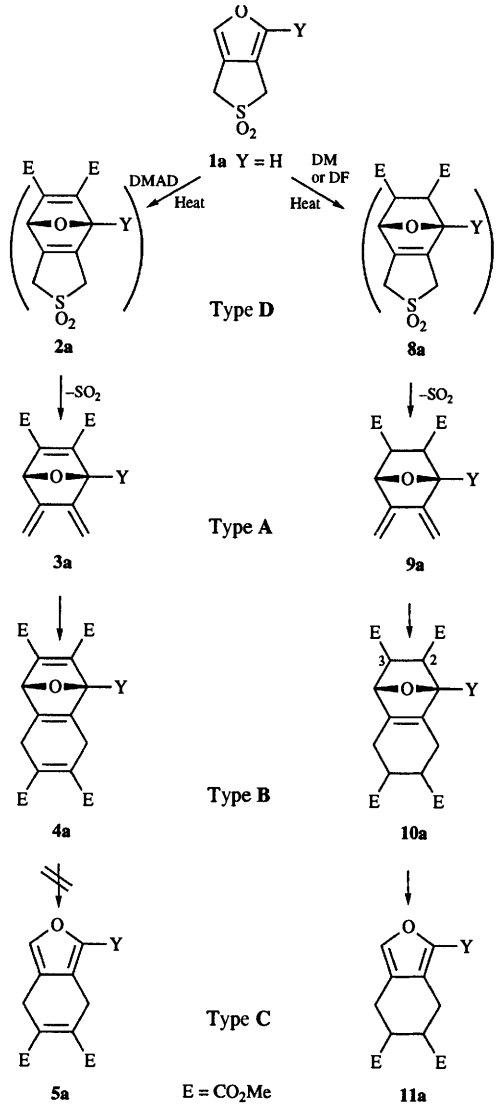
Furansulfolene, 4*H*,6*H*-dihydrothieno[3,4-*c*]furan 5,5-dioxide **1a** (Y = H), appears to be a useful masked bis-diene exhibiting versatility in Diels–Alder reactions. Depending on the reaction conditions and dienophiles, **1a** sequentially reacted with the latter to produce four types of cycloadducts.[1] The 3-sulfolene function of **1a** reacts not only as a s-*cis* diene in Diels–Alder reactions but also widens the scope of such reactions for the furan moiety to react with dienophiles as a result of its desulfonylation to form a s-*cis* diene. Thus, the furansulfolene **1a** reacts with dienophiles such as dimethyl maleate, dimethyl fumarate and *p*-benzoquinone to give Diels–Alder adducts of furan not accessible under thermal conditions. Scheme 1 illustrates the Diels–Alder reaction of **1a** with dimethyl acetylenedicarboxylate (DMAD), dimethyl maleate (DM) and dimethyl fumarate (DF) under thermal conditions. The formation of a type **C** adduct was observed only when 2*endo*,3*endo*-**10a** (type **B**) was heated at 150 °C for 1 h. Treatment of other type **B** adducts, **4** and **10**, under more drastic conditions gave recovery of starting material.

As a continuation of our studies on the chemistry of furansulfolene for the syntheses of variously substituted multicyclic molecules, we have investigated the reactivity of its furan moiety having substituents at the α-position in Diels–Alder reactions. Here we report the preparation of **1b–e** and the results of Diels–Alder reactions.

Results and discussion

Modification of the furan ring

Bromination, acetylation and alkylation of furan rings is usually achieved *via* lithiofuran,[2] but this was not possible for the furansulfolene **1a** because of the activated α-methylene adjacent to the SO_2 group. Bromination of **1a** by NBS (1.1 equiv.) in benzene at 100 °C gave the desired monobromide **1b** (Y = Br) (24%) together with a dibromide (17%) and recovered **1a** (17%). The best yield (35%) of the bromofuransulfolene **1b** was obtained on treating **1a** with Br_2–dioxane complex in dioxane.[3] Since acetylation of furan rings is usually achieved with acetic toluene-*p*-sulfonic anhydride,[4] we tried initially to prepare this reagent by the reported method from acetyl chloride and toluene-*p*-sulfonic anhydride, but failed. Thus, reaction of toluene-*p*-sulfonyl chloride and silver acetate in acetonitrile at 130 °C for 1 h gave an unsatisfactory yield of the reagent (^{1}H NMR measurement) and afforded only 16% yield of the desired acetylfuransulfolene (the recovery of **1a** was 82%). In contrast, the facile acetylation of **1a** with acetic toluene-*p*-sulfonic anhydride, prepared conveniently from acetyl chloride and silver toluene-*p*-sulfonate, in acetonitrile at 50 °C for 9 h gave acetylfuransulfolene **1d** (Y = Ac) in 80% yield. The nitration of **1a** with nitronium tetrafluoroborate[5] in diethyl ether at 0 °C resulted only in consumption of **1a**. A simple method for generating nitronium trifluoromethanesulfonate from nitronium tetrafluoroborate and silver trifluoromethanesulfonate in the presence of **1a** at −40 °C afforded a 37% yield of the desired nitrofuransulfolene **1e** (Y = NO_2).



Scheme 1

Table 1 Reaction of furansulfonenes **1b–c** with dienophiles at 120 °C

No.	Sulfolene	Dienophile	React. time (h)	Products (isolated yield, %) Type A	Type B	Type C	Others	Total yield (%)
1	**1b** (Y = Br)	DMAD[a]	4.5	**3b** (58)	**4b** (17)			75
2	**1c** (Y = Ar[c])	DMAD	4.5	**3c** (31)	**4c** (27)			58
3	**1d** (Y = Ac)	DMAD	6.0	**3d** (14)	**4d** (57)	**5d** (16)		87 (10)[b]
4	**1e** (Y = NO_2)	DMAD	24.0				**7e** (14)	14
5	**1b**	DM[d]	22.0	**9b** (*cis-endo* 49) (*cis-exo* 4)				53
6	**1d**	DM	24.0	**9d** (*cis-endo* 13) (*cis-exo* 4)				17 (70)[b]
7	**1e**	DM	24.0	**9e** (*cis-endo* 10)				10
8	**1b**	DF[e]	20.0	**9b** (2*endo*,3*exo* 13) (2*exo*,3*endo* 7)		**11b** (11)		31
9	**1d**	DF	20.0	**9d** (2*endo*,3*exo* 7) (2*exo*,3*endo* 5)		**11d** (10)		22 (73)
10	**1e**	DF	24.0			**11e** (11)		11

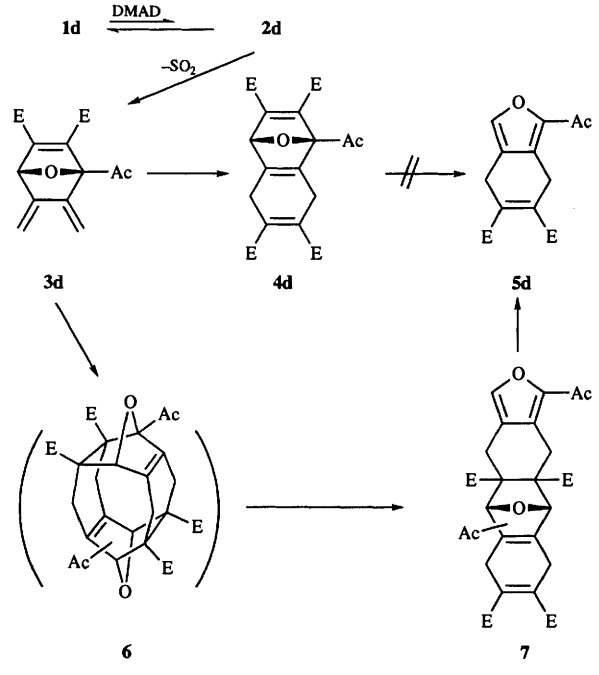
[a] DMAD = dimethyl acetylenedicarboxylate. [b] Recovery of the furansulfolene. [c] Ar = *p*-$MeOC_6H_4$. [d] DM = dimethyl maleate. [e] DF = dimethyl fumarate.

The tetrakis(triphenylphoshine)palladium(0)-catalysed cross-coupling of **1b** with *p*-methoxyphenyl(trimethyl)tin[6] in dioxane at 105 °C proceeded smoothly to afford phenylfuransulfolene **1c** (Y = *p*-$MeOC_6H_4$) in 57% yield. The structures of all new furansulfolenes were confirmed from their spectral results.

Diels–Alder reaction of the furansulfolenes with DMAD

The Diels–Alder reaction of the bromofuransulfolene **1b** with DMAD (3 equiv.) took place at 120 °C (benzene; sealed tube) to afford two types of cycloadducts, type **A 3b** (58%) and type **B 4b** (17%) in 75% total yield (Table entry 1).

As compared with the 1 h reaction of the non-substituted furansulfolene **1a** with DMAD, the reaction of **1b** at the same temperature needed 6 h.[1] A similar reaction of the phenyl-substituted **1c** with DMAD produced the same type adducts, **3c** and **4c**, containing the hoped for skeletal features of lignan lactones of the podophyllotoxin series (entry 2). In striking contrast to reports that furans containing electron-withdrawing groups, such as furfural and 2-acetylfuran, are poor dienes in Diels–Alder reactions,[7] we found that 1-acetylfuransulfolene **1d** was very reactive towards DMAD giving not only **3d** and **4d** but also the unexpected monocycloadduct **5d** in high total yield (entry 3). The formation of the type **C** adduct **5d** under these reaction conditions (120 °C, 6 h) was of interest because the isolated type **B** adduct **4d** failed to undergo the retro-Diels–Alder reaction to afford the type **A** adduct **3d** or the type **C** adduct **5d** under more drastic conditions (150 °C for 2 h, 180 °C for 2 h and 200 °C for 2 h). In these reactions, only slow decomposition was observed and **4d** was recovered (86%). The treatment of **5d** with DMAD (1.5 equiv.) in benzene at 120 °C for 6 h (sealed tube) gave only recovery of **5d**. Treatment of the type **A** adduct **3d** with DMAD (1.5 equiv.) in benzene at 120 °C for 6 h (sealed tube) gave the type **C** adduct **5d** (21%) and the type **B** adduct **4d** (36%). Furthermore, the treatment of **3d** in benzene at 120 °C for 6 h (sealed tube) afforded **5d** in 73% yield. Formation of **5d**, therefore, may be rationalized in terms of a reaction pathway *via* **3d**; first, two molecules of **3d** undergo an intermolecular Diels–Alder reaction to afford a cyclic dimer, which is then converted into a linear dimer **7**; a retro-Diels–Alder reaction of this linear dimer then affords a type **C** adduct **5d** (Scheme 2).†



Scheme 2

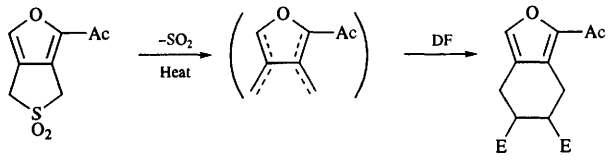
Incorporation of an acetyl group into the bridgehead of the type **A** adduct made the endocyclic olefin a favourable dienophile. Similarly, the nitrofuransulfolene **1e** resulted in a linear dimer **7e** (entry 4), but the reaction was complex. The carbon framework of **7e** was confirmed on the basis of its ^{13}C NMR spectrum; 4 carbonyl carbons (δ 169.9, 167.4, 167.3 and 161.2

† The possibility of the formation of **5d** *via* **12d** (3,4-dimethylenefuran, Scheme 3), formed by retro-Diels–Alder elimination of DMAD from **3d**, cannot be rejected.

ppm), 10 quaternary carbons (δ 161.1, 150.9, 149.5, 149.4, 142.7, 140.6, 132.6, 131.1, 122.6 and 121.8 ppm), 2 methyne carbons (δ 147.6 and 81.2 ppm), 4 methyl carbons (δ 53.2, 53.1, 52.6 and 50.9 ppm) and 4 methylene carbons (δ 27.5, 27.3, 26.8 and 26.3 ppm). Its ^{1}H NMR spectrum showed 1 aromatic proton as a singlet at δ 8.08 ppm, the bridgehead proton as a singlet at δ 5.97 ppm, as well as signals for the remaining 12 methyl and 8 methylene protons.

Diels–Alder reaction of the furansulfolenes with ethylenedicarboxylate

With dimethyl maleate as a dienophile, the bromofuransulfolene **1b** reacted at 120 °C for 22 h to give two isomers of type **A** adduct, *endo*- and *exo*-**9b**, in 53% total yield (entry 5). At the same temperature, the acetylfuransulfolene **1d** gave **9d** in 56.6% yield (based on the consumption of **1d**) (entry 6). These results showed that bromo and acetyl substituents in the furansulfolene did not prevent the Diels–Alder reaction of the furan with dimethyl maleate. The reaction of the nitrofuransulfolene **1e** with dimethyl maleate was complex and gave *endo*-**9e** (10%) (entry 7). Interestingly, in contrast to the reaction of dimethyl maleate these furansulfolenes reacted with dimethyl fumarate to give the adducts **11**. These results were in contrast to our experience with the type **B** adduct **10a** obtained from **1a** and dimethyl fumarate which was resistant to retro-Diels–Alder reactions, the formation of a type **C** adduct not being observed. Cycloaddition of the acetylfuransulfolene **1d** to dimethyl fumarate was slow but gave the type **C** adduct **11d** (37% yield based on the consumption of **1d**) and a type **A** adduct **9d** (44% yield based on the consumption of **1d**). Similarly, **1b** and dimethyl fumarate gave **9b** and **11b**. Furthermore, the nitro-substituted type **C** adduct **11e** was obtained in 11% yield (entry 10). Treatment of the isolated **9d** with dimethyl fumarate at the same temperature gave only recovery of starting material. This result suggested that the type **C** adduct **11d** was not formed *via* a retro-Diels–Alder product of the corresponding type **B** adduct but, rather, by reaction of the sulfolene moiety with dimethyl fumarate (Scheme 3).‡



1d **12d** **11d**

Scheme 3

In summary, we have developed new and simple methods for the acetylation and nitration of furansulfolene. The acetyl and nitro electron-withdrawing substituents in the furan moiety diminished its reactivity toward DMAD very little compared with the corresponding furans. The key to a favourable equilibrium for product formation lies in rapid SO_2 extrusion from the initially formed adducts **4**. Acetyl and nitro substituents in type **A** adducts made the endocyclic olefins more powerful than DMAD, and this led to the formation of type **C** adducts. In the reaction with dimethyl fumarate, and 1-substituted furansulfolenes acted like the corresponding 3,4-dimethylenefurans.[8]

Experimental

The melting points (Yamaco Micro Melting Point apparatus) are uncorrected. The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were determined for $CDCl_3$ solutions containing *ca.* 1% TMS as an internal standard with a JEOL GSX-400 spectrometer; J values are given in Hz. Column chromatography was performed on silica gel (Wakogel C-200). All reactions were conducted under an argon atmosphere unless otherwise stated.

Bromination of 1a

To a solution of **1a** (50.0 mg, 0.32 mmol) in dioxane (1 cm^3) was added Br_2–dioxane complex (87 mg, 1.1 equiv.) and the mixture was heated at 50 °C for 1.5 h. It was then diluted with $CHCl_3$, washed with brine, dried ($MgSO_4$) and evaporated. The residual oil was chromatographed on silica gel. Elution with ethyl acetate–hexane (1:4) afforded compound **1b** (26.5 mg, 35.0%) as a colourless oil and **1a** (14%).

1-*Bromo*-4H,6H-*thieno*[3,4-c]*furan* 5,5-*dioxide* **1b**: δ_H 4.06 (2 H, s, 6-H), 4.21 (2 H, d, J 1.53, 4-H) and 7.48 (1 H, t, J 1.53, 3-H); δ_C 51.22 (t, 4-C), 52.35 (t, 6-C), 117.09 (s, 6a-C), 118.01 (s, 3a-C or 1-C), 118.93 (s, 1-C or 3a-C) and 139.41 (d, 3-C); *m/z* 238, 236 (M$^+$, 3.09, 3.13%), 174, 172 (M$^+$ − SO_2, 17.40, 17.05%) [Found (HRMS): *m/z* 235.9165. Calc. for $C_6H_5O_3BrS$: 235.9142].

Cross-coupling of the dioxide 1b

p-Methoxyphenyl(trimethyl)tin, obtained by [Pd(PPh$_3$)$_4$]-catalysed reaction of *p*-iodoanisole and hexamethylditin (2 equiv.) in toluene at 115 °C for 15 h, was used without purification. To a solution of **1b** (24 mg, 0.10 mmol) in dioxane (1 cm^3), *p*-methoxyphenyl(trimethyl)tin (60 mg, 2 equiv.) and [Pd(PPh$_3$)$_4$] were added and the mixture was heated and stirred at 105 °C for 24 h in a sealed tube. The mixture was then diluted with Et_2O, filtered through a short column of aluminum oxide and evaporated to give a residue which was chromatographed on silica gel. Elution with ethyl acetate–hexane (1:4) gave compound **1c** (15 mg, 57%) as a viscous yellow oil.

1-(4-*Methoxyphenyl*)-4H,6H-*thieno*[3,4-c]*furan* 5,5-*dioxide* **1c**: δ_H 3.85 (3 H, s, CH_3O), 4.19 (2 H, d, J 1.60, 4-H), 4.33 (2 H, s, 6-H), 6.97 (2 H, d, J 9.0, benzene ring H), 7.42 (1 H, t, J 1.60, 3-H) and 7.47 (2 H, d, J 9.0, benzene ring H); *m/z* 264 (M$^+$, 14.70%) and 200 (M$^+$ − SO_2, 68.48%) [Found (HRMS): *m/z* 264.0457. Calc. for $C_{13}H_{12}O_4S$: 264.0456].

Acetylation of 1a

To a solution of TsOAg (558 mg, 2 mmol) in dry CH_3CN (2 cm^3) was added acetyl chloride (0.142 cm^3, 2 equiv.) and the mixture, in a sealed tube, was heated at 130 °C for 1 h. It was then allowed to cool to room temperature and **1a** (158 mg, 1 mmol) was added to it. The mixture was stirred and heated at 50 °C for 9 h after which it was diluted with $CHCl_3$, washed with sat. aqueous $NaHCO_3$ and brine, dried (Na_2SO_4) and evaporated. The residue was purified by silica gel chromatography (20% ethyl acetate in hexane) to give the desired product **1d** (160 mg, 80%) as colourless plates and **1a** (14%).

1-*Acetyl*-4H,6H-*thieno*[3,4-c]*furan* 5,5-*dioxide* **1d**: mp 132.0–134 °C (benzene); δ_H 2.52 (3 H, s, CH_3CO), 4.18 (2 H, d, J 1.53, 4-H), 4.38 (2 H, s, 6-H) and 7.53 (1 H, t, J 1.53, 3-H); δ_C 26.19 (q, *C*H$_3$CO), 51.01 (t, 4-C), 52.91 (t, 6-C), 119.57 (s, 6a-C or 3a-C), 123.52 (s, 3a-C or 6a-C), 139.35 (d, 3-C), 147.35 (s, 1-C) and 187.25 (s, CH$_3$*C*O); *m/z* 200 (M$^+$, 5.59%) and 136 (M$^+$ − SO_2, base); ν_{max}($CHCl_3$)/cm^{-1} 1680, 1330, 1130 and 928 [Found (HRMS): *m/z* 200.0140. Calc. for $C_8H_8O_4S$: 200.0143].

Nitration of 1a

To a solution of nitronium tetrafluoroborate (84 mg, 1.0 equiv.) in dry acetonitrile (1 cm^3) at −40 °C were added **1a** (100 mg, 0.63 mmol) and silver trifluoromethanesulfonate (162 mg, 1.0 equiv.). After being stirred at the same temperature for 1.5 h, the mixture was diluted with $CHCl_3$, washed with 10% aqueous Na_2CO_3 and brine, dried (Na_2SO_4) and evaporated. Column

‡ When suitable dienophiles coexist, the Diels–Alder reaction of the furan moiety of **1** with them predominates over the desulfonylation of the sulfolene part of **1**. In the case of no suitable dienophiles, the desulfonylation proceeds to form 3,4-dimethylenefuran **12**.

chromatography of the residue on silica gel yielded compound **1e** (47 mg, 37.0%) as yellow plates. When the reaction temperature was higher than −40 °C, the yield of **1e** was lower (0 °C, 10%; −20 °C, 15%). Nitration of **1a** with nitronium tetrafluoroborate in ether at 0 °C was complex and failed to afford **1e**.

1-*Nitro*-4H,6H-*thieno*[3,4-c]*furan* 5,5-*dioxide* **1e**: 194.0–196.0 °C (from ethyl acetate); δ_H 4.27 (2 H, d, *J* 1.52, 4-H), 4.50 (2 H, s, 6-H) and 7.57 (1 H, t, *J* 1.52, 3-H); δ_C 51.90 (t, 4-C), 52.98 (t, 6-C), 121.49 (s, 3a-C or 6a-C), 122.63 (s, 6a-C or 3a-C) and 141.20 (d, 3-C); 1-C singlet signal was not observed; *m/z* 203 (M^+, 1.07%), 139 ($M^+ - SO_2$, 5.94%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1530, 1370, 1345, 1135, 1010 and 840 [Found (HRMS): *m/z* 202.9866. Calc. for $C_6H_5O_4NS$: 202.9888].

Diels–Alder reaction of 1b with DMAD

A solution of **1b** (30 mg, 0.13 mmol), 4-methoxyphenol (5 mg) and DMAD (0.047 cm^3, 3 equiv.) in dry benzene (1 cm^3) was heated at 120 °C for 4.5 h in a sealed tube. After concentration of the mixture, the residue was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give compound **3b** (23 mg, 58%) and compound **4b** (10 mg, 17%) as yellow oils.

Dimethyl 1-bromo-5,6-dimethylidene-7-oxabicyclo[2.2.1]-hept-2-ene-2,3-dicarboxylate **3b**; δ_H 3.80 (3 H, s, CH_3OCO), 3.86 (3 H, s, CH_3OCO), 5.36 [1 H, s, C*H*H=C(5 or 6)], 5.46 [1 H, s, C*H*H=C(5 or 6)], 5.51 [1 H, s, C*H*H=C(5 or 6)], 5.62 [1 H, s, C*H*H=C(5 or 6)] and 5.64 [1 H, s, C*H*H=C(5 or 6)]; δ_C 52.7 (q, *C*H_3OCO), 52.9 (q, *C*H_3OCO), 82.4 (d, 4-C), 106.3 [t, *C*H_2=C(5 or 6)], 108.8 [t, *C*H_2=C(5 or 6)], 138.6 (s, 2-, 3-, 5- or 6-C), 139.7 (s, 2-, 3-, 5- or 6-C), 141.9 (s, 2-, 3-, 5- or 6-C), 147.1 (s, 2-, 3-, 5- or 6-C), 160.8 (s, *C*OOMe), 162.7 (s, *C*OOMe). The ^{13}C NMR spectrum of **3b** showed only four singlet signals for the quaternary carbons of the ring, that for 1-C-Br probably not being observed; *m/z* 316, 314 (M^+, 0.29, 0.32%), 257, 255 (M^+ − COOMe, 4.19, 4.17%) and 235 (M^+ − Br) [Found (HRMS): *m/z* 315.6784. Calc. for $C_{12}H_{11}O_5Br$: 315.9769].

Tetramethyl 1-bromo-1,4-epoxy-1,4,5,8-tetrahydronaphthalene-2,3,6,7-tetracarboxylate **4b**: δ_H 3.14–3.16 (1 H, m, 5- or 8-H), 3.18–3.22 (1 H, m, 5- or 8-H), 3.42–3.45 (1 H, m, 5- or 8-H), 3.47–3.50 (1 H, m, 5- or 8-H), 3.79 (3 H, s, CH_3OCO), 3.81 (6 H, s, 2 × CH_3OCO), 3.90 (3 H, s, CH_3OCO) and 5.57 (1 H, s, 4-H); δ_C 26.3 (t, 5-C or 8-C), 27.7 (t, 5-C or 8-C), 52.5 (q, *C*H_3OCO), 52.7 (q, *C*H_3OCO), 52.8 (q, *C*H_3OCO), 52.9 (q, *C*H_3OCO) and 83.7 (d, 4-C); although a singlet for 1-C-Br was not observed, 11 singlets for 7 quaternary carbons of the ring and 4 carbonyl carbons were observed as follows: 132.1 (s), 132.5 (s), 145.8 (s), 146.6 (s), 149.2 (s), 156.0 (s), 161.9 (s), 163.7 (s), 167.8 (s), 168.1 (s) and 208.3 (s); *m/z* 427, 425 (M^+ − OMe, 3.15, 3.25%), 346 (M^+ − OMe − **Br**, 4.32%), (CI) 458 and 456 (M^+) [Found (HRMS): *m/z* 424.9709. Calc. for $C_{18}H_{17}O_9Br$: 424.9871].

Diels–Alder reaction of 1c with DMAD

A solution of **1c** (20 mg, 0.08 mmol), 4-methoxyphenol (2 mg) and DMAD (0.028 cm^3, 3 equiv.) in dry benzene (1 cm^3) was heated at 120 °C for 4 h in a sealed tube. After concentration, the residue was purified by silica gel column chromatography (hexane–AcOEt, 9:1) to give compound **3c** (8 mg, yield 31%) and compound **4c** (10 mg, 27%) as yellow oils.

Dimethyl 1-(4′-methoxyphenyl)-5,6-dimethylidene-7-oxabicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate **3c**: δ_H 3.78 (3 H, s, CH_3O), 3.80 (3 H, s, CH_3O), 3.83 (3 H, s, CH_3O); 5 singlets for 4-H and CH_2=C(5) and CH_2=C(6) were observed as follows: 5.24 (1 H, s), 5.35 (1 H, s), 5.44 (1 H, s), 5.54 (1 H, s), 5.63 (1 H, s), 6.94 (2 H, d, *J* 8.0, benzene ring) and 7.45 (2 H, d, *J* 8.0, benzene ring); *m/z* 342 (M^+, 12.23%), 311 (M^+ − OMe, 1.27%).

Tetramethyl 1,4-epoxy-(4′-methoxyphenyl)-1,4,5,8-tetrahydronaphthalene-2,3,6,7-tetracarboxylate **4c**: δ_H 3.20 (1 H, m, 5- or 8-H), 3.32 (1 H, m, 5- or 8-H), 3.48 (1 H, m, 5- or 8-H), 3.62 (1 H, m, 5- or 8-H), 3.73 (3 H, s, CH_3O), 3.76 (3 H, s, CH_3O), 3.79 (3 H, s, CH_3O), 3.81 (3 H, s, CH_3O), 3.83 (3 H, s, CH_3O), 5.66 (1 H, s, 4-H), 6.93 (2 H, d, *J* 9.2, benzene ring) and 7.36 (2 H, s, *J* 9.2, benzene ring); *m/z* 484 (M^+, 14.34%), 453 (M^+ − OMe, 5.34%) and 425 (M^+ − COOMe, 1.01%).

Diels–Alder reaction of 1d with DMAD

A solution of **1d** (50 mg, 0.25 mmol), 4-methoxyphenol (5 mg) and DMAD (0.092 cm^3, 3 equiv.) in dry benzene (1 cm^3) was heated at 120 °C for 6 h in a sealed tube. After concentration, the residue was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give as yellow oils **3d** (10 mg, 14%), **4d** (60 mg, 57%) and **5d** (11 mg, 16%) together with recovered **1d**.

Dimethyl 1-acetyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]-hept-2-ene-2,3-dicarboxylate **3d**: δ_H 2.31 (3 H, s, CH_3CO), 3.76 (3 H, s, CH_3OCO), 3.85 (3 H, s, CH_3OCO); 5 singlets for 4-H and CH_2=C(5) and CH_2=C(6) were observed as follows: 5.28 (1 H, s), 5.40 (1 H, s), 5.46 (1 H, s), 5.51 (1 H, s) and 5.53 (1 H, s); δ_C 26.4 (q, *C*H_3CO), 52.5 (q, *C*H_3OCO), 52.8 (q, *C*H_3OCO), 82.4 (d, 4-C), 96.3 (s, 1-C), 106.2 [t, *C*H_2=C(5 or 6)], 106.3 [t, *C*H_2=C(5 or 6)]; 4 singlets for the 4 quaternary carbons in the ring were observed as follows: 137.8 (s), 139.5 (s), 139.6 (s) and 146.5 (s); 161.3 (s, CO), 163.5 (s, CO) and 201.2 (s, CO); *m/z* 235 (M^+ − Ac, 9.94%), 176 (M^+ − Ac − COOMe, 18.36%) and (CI) 278 (M^+) [Found (HRMS): *m/z* 235.0602. Calc. for $C_{12}H_{11}O_5$: 235.0606].

Tetramethyl 1-acetyl-1,4-epoxy-1,4,5,8-tetrahydronaphthalene-2,3,6,7-tetracarboxylate **4d**: δ_H 2.32 (3 H, s, CH_3CO), 3.32 (4 H, m, 5-H and 8-H), 3.78 (3 H, s, CH_3OCO), 3.79 (3 H, s, CH_3OCO), 3.80 (3 H, s, CH_3OCO), 3.82 (3 H, s, CH_3OCO) and 5.61 (1 H, s, 4-H); δ_C 26.8 (t, 5-C or 8-C), 26.9 (q, *C*H_3CO), 27.3 (t, 8-C or 5-C), 52.4 (q, *C*H_3OCO), 52.5 (q, *C*H_3OCO), 52.6 (q, *C*H_3OCO), 52.7 (q, *C*H_3OCO), 84.4 (d, 4-C) and 98.9 (s, 1-C); 6 singlets for 6 sp^2 carbons of the ring were observed as follows: 131.4 (s), 133.3 (s), 144.2 (s), 146.8 (s), 148.6 (s) and 154.9 (s); 5 singlets for carbonyl carbons were observed as follows: 162.3 (s), 163.2 (s), 167.5 (s), 167.9 (s) and 201.9 (s); *m/z* 389 (M^+ − OMe, 1.89%) and 346 (M^+ − OMe − Ac, 1.89%) [Found (HRMS): *m/z* 389.0869. Calc. for $C_{19}H_{17}O_9$: 389.0871].

Dimethyl 1-acetyl-4,7-dihydrobenzo[*c*]furan-5,6-dicarboxylate **5d**: δ_H 2.48 (3 H, s, CH_3CO), 3.55 (2 H, d, *J* 1.22, 4-H), 3.82 (3 H, s, CH_3OCO), 3.83 (2 H, s, 7-H), 3.84 (3 H, s, CH_3OCO) and 7.37 (1 H, t, *J* 1.22, 3-H); δ_C 22.2 (t, 4-C), 25.2 (t, 7-C), 26.4 (q, *C*H_3CO), 52.4 (q, *C*H_3OCO), 52.5 (q, *C*H_3OCO), 120.0 (s, 3a-C or 6a-C), 125.6 (s, 6a-C or 3a-C); 3 singlets for 1- and 5- and 6-C were observed as follows: 131.1 (s), 133.6 (s) and 133.7 (s) and 140.1 (d, 3-C); 3 carbonyl carbons were observed as follows: 167.8 (s), 168.0 (s) and 188.3 (s); *m/z* 278 (M^+, 5.86%), 219 (M^+ − COOMe, 29.31%) [Found (HRMS): 278.0765. Calc. for $C_{14}H_{14}O_6$: 278.0789].

Diels–Alder reaction of 1e with DMAD

A solution of **1e** (43 mg, 0.21 mmol), 4-methoxyphenol (5 mg) and DMAD (0.077 cm^3, 3 equiv.) in dry benzene (1 cm^3) was heated in a sealed tube at 120 °C for 24 h and then concentrated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 9:1) to give **7e** (6 mg, 14%) as a yellow oil.

Tetramethyl 5,10-epoxy-1,*n*-dinitro-4,4a,5,6,9,10,10a,11-octahydroanthro[2,3-*c*]furan-4a,7,8,10a-tetracarboxylate **7e** (*n* = 5 or 10): δ_H 3.30 (2 H, m, 6- or 9-H), 3.59 (2 H, m, 6- or 9-H), 3.75 (6 H, s, CH_3OCO × 2), 3.80 (3 H, s, CH_3OCO), 3.83 (3 H, s, CH_3OCO), 3.90 (4 H, s, 4- and 11-H), 5.97 (1 H, s, 5- or 10-H) and 8.08 (1 H, s, 3-H); δ_C 26.3 (t, 4-, 6-, 9- or 11-C), 26.8 (t, 4-, 6-, 9- or 11-C), 27.3 (t, 4-, 6-, 9- or 11-C), 27.5 (t, 4-, 6-, 9- or 11-C), 50.9 (q, *C*H_3OCO), 52.6 (q, *C*H_3OCO), 53.1 (q, *C*H_3OCO), 53.2 (q, *C*H_3OCO), 81.2 (d, 5- or 10-C), 147.6 (d, 3-C); 4 carbonyl carbons and 10 quaternary carbons had signals as described in the text; *m/z* 420 ($M^+ - C_6H_6O_4$, 3.28%), 374

($M^+ - C_6H_6O_4 - NO_2$, 7.71%) and (CI) 580 $(M + NH_4)^+$ [Found (HRMS): *m/z* 420.0756. Calc. for $C_{24}H_{22}O_{14}N_2$: 420.0804].

Diels–Alder reaction of 1b with dimethyl maleate

A solution of **1b** (50 mg, 0.21 mmol), 4-methoxyphenol (5 mg) and dimethyl maleate (0.079 cm^3, 3 equiv.) in dry benzene (1 cm^3) was heated in a sealed tube at 120 °C for 22 h after which it was concentrated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give *cis-endo*-**9b** (32.3 mg, 48%) and *cis-exo*-**9b** (2.9 mg, 4%) as colourless oils.

Dimethyl 1-bromo-5,6-dimethylidene-7-oxabicyclo[2.2.1]-heptane-2*endo*,3*endo*-dicarboxylate *cis-endo*-**9b**: δ_H 3.60 (1 H, d, *J* 12.0, 2-H), 3.63 (3 H, s, CH_3OCO), 3.68 (3 H, s, CH_3OCO), 3.71 (1 H, dd, *J* 12.0, 5.5, 3-H), 5.04 (1 H, d, *J* 5.5, 4-H), 5.10 [1 H, s, CH_2=C(5 or 6)], 5.45 [1 H, s, CH_2=C(5 or 6)], 5.47 [1 H, s, CH_2=C(5 or 6)] and 5.63 [1 H, s, CH_2=C(5 or 6)]; δ_C 50.2 (d, 3-C), 51.9 (q, CH_3OCO), 52.0 (q, CH_3OCO), 56.6 (d, 2-C), 80.8 (d, 4-C), 93.2 (s, 1-C), 105.4 [t, CH_2=C(5)], 108.8 [t, CH_2=C(6)], 141.5 (s, 5-C), 144.5 (s, 6-C), 168.1 (s, CO) and 168.5 (s, CO); *m/z* 318, 316 (M^+, 3.62, 3.64%), 287, 265 (M^+ – OMe, 5.80, 5.94%) and 237 (M^+ – Br, 15.71%) [Found (HRMS): *m/z* 315.9911. Calc. for $C_{12}H_{13}O_5Br$: 315.9945].

Dimethyl 1-bromo-5,6-dimethylidene-7-oxabicyclo[2.2.1]-heptane-2*exo*,3*exo*-dicarboxylate *cis-exo*-**9b**: δ_H 3.11 (1 H, d, *J* 9.5, 3-H), 3.51 (1 H, d, *J* 9.5, 2-H), 3.70 (3 H, s, CH_3OCO) and 3.75 (3 H, s, CH_3OCO); 4 singlets for CH_2=C(5), CH_2=C(6) and 4-H were observed as follows: 5.13 (1 H, s), 5.33 (1 H, s), 5.46 (2 H, s) and 5.51 (1 H, s); δ_C 52.5 (d, 3-C), 52.7 (q, CH_3OCO), 52.8 (q, CH_3OCO), 58.3 (d, 2-C), 80.4 (d, 4-C), 93.1 (s, 1-C), 103.5 [t, CH_2=C(5)], 106.8 [t, CH_2=C(6)], 143.3 (s, 5-C), 147.5 (s, 6-C), 169.5 (s, CO) and 169.7 (s, CO); *m/z* 287, 285 (M^+ – OMe, 1.23, 1.32%) and 237 (M^+ – Br, 4.01%) [Found (HRMS): *m/z* 284.9771. Calc. for $C_{11}H_{10}O_4Br$: 284.9762].

Diels–Alder reaction of 1d with dimethyl maleate

A solution of **1d** (50 mg, 0.25 mmol), 4-methoxyphenol (5 mg) and dimethyl maleate (0.094 cm^3, 3 equiv.) in dry benzene (1 cm^3) was heated in a sealed tube at 120 °C for 24 h after which it was concentrated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give *cis-endo*-**9d** (9.1 mg, 14%) and *cis-exo*-**9d** (2.8 mg, 4%) as colourless oils together with recovered **1d** (70%).

Dimethyl 1-acetyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane-2*endo*,3*endo*-dicarboxylate *cis-endo*-**9d**: δ_H 2.30 (3 H, s, CH_3CO), 3.35 (1 H, d, *J* 11.6, 2-H), 3.56 (1 H, dd, *J* 11.6, 5.6, 3-H), 3.63 (3 H, s, CH_3OCO), 3.67 (3 H, s, CH_3OCO) and 5.06 (1 H, d, *J* 5.6, 4-H); 4 singlets for CH_2=C(5) and CH_2=C(6) were observed as follows: 5.01 (1 H, s) 5.19 (1 H, s), 5.51 (1 H, s) and 5.52 (1 H, s); *m/z* 280 (M^+, 7.33%). 249 (M^+ – OMe, 11.6%) and 237 (M^+ – Ac, 5.86%).

Dimethyl 1-acetyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane-2*exo*,3*exo*-dicarboxylate *cis-exo*-**9d**: δ_H 2.45 (3 H, s, CH_3CO), 3.22 (1 H, d, *J* 10.0, 3-H), 3.49 (1 H, d, *J* 10.0, 2-H), 3.65 (3 H, s, CH_3OCO) and 3.70 (3 H, s, CH_3OCO); 5 singlets for 4-H, CH_2=C(5) and CH_2=C(6) were observed as follows: 5.05 (1 H, s), 5.18 (1 H, s), 5.28 (1 H, s), 5.35 (1 H, s) and 5.36 (1 H, s); *m/z* 280 (M^+, 2.01%), 249 (M^+ – OMe, 4.18%) and 237 (M^+ – Ac, 1.81%).

Diels–Alder reaction of 1e with dimethyl maleate

A solution of **1e** (50 mg, 0.25 mmol), 4-methoxyphenol (5 mg) and dimethyl maleate (0.092 cm^3, 3 equiv.) in dry benzene (1 cm^3) was heated in a sealed tube at 120 °C for 24 h after which it was concentrated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give *cis-endo*-**9e** (7.1 mg, 10%).

Dimethyl 5,6-dimethylidene-1-nitro-7-oxabicyclo[2.2.1]heptane-2*endo*,3*endo*-dicarboxylate *cis-endo*-**9e**: δ_H 3.44 (1 H, t, *J* 5.5, 3-H), 3.73 (3 H, s, CH_3OCO), 3.75 (1 H, d, *J* 5.5, 2-H), 3.78 (3 H, s, CH_3OCO), 5.06 (1 H, d, *J* 5.5, 4-H). 5.10 (1 H, s), 5.12 (1 H, s), 5.36 (1 H, s) and 5.37 (1 H, s); *m/z* 283 (M^+, 9.69%) and 206 (M^+ – NO_2 – OMe, 3.22%).

Diels–Alder reaction of 1b with dimethyl fumarate

A solution of **1b** (50 mg, 0.21 mmol), 4-methoxyphenol (5 mg) and dimethyl fumarate (91 mg, 3 equiv.) in dry benzene (1 cm^3) was heated in a sealed tube at 120 °C for 20 h after which it was concentrated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give 2*endo*,3*exo*-**9b** (8.6 mg, 13%) and 2*exo*,3*endo*-**9b** (4.3 mg, 7%).

Dimethyl 1-bromo-5,6-dimethylidene-7-oxabicyclo[2.2.1]-heptane-2*endo*,3*exo*-dicarboxylate 2*endo*,3*exo*-**9b**: δ_H 3.40 (1 H, d, *J* 4.8, 2-H), 3.73 (3 H, s, CH_3OCO), 3.78 (3 H, s, CH_3OCO) and 3.89 (1 H, d, *J* 4.8, 3-H); 5 protons of 4-H, CH_2=C(5) and CH_2=C(6) were observed as follows: 5.19 (1 H, s), 5.21 (1 H, s), 5.32 (1 H, s), 5.38 (1 H, s) and 5.50 (1 H, s); δ_C 52.4 (q, CH_3OCO), 52.6 (d, 3-C), 52.7 (q, CH_3OCO), 55.9 (d, 2-C), 80.5 (d, 4-C), 94.1 (s, 1-C), 105.6 [t, CH_2=C(5 or 6)], 105.9 [t, CH_2=C(5 or 6)], 141.4 (s, 5- or 6-C), 147.4 (s, 5- or 6-C), 169.0 (s, CO) and 170.7 (s, CO); *m/z* 318. 316 (M^+, 4.43, 4.53%), 287, 285 (M^+ – OMe, 2.72, 2.70%) and 237 (M^+ – Br; 2.50%) [Found (HRMS): *m/z* 315.9956. Calc. for $C_{12}H_{13}O_5Br$: 315.9945].

Dimethyl 1-bromo-5,6-dimethylidene-7-oxabicyclo[2.2.1]-heptane-2*exo*,3*endo*-dicarboxylate 2*exo*,3*endo*-**9b**: δ_H 3.53 (1 H, d, *J* 5.2, 2-H), 3.68 (3 H, s, CH_3OCO), 3.81 (3 H, s, CH_3OCO), 3.91 (1 H, dd, *J* 5.6, 5.2, 3-H), 5.16 (1 H, d, *J* 5.6, 4-H); 4 singlets for CH_2=C(5 and 6) were observed as follows: 5.07 (1 H, s), 5.39 (1 H, s), 5.43 (1 H, s) and 5.47 (1 H, s); δ_C 52.3 (q, CH_3OCO), 52.6 (d, 2- or 3-C), 52.8 (q, CH_3OCO), 59.2 (d, 2- or 3-C), 84.4 (d, 4-C), 92.6 (s, 1-C), 104.1 [t, CH_2=C(5 or 6)], 107.4 [t, CH_2=C(5 or 6)], 142.6 (s, 5- or 6-C), 144.8 (s, 5- or 6-C), 168.9 (s, CO) and 170.8 (s, CO); *m/z* 318, 316 (M^+, 2.64, 2.56%), 287, 285 (M^+ – OMe, 5.62, 5.96%) and 237 (M^+ – Br; 6.62%) [Found (HRMS): *m/z* 315.9937. Calc. for $C_{12}H_{13}O_5Br$: 315.9945].

Diels–Alder reaction of 1d with dimethyl fumarate

A solution of **1d** (30 mg, 0.15 mmol), 4-methoxyphenol (5 mg) and dimethyl fumarate (65 mg, 3 equiv.) in dry benzene (1 cm^3) was heated in a sealed tube at 120 °C for 20 h after which it was concentrated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give 2*endo*,3*exo*-**9d** (3 mg, 7%), 2*exo*,3*endo*-**9d** (2 mg, 5%) as pale yellow oils, *trans*-**11d** (4 mg, 10%) as a colourless oil together with recovered **1d** (22 mg, 73%).

Dimethyl 1-acetyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane-2*endo*,3*exo*-dicarboxylate 2*endo*,3-*exo*-**9d**: δ_H 2.34 (3 H, s, CH_3CO), 3.34 (1 H, d, *J* 4.8, 2- or 3-H), 3.67 (1 H, d, *J* 4.8, 2- or 3-H), 3.69 (3 H, s, CH_3OCO) and 3.78 (3 H, s, CH_3OCO); 5 protons of 4- and 2 × CH_2=C appeared as singlets: 5.18 (2 H, s), 5.23 (1 H, s), 5.37 (1 H, s), and 5.47 (1 H, s); δ_C 27.2 (q, CH_3CO), 52.2 (q, CH_3OCO), 53.7 (d, 3-C), 80.9 (d, 2- or 4-C), 83.2 (d, 4- or 2-C), 94.6 (s, 1-C), 103.9 [t, CH_2=C(5 or 6)], 105.2 [t, CH_2=C(5 or 6)], 142.8 (s, 5- or 6-C), 143.0 (s, 5- or 6-C), 169.2 (s, CO), 172.1 (s, CO) and 204.6 (s, CO); *m/z* 280 (M^+, 2.09%), 249 (M^+ – OMe, 5.71%) and 237 (M^+ – Ac, 3.19%) [Found (HRMS): *m/z* 280.0942. Calc. for $C_{14}H_{16}O_6$: 280.0946].

Dimethyl 1-acetyl-5,6-dimethylidene-7-oxabicyclo[2.2.1]heptane-2*exo*,3*endo*-dicarboxylate 2*exo*,3*endo*-**9d**: δ_H 2.35 (3 H, s, CH_3CO), 3.35 (1 H, d, *J* 4.6, 2-H), 3.44 (1 H, dd, *J* 5.8, 4.6, 3-H), 3.68 (3 H, s, CH_3OCO), 3.70 (3 H, s, CH_3OCO) and 5.12 (1 H, d, *J* 5.8); 4 protons for CH_2=C(5 and 6) appeared as singlets at 5.06 (1 H, s), 5.10 (1 H, s), 5.36 (1 H, s) and 5.37 (1 H, s); δ_C 29.7 (q, CH_3CO), 52.1 (d, 2- or 3-C), 52.3 (q, CH_3OCO), 52.5 (d, 2- or 3-C), 83.2 (d, 4-C), 103.3 [t, CH_2=C(5 or 6)], 106.1 [t, CH_2=C(5 or 6)]; 3 quaternary carbons, 1-, 5- and 6-C were observed as singlets at 141.5 (s), 143.2 (s) and 144.0 (s); 165.2 (s, CO), 165.4 (s, CO) and 189.3 (s, CO); *m/z* 280 (M^+,

3.92%), 249 (M^+ − OMe, 12.87%), 237 (M^+ − Ac, 8.22%) [Found (HRMS): *m/z* 280.0975. Calc. for $C_{14}H_{16}O_6$: 280.0946].

Dimethyl 1-acetyl-4,5,6,7-tetrahydrobenzo[*c*]furan-*trans*-5,6-dicarboxylate *trans*-**11d**. δ_H 2.45 (3 H, s, CH_3CO), 2.70 (1 H, dd, *J* 17.9, 9.5, 4-H), 2.91 (1 H, dd, *J* 17.9, 9.5, 4-H), 3.03 (3 H, m, 5-, 6- and 7-H), 3.41 (1 H, dd, *J* 18.0, 4.2, 7-H), 3.73 (6 H, s, $CH_3OCO \times 2$), 7.28 (1 H, s, 3-H); δ_C 22.3 (t, 4- or 7-C), 24.8 (t, 7- or 4-C), 26.5 (q, CH_3CO), 41.6 (d, 5- or 6-C), 41.7 (d, 5- or 6-C), 52.2 (q, CH_3OCO), 52.5 (q, CH_3OCO), 128.1 (s, 3a- or 7a-C), 128.2 (s, 3a- or 7a-C), 140.2 (d, 3-C), 147.6 (s, 1-C), 174.3 (s, CO), 174.4 (s, CO) and 188.4 (s, CO); *m/z* 280 (M^+, 2.30%), 249 (M^+ − OMe, 7.03%), 221 (M^+ − CO_2Me, 5.35%) [Found (HRMS): *m/z* 280.0943. Calc. for $C_{14}H_{16}O_6$: 280.0946].

Diels–Alder reaction of 1e with dimethyl fumarate

A solution of **1e** (50 mg, 0.25 mmol), 4-methoxyphenol (5 mg) and dimethyl fumarate (106 mg, 3 equiv.) in dry benzene (1 cm^3) was heated in a sealed tube at 120 °C for 24 h after which it was concentrated. The residue was purified by silica gel column chromatography (hexane–AcOEt, 4:1) to give *trans*-**11e** (8 mg, 11%) as a yellow oil.

Dimethyl 1-nitro-4,5,6,7-tetrahydrobenzo[*c*]furan-*trans*-5,6-dicarboxylate *trans*-**11e**: δ_H 2.81 (1 H, dd, *J* 16.9, 3.8, 7-H), 2.98 (1 H, dd, *J* 15.9, 5.3, 4-H), 3.15 (3 H, m, 4-, 5- and 6-H), 3.41 (1 H, dd, *J* 16.9, 3.8, 7-H), 3.74 (6 H, s, $CH_3OCO \times 2$) and 7.31 (1 H, m, 3-H); *m/z* 252 (M^+ − OMe, 7.49%), 206 (M^+ − OMe − NO_2, 24.82%) and (CI) 301 $(M + NH_4)^+$ [Found (HRMS): *m/z* 252.0513. Calc. for $C_{12}H_{13}O_7N$: 252.0507].

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