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Site and Stereoselectivities in the High Pressure Reaction of Furan with Dimethyl 7-isopropylidenebicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate and Tetramethyl 7-isopropylidenebicyclo[2.2.1]hepta-2,5-diene-2,3,5,6-tetracarboxylate

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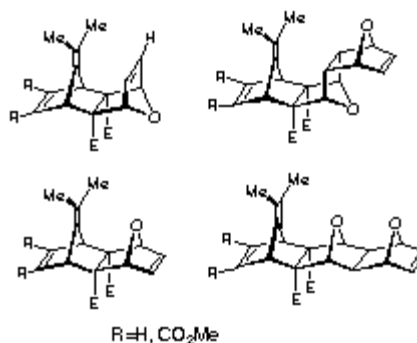
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Abstract

Furan **16** is shown to react under high pressure (14 kbar) with dimethyl 7-isopropylidene norbornadiene-2,3-dicarboxylate **4** to form two 1:1-adducts **17** and **19** (only **17** isolated) by exclusive reaction at the ester-substituted p-bond and 2:1-products **18** and **20** (X-ray analysis) by further *in situ* cycloaddition of furan **16** at the newly formed 7-oxa norbornene p-bond of the 1:1-adducts. Similar 1:1-adducts **26**, **27** and 2:1-adducts **28**, **29** were obtained in the high pressure addition of furan **16** with tetramethyl 7-isopropylidene norbornadiene-2,3,5,6-tetracarboxylate **5**.



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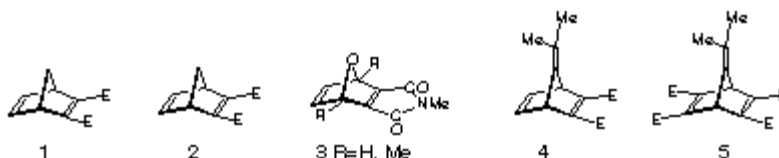
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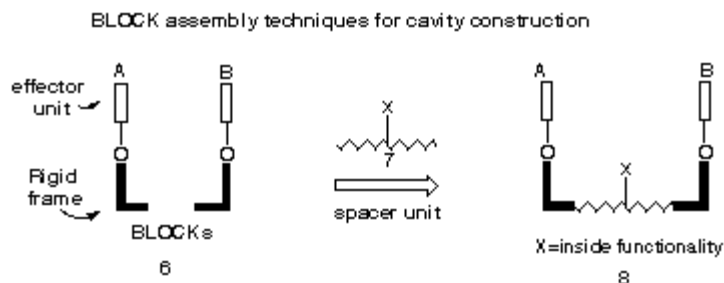
1. Introduction

The incorporation of ester substituents at the p-bond position of norbornadiene serves to activate the system as a dienophile in regular electron-demand Diels-Alder reactions.¹ The resultant dimethyl norbornadiene-2,3-dicarboxylate **1** is an ambident dienophile where cycloaddition can occur, in principle, at either of two different p-sites. Reaction of **1** with tropone or 9,10-dimethyl anthracene has been reported to occur with exclusive site selectivity at the unsubstituted p-centre.² In the corresponding dimethyl 7-oxanorbornadiene-2,3-dicarboxylate **2**, tropone again forms an adduct by reaction at the unsubstituted p-bond.³ However, when the diene is changed to furan, oxanorbornadiene **2** gives adducts resulting from attack at each of the p-centres.⁴ The furan reaction was studied subsequently in more detail, including the effect of Lewis acids,^{5,6} and it is now accepted that adducts derived from attack at the ester-substituted p-bond of **2** are under kinetic control.⁶ The initially-formed furan adducts readily undergo retro Diels-Alder under the conditions of the reaction, so secondary adducts are formed by attack at the unsubstituted p-bond (thermodynamic control). These results are in accord with FMO prediction and calculated heats of formation.⁶ More recently, we have studied cycloadditions to the maleimide-fused 7-oxanorbornadienes **3** where exclusive attack occurs at the maleimide p-centre with cyclopentadiene, furan and 2,6-dimethylfuran,⁷ and more recently with *N*-Cbz pyrrole.⁸ Semi-empirical and *ab initio* calculations have been used to assess this site selectivity and also transition state energies have been employed to predict the stereoselectivities of these reactions, with excellent precision.^{7,8}



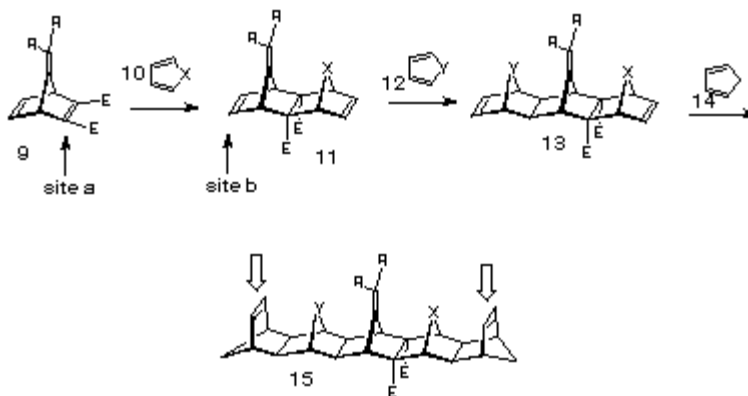
Scheme 1

In the present study, we have examined the cycloaddition reaction of furan **16** with the ester-activated ambident dienophiles **4** and **5**. Our objective has been to determine what influence the isopropylidene bridge has on the site selectivity and stereoselectivity when a regular electron-demand Diels-Alder 1,3-diene is involved. Already, it has been reported that dienophile **4** is attacked exclusively at the unsubstituted p-bond when reacted with inverse electron-demand dienes such as *s*-tetrazine **23** (see later),⁹ but no other information is available on the cycloaddition reactions of **4** or **5**.



Scheme 2

A major driving force for this study is related to our ongoing program directed at the production of inside-functionalised U-type cavity structures¹⁰ of type **8**, since we wanted to evaluate the potential for the 7-methylene group to act as an inner linking point for attachment of functionality. In this respect the strategy shown in scheme 3 represents an ideal situation in which the *syn*-facial product **13**, formed by selective addition of furan or a *N*-substituted pyrrole, would yield the turn-frame adduct **15** stereoselectively on treatment with cyclopentadiene. In this way, the exocyclic bridge methylene is centrally located and the R groups attached thereto can be used for the attachment of effector groups.



Scheme 3

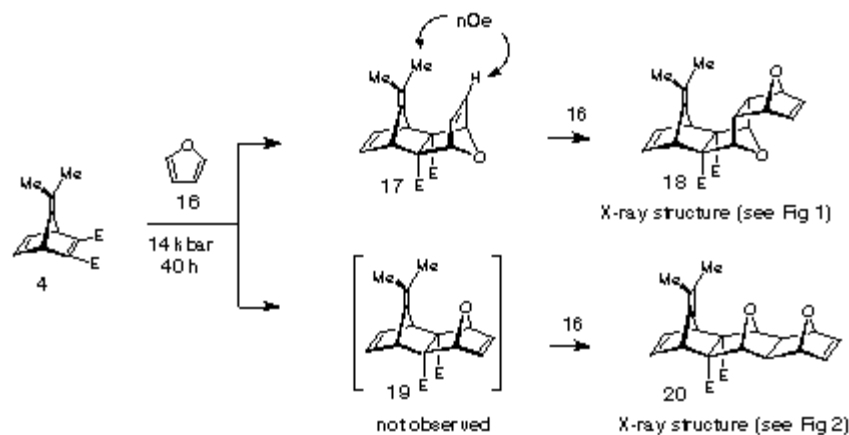
In practice, no reaction was observed to occur between furan **16** and the ester-activated bicyclic dienophiles **4** or **5** under thermal conditions, even in the presence of Lewis acids. Accordingly, we have conducted the reactions under high-pressure (14 kbar), since this has been reported to promote other furan cycloadditions.¹¹ The results of this study constitute the basis of this paper.

2. Results

2.1 Reaction of the diester **4** with furan **6**.

Reaction of 7-isopropylidene-norbornadiene-2,3-diester **4**¹² with furan **16** under high pressure did proceed at room temperature, but was slow (14 kbar, 40 h, 88%).

Several products were observed in the crude reaction mixture when excess furan was employed, from which one 1:1-adduct (**17**) and two 2:1-adducts (**18** and **20**) were separated by chromatography and purified by recrystallisation. The structures of the 2:1-adducts **18** and **20** were solved by X-ray crystallographic methods (Figure 1), while the decision in favour of 1:1-adduct **17** was made on ¹H NMR chemical shift and nOe data (*vide infra*).



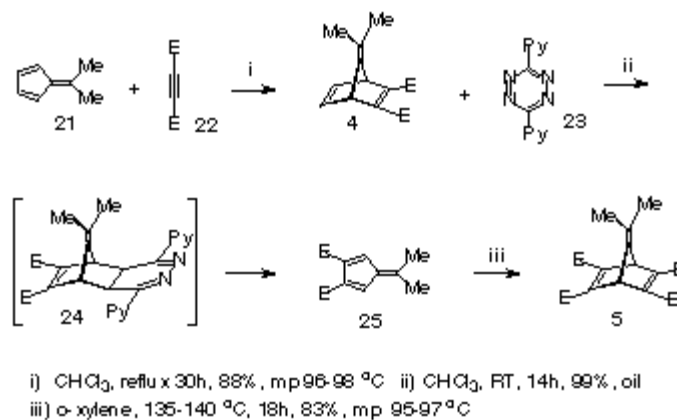
Scheme 4

2.2 Reaction of the tetraester **5** with furan **16**.

As no reaction occurred at the unsubstituted p-bond of **4**, and forcing conditions promoted preferential cycloaddition at the 7-oxanorbornene p-bond, it was necessary to find some way to promote reaction at this second p-bond if it was going to be useful for the development of cavity systems.

In an attempt to promote reaction at both p-centres of the 7-isopropylidene norbornadiene, activating ester-substituents were introduced onto both the p-bonds (Scheme 5). The required 7-isopropylidene-norbornadiene-2,3,5,6-tetraester **5** ($m/z = 364$) was prepared by reaction of fulvene diester **25** with DMAD **22** at 135-140 °C. The high symmetry of the fulvene tetraester **5** was reflected in the ^{13}C NMR (7 lines) while the ^1H NMR was even simpler, being comprised of three singlets (d 1.52, C-Me; d 3.81, ester, O-Me; d 4.75, CH).

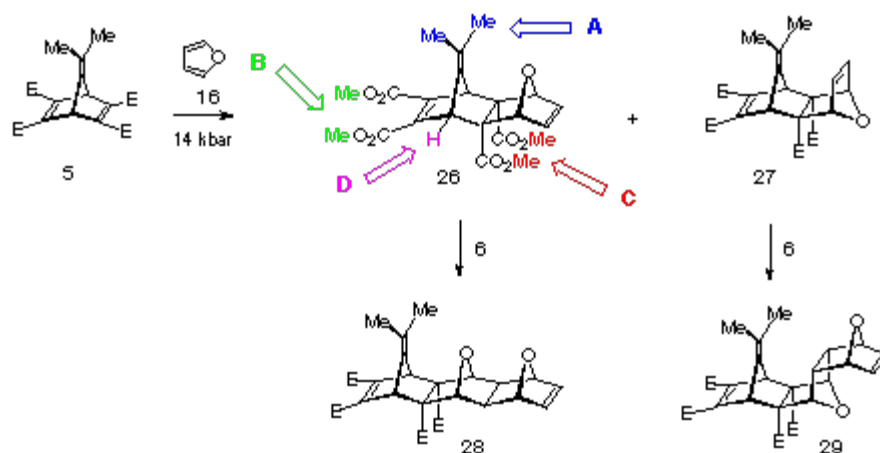
The requisite fulvene diester **25**, used for the synthesis of **5**, was itself prepared using a cycloaddition/fragmentation route developed by us earlier and which is outlined in Scheme 3. Site selective attack of the *s*-tetrazine **23** at the unsubstituted p-bond of the 7-isopropylidene-norbornadiene **4** occurred at room temperature to produce intermediate **24**, which fragmented spontaneously to yield 6,6-dimethylfulvene-3,4-diester **25** in 99% yield.⁹ It is pertinent to note that *s*-tetrazine **23**, an inverse-electron demand diene, reacts at the *unsubstituted* p-bond of **4**, whereas the regular electron-demand dienes react site-selectively at the *ester-activated* p-bond of **4**.



Scheme 5

A similar high-pressure reaction with furan **16** was conducted on the norbornadiene tetraester **5** and while a mixture of 1:1-adducts **26** and **27** and 2:1-adducts **28** and **29** was again produced, no product arising from attack at the alternative p-centre of **5** was observed. This time, two stereoisomeric 1:1-adducts were isolated, together with the corresponding

2:1 products formed by further addition of furan at the 7-oxanorbornene p-bond of the 1:1-adducts (Scheme 6).



Scheme 6

Table 1 ^1H NMR chemical shifts for adducts 17, 26 and 27

structural feature		26	27	17
A	exocyclic methyls CH_3	δ 1.59	δ 1.46 \uparrow	δ 1.41 \uparrow
B	vinyllic esters OCH_3	δ 3.77	δ 3.77	-
C	ester methyl OCH_3	δ 3.57 \uparrow	δ 3.69	δ 3.68
D	bridgehead CH	δ 3.99	δ 3.63 \uparrow	δ 3.14 \uparrow
E	alkene	δ 6.59	δ 6.25	δ 6.49

\uparrow = upfield shift resulting from geometric relationship of the anisotropic oxanorbornene π -bond

The stereochemistry of the 1:1-adducts **17**, **26** and **27** were determined by ^1H NMR chemical shift data, where the anisotropy of the 7-oxanorbornene p-bond played a key role in the structural assignment (see Table 1 and Scheme 6). Fortunately, both isomers in the tetraester series were available so that relative shift data allowed comparisons for several different sets of protons. The methyl groups of the 7-isopropylidene unit were affected by the proximate 7-oxanorbornene p-bond and this caused an upfield shift of 0.13 ppm in **27** relative to isomer **26**. A related effect of the proximate 7-oxanorbornene p-bond on the bridgehead protons of the all-carbon bridge (designated Hb in Figure 1) in **27** resulted in a shielding (0.36 ppm) relative to those in isomer **26**. In this case molecular modelling (see later) confirms that protons Hb fall within the shielding cone of the p-bond. The upfield shift (0.12 ppm) of the centrally located ester methyl groups in **26** reflect the additional shielding provided by the second p-bond, relative to **27**. While these shifts are not large, in combination they provide strong evidence for the assignments.

A comparison between these chemical shift data for **26** and **27**, with the 1:1-adduct **17** formed from furan **16** and **4** (Table 2) allowed confirmation of the stereochemistry. The assignment was supported further by the observation of a nOe between the vinyl proton Ha and the methyl substituents of the isopropylidene group.

The structures for the 2:1-adducts **28** and **29** were assigned by comparison between the ^1H NMR chemical shifts

displayed by the corresponding adducts **18** and **20** formed from the reaction of **16** with **4** for which X-Ray structures have been obtained. These comparisons are tabulated in Table 2 and place the new structures on firm ground.

Table 2 ^1H NMR data for the 2:1-adducts **18** and **20** (established by X-Ray structure) and unknown adducts **28** and **30**.

structural feature	Syn-facial pair		Bent-frame pair	
	18	29	20	28
exocyclic methyls CH_3	1.56	1.58	1.64	1.68
vinyllic esters OCH_3	-	3.75		3.77
ester methyl OCH_3	3.66	3.60	3.63	3.62
bridgehead CH	3.52; 4.42; 4.86	3.95; 4.49; 4.88	3.32; 4.40; 4.84	3.78; 4.54; 4.81
frame CH	2.24	2.31	2.53	2.45
alkene	6.28; 6.33	6.34	6.27; 6.54	6.28

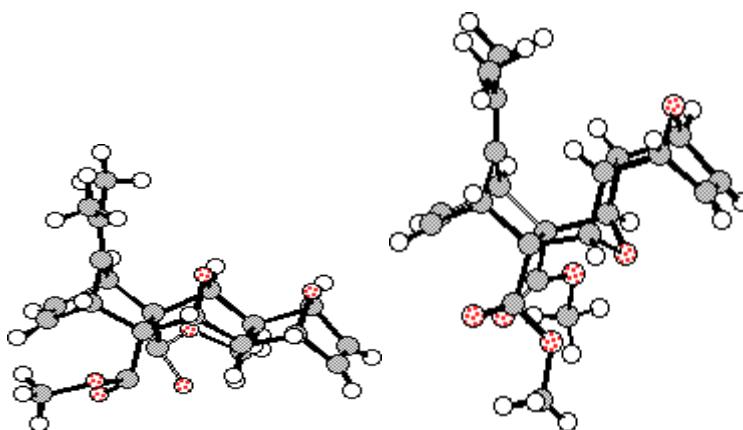


Figure 2. X-Ray structures for *bis*-adducts **28** and **29**.

3. Molecular Modelling and X-Ray Data

Molecular modelling experiments on compounds **18** and **20** were conducted at the AM1 level (Table 4). These results show excellent agreement with the x-ray data for these same compounds. Accordingly, we have confidence in using the AM1 figures when assessing the structures of other key compounds in this series.

Table 3. Crystal data for compound **20** and **18**

Compound	20	18
Formula	$\text{C}_{22}\text{H}_{24}\text{O}_6$	$\text{C}_{22}\text{H}_{24}\text{O}_6$

Formula weight	384.4	384.4
Crystal system	monoclinic	monoclinic
Space group	P21/c	P21/c
a (Å)	14.980(4)	13.473(2)
b (Å)	14.900(5)	8.059(4)
c (Å)	8.698(3)	17.442(2)
b (°)	95.83(2)	99.420(9)
V (Å ³)	1931.3(9)	1868.2(8)
Z	4	4
Crystal size (mm)	0.08 x 0.13 x 0.29	0.32 x 0.32 x 0.48
D _c (g cm ⁻³)	1.322	1.367
F(000)	816	816
μ (cm ⁻¹)	0.96	0.99
trans. factors	0.890 - 1	0.955 - 1
No. of data collected	3814	3725
θ _{max} (°)	25.0	25.0
No. of unique data	3570	3566
No. of reflections with I ≥ 3σ(I)	1459	2339
R	0.052	0.035
R _w	0.045	0.035
Residual rmax (e ⁻³)	0.27	0.16

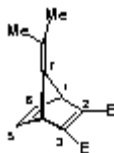
Table 4. Comparison of experimental and calculated bond length (Å) at AM1 theory.

parameter	observed (X-ray)	calculated 20	D	observed (X-ray)	calculated 18	D
O15-C1	1.438	1.454	0.016	1.436	1.458	0.022
O15-C8	1.430	1.450	0.020	1.436	1.454	0.018
O18-C10	1.443	1.464	0.021	1.442	1.471	0.029
O18-C13	1.437	1.466	0.029	1.445	1.472	0.028
C1-C2	1.568	1.564	0.040	1.563	1.572	0.009

C1-C14	1.523	1.545	0.022	1.528	1.534	0.006
C2-C3	1.570	1.567	0.003	1.582	1.555	0.027
C2-C7	1.586	1.608	0.022	1.586	1.613	0.027
C3-C4	1.526	1.532	0.008	1.523	1.537	0.014
C3-C16	1.515	1.530	0.015	1.512	1.532	0.020
C4-C5	1.319	1.354	0.035	1.313	1.354	0.041
C5-C6	1.520	1.528	0.008	1.526	1.535	0.009
C6-C7	1.593	1.563	0.030	1.568	1.558	0.010
C6-C16	1.520	1.533	0.013	1.523	1.532	0.009
C7-C8	1.546	1.565	0.019	1.570	1.566	0.004
C8-C9	1.535	1.543	0.008	1.520	1.536	0.016
C9-C10	1.553	1.553	0.000	1.562	1.555	0.007
C9-C14	1.563	1.585	0.022	1.545	1.587	0.042
C10-C11	1.520	1.535	0.015	1.502	1.529	0.027
C11-C12	1.318	1.353	0.035	1.314	1.354	0.040
C12-C13	1.513	1.535	0.022	1.504	1.529	0.025
C13-C14	1.543	1.553	0.010	1.564	1.555	0.009
C17-Me	1.511	1.485	0.036	1.506	1.485	0.021
C16-C17	1.315	1.332	0.017	1.321	1.334	0.013

4. Experimental

Dimethyl-7-isopropylidenebicyclo[2.2.1]hepta-2,5-dien-2,3-dicarboxylate (**4**)

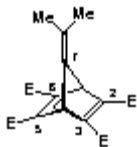


A solution of 6,6-dimethylfulvene (2.00 g, 18.87 mmol) and DMAD (5.36 g, 37.74 mmol) in CHCl_3 (15 ml) was heated under reflux for 30 h. The solvent was removed and the resultant yellow-coloured residue slowly solidified. This solid was recrystallised from EtOAc to give a colourless crystalline product (3.59 g, 77%). m.p. 96-98 °C (lit. 21190% yield, m.p. 101 °C); ^1H nmr (CDCl_3) δ : 1.48 (6H, s, $\text{CH}_3 \times 2$), 3.79 (6H, s, OCH_3), 4.42 (2H, t, $J = 2.3$ Hz, H1,4), 7.00 (2H, t, $J = 2.3$ Hz, H5,6).

The above diester **4** (1.29 g, 5.59 mmol) was treated with furan (5 ml) and compressed at 14 kbar pressure for 40 h. The excess furan was evaporated off under reduced pressure below 30 °C and the resultant colourless residue was

chromatographed (silica gel, EtOAc/PE, 3:4, v/v) to provide the 1:1 adduct **17** in the first fractions, followed by the 2:1 *exo,exo;exo,exo*-adduct **20** and 2:1 *exo,endo;exo,endo*-adduct **21**.

Tetramethyl-7-isopropylidenebicyclo[2.2.1]hepta-2,5-dien-2,3,5,6-tetracarboxylate (**5**)



A mixture of the above compound **15** (0.58 g, 2.61 mmol) and DMAD (1.56 g, 11.00 mmol) in *o*-xylene (2 ml) was heated at reflux for 18 h. The solvent was removed. The resultant residue was chromatographed (silica gel, EtOAc/PE, 5:6, v/v) to afford the crude product, which was crystallised from EtOAc as colourless crystals (0.79 g, 83%);

m.p. 95-97 °C (lit.241 m.p. 100 °C, yield 99%);

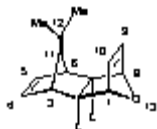
¹H NMR (CDCl₃) d: 1.52 (6H, s, CH₃x2), 3.81 (12H, s, OCH₃x4), 4.75 (2H, s, H1,4);

¹³C NMR (CDCl₃) d: 18.53 (CH₃), 52.33 (OCH₃), 56.15 (C1,4), 105.49 (C8), 150.45 (C2,3,5,6), 158.65 (C7), 163.79 (OCO).

Mass spectrum: *m/z* 364 (M⁺, 17.3%), 333 (18), 332 (65), 317 (13), 305 (43), 304 (34), 289 (12), 285 (12), 273 (37), 272 (37), 261 (26), 246 (12), 245 (45), 244 (26), 242 (10), 241 (39), 235 (10), 222 (24), 217 (11), 214 (17), 213 (24), 201 (10), 192 (13), 191 (100), 187 (11), 159 (14), 155 (10), 143 (13), 129 (15), 128 (25), 127 (18), 115 (28), 105 (13), 103 (28), 91 (19), 85 (11), 83 (18), 79 (11), 78 (13), 77 (30), 59 (78), 41 (23) ;

The above tetracarboxylate **5** (0.677 g, 1.86 mmol) was treated with furan **16** (4 ml) under 14 kbar for 16 h. The excess furan was evaporated under reduced pressure below 30 °C and the resultant residue was chromatographed (silica gel, EtOAc/PE, 5:2, v/v) to afford the 1:1 adducts in the first fractions, followed by 2:1 *exo,exo,exo*-adduct and *exo,endo,exo*-adduct, respectively.

(1a,2a,3b,6b,7a,8a,9b) Dimethyl-11-isopropylidene-13-oxatetracyclo [6.2.1.1^{3,6}.0^{2,7}]dodeca-4,10-dien-2,7-dicarboxylate (**17**)



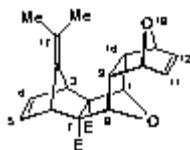
m.p. 176-178 °C;

¹H NMR (CDCl₃) d: 1.41 (6H, s, CH₃ x 2), 3.14 (2H, dd, *J* = 2.3, 1.8 Hz, H3,6), 3.68 (6H, s, OCH₃ x2), 5.07 (2H, t, *J* = 1.0 Hz, H1,8), 6.22 (2H, t, *J* = 1.0 Hz, H9,10), 6.49 (2H, dd, *J* = 2.3, 1.8 Hz, H4,5);

¹³C NMR (CDCl₃) d: 19.38 (CH₃), 47.15 (C3,6), 52.17 (OCH₃), 69.82 (C2,7), 83.67 (C1,8), 110.01 (C12), 132.38 (C9,10), 139.45 (C4,5), 147.80 (C11), 174.00 (OCO).

Analysis: C₁₈H₂₀O₅ requires: C, 68.34; H, 6.31%. Found: C, 68.20; H, 5.82%.

(1b,2b,3a,6a,7b,8b,9a,10a,13a,14a)-Dimethyl-16-isopropylidene-15,18-dioxahexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,3,14}]octadeca-4,11-diene-2,7-dicarboxylate (18)



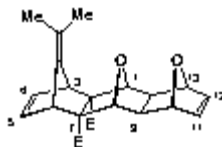
m.p. 179-180 ° C;

¹H NMR (CDCl₃) d: 1.64 (6H, s, CH₃x2), 2.53 (2H, dd, *J* = 1.6, 3.2 Hz, H9,14), 3.32 (2H, t, *J* = 2.1 Hz, H3,6), 3.63 (6H, s, OCH₃), 4.40 (2H, s, H1,8), 4.82 (2H, m, H10,13), 6.27 (2H, m, H11,12), 6.54 (2H, t, *J* = 2.1 Hz, H4,5);

¹³C NMR (CDCl₃) d: 20.32 (CH₃), 45.33 (C9,14), 46.34 (C3,6), 52.17 (OCH₃), 74.57 (C2,7), 79.98 (C10,13), 80.16 (C1,8), 110.17 (C17), 134.52(C11,12), 140.33 (C4,5), 146.04 (C16), 173.52 (OCO).

Analysis: Calc. for C₂₂H₂₄O₆ requires: C, 68.74; H, 6.29. Found: C, 68.57; H, 6.19.

(1a,2b,3a,6a,7b,8a,9b,10a,13a,14b)-Dimethyl-16-isopropylidene-15,18-dioxahexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]octadeca-4,11-diene-2,7-dicarboxylate (20)



m.p. 173-174 ° C;

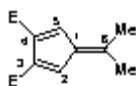
¹H NMR (CDCl₃) d: 1.56 (6H, s, CH₃ x2), 2.24 (2H, s, H9,14), 3.52 (2H, t, *J* = 1.8 Hz, H3,6), 3.66 (6H, s, OCH₃ x2), 4.42 (2H, s, H1,8), 4.86 (2H, m, H10,13), 6.28 (2H, t, *J* = 1.8 Hz, H4,5), 6.33 (2H, m, H11,12);

¹³C NMR (CDCl₃) d: 19.80 (CH₃), 46.50 (C9,14), 51.60 (C3,6), 51.68 (OCH₃), 70.01 (C2,7), 80.78 (C10,13), 84.24 (C1,8), 107.64 (C17), 137.17 (C11,12), 137.93 (C4,5), 143.29 (C16), 170.93 (OCO).

Mass spectrum: *m/z* 384 (M⁺, 0.8%), 17 (18), 106 (100), 91 (47), 77 (10.6), 68 (20);

Analysis: C₂₂H₂₄O₆ requires: C, 68.74; H, 6.29. Found: C, 68.37; H, 6.19.

Dimethyl-6,6-dimethylfulvene-3,4-dicarboxylate (25)

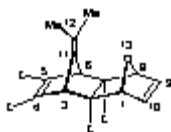


A solution of dicarboxylate **4** (1.04 g, 4.81 mmol) and *s*-tetrazine (1.02 g, 4.32 mmol) in CHCl₃ (6 ml) was stirred at room temperature for 14 h. The solution was diluted with CHCl₃. The organic layer was washed with aqueous HCl (50%), water, dried and the solvent was removed to produce a yellow gum in quantitative yield (lit.241 yield 99%).

$^1\text{H NMR}$ (CDCl_3) d: 2.31 (6H, s, $\text{CH}_3 \times 2$), 3.82 (6H, s, OCH_3), 7.14 (2H, s, H2,5);

$^{13}\text{C NMR}$ (CDCl_3) d: 23.95 (CH_3), 51.70 (OCH_3), 127.44 (C2,5), 133.56 (C6), 139.57 (C1), 164.00 (C4,5), 165.10 (OCO).

(1a,2b,3a,6a,7b,8a,9a) Tetramethyl-12-isopropylidene-11-oxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7,4,5-tetracarboxylate (**26**)



1:1 Adduct **26** (minor product):

m.p. 175-178 °C;

$^1\text{H NMR}$ (CDCl_3): 1.59 (6H, s, $\text{CH}_3 \times 2$), 3.57 (6H, s, $\text{OCH}_3 \times 2$), 3.77 (6H, s, $\text{OCH}_3 \times 2$), 3.99 (2H, s, H3,6), 4.86 (2H, t, $J = 0.9$ Hz, H1,8), 6.59 (2H, t, $J = 0.9$ Hz, H9,10);

$^{13}\text{C NMR}$ (CDCl_3) d: 19.63 (CH_3), 51.87 (OCH_3), 51.90 (OCH_3), 53.84 (C3,6), 70.53 (C2,7), 84.23 (C1,8), 111.61 (C13), 138.02 (9,10), 143.00 (C4,5), 146.56 (C12), 164.17 (OCO), 170.80 (OCO).

(1a,2a,3b,6b,7a,8a,9b) Tetramethyl-12-isopropylidene-11-oxatetracyclo [6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7,4,5-tetracarboxylate (**27**)



1:1 Adduct **27**(major product):

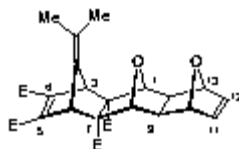
m.p. 176-178 °C;

$^1\text{H NMR}$ (CDCl_3) d: 1.46 (6H, s, $\text{CH}_3 \times 2$), 3.63 (2H, s, H3,6), 3.69 (6H, s, $\text{OCH}_3 \times 2$), 3.77 (6H, s, $\text{OCH}_3 \times 2$), 5.23 (2H, t, $J = 0.9$ Hz, H1,8), 6.25 (2H, t, $J = 0.9$ Hz, H9,10);

$^{13}\text{C NMR}$ (CDCl_3) d: 19.40 ($\text{CH}_3 \times 2$), 50.79 (C3,6), 51.97 (OCH_3), 52.58 (OCH_3), 68.52 (C2,7), 83.98 (C1,8), 113.84 (C13), 134.42 (C9,10), 144.33 (C4,5), 147.33 (C12), 164.09 (OCO), 172.93 (OCO).

Analysis: Calc. for $\text{C}_{22}\text{H}_{24}\text{O}_9$ requires: C, 61.11; H, 5.59. Found: C, 60.91; H, 5.35.

(1a,2b,3a,6a,7b,8a,9b,10a,13a,14b)- Tetramethyl-16-isopropylidene-15,18-dioxahexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]octadeca-4,11-dien-2,7,4,5-tetracarboxylate (**28**)



m.p. 173 °C (dec.);

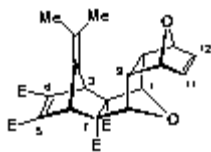
¹H NMR (CDCl₃) δ: 1.58 (6H, s, CH₃x2), 2.31 (2H, s, H_{9,14}), 3.60 (6H, s, OCH₃x2), 3.75 (6H, s, OCH₃x2), 3.95 (2H, s, H_{3,6}), 4.49 (2H, s, H_{1,8}), 4.88 (2H, m, H_{10,13}), 6.34 (2H, m, H_{11,12});

¹³C NMR (CDCl₃) δ: 19.72 (CH₃), 46.31 (C_{9,14}), 51.97 (OCH₃), 51.82 (OCH₃), 54.49 (C_{3,6}), 69.30 (C_{2,7}), 80.80 (C_{10,13}), 84.54 (C_{1,8}), 111.25 (C₁₇), 137.16 (C_{11,12}), 141.70 (C₁₆), 145.47 (C_{4,5}), 164.09 (OCO), 169.84 (OCO).

Mass spectrum *m/z* 500 (M⁺, 1.4%), 223 (14), 222 (84), 192 (14), 191 (100), 77 (12), 68 (39), 66 (10), 41 (16);

Analysis: Calc. for C₂₆H₂₈O₁₀·0.25H₂O requires: C, 61.84; H, 5.69. Found: C, 61.70; H, 5.24.

(1b,2b,3a,6a,7b,8b,9a,10a,13a,14a)-Tetramethyl-16-isopropylidene-15,18-dioxahexacyclo[6.6.1.1^{3,6}.1^{10,13}.0^{2,7}.0^{9,14}]octadeca-4,11-dien-2,7,4,5-tetracarboxylate (29)



m.p. 199-200 °C;

¹H NMR (CDCl₃) δ: 1.68 (6H, s, CH₃x2), 2.45 (2H, dd, *J* = 1.6, 3.1 Hz, H_{9,14}), 3.62 (6H, s, OCH₃x2), 3.77 (6H, s, OCH₃x2), 3.78 (2H, s, H_{3,6}), 4.54 (2H, s, H_{1,8}), 4.81 (2H, br, H_{10,13}), 6.28 (2H, m, H_{11,12});

¹³C NMR (CDCl₃) δ: 20.32 (CH₃), 45.45 (C_{9,14}), 49.86 (C_{3,6}), 52.00 (OCH₃), 52.53 (OCH₃), 73.46 (C_{2,7}), 79.95 (C_{10,13}), 80.43 (C_{1,8}), 114.12 (C₁₇), 134.62 (C_{11,12}), 144.57 (C_{4,5}), 147.96 (C₁₆), 163.99 (OCO), 172.53 (OCO).

Analysis: Calc. for C₂₆H₂₈O₁₀ requires: C, 62.39; H, 5.64. Found: C, 62.35; H, 5.26.

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