

Synthesis and Tandem Diels-Alder Reactivity of 1,3-Dimethoxy-5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene

Gerald Burnier and Pierre Vogel*

Abstract: The synthesis of 1,3-dimethoxy-5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (**13**) is presented. **13** added one equivalent of ethylenetetracarbonitrile (TCNE) to give the corresponding monoadduct **18** ($k_1^{II} = 204 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C , $\Delta H_1^\ddagger = 10.7 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta S_1^\ddagger = -26 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$). **18** added another equivalent of TCNE and afforded the bisadduct **19** ($k_2^{II} = 0.6 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C , $\Delta H_2^\ddagger = 14 \pm 1 \text{ kcal mol}^{-1}$, $\Delta S_2^\ddagger = -26 \pm 4 \text{ cal K}^{-1} \text{ mol}^{-1}$). The tandem Diels-Alder reactivity of **13** given by the rate constant ratio $k_1^{II}/k_2^{II} = 340$ (at 25°C) is compared with that reported for 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**3**), 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (**4**), and [2.2.2]hericene (**5**).

Kinetic data^[1] obtained for the Diels-Alder additions of ethylenetetracarbonitrile (TCNE: tetracyanoethylene) to 2,3-dimethylidenebicyclo[2.2.2]octane (**1**), 5,6-dimethylidenebicyclo[2.2.2]oct-2-ene (**2**), 2,3,5,6-tetramethylidenebicyclo[2.2.2]octane (**3**), 5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (**4**), and [2.2.2]hericene (**5**) reveal relatively small reactivity difference between these exocyclic polyenes. This observation is in agreement with the hypothesis that Diels-Alder reactivity of strong dienophiles such as TCNE depends mostly upon the ionization energies (*IE*) of the dienes^[2] if the latter have comparable geometries and flexibilities^[3], as in the case of **1–5**^[1], since very similar ionization energies were measured for these polyenes (Scheme 1).

Although the UV absorption^[7,8] and Photoelectron (PE) spectra^[5,6] confirmed the existence of significant transannular interaction between the homoconjugated *s-cis*-butadiene moieties in **3**, **4**, and **5**, their Diels-Alder reactivity is not affected by it as **3**, **4**, and **5**, added to TCNE with about the same rates as the parent diene **1** or triene **2**. Moreover, a hypothetical bishomoaromaticity due to through-space or/and through-bond^[9] interactions between an endocyclic double bond and an exocyclic *s-sis*-butadiene moiety, as in **2** and **4**, appears to be insignificant by comparing kinetic and PE data of the polyene pairs **1/2** and **3/4**.

In light of these results, the three successive cycloadditions of TCNE to the triple diene **5** giving the corresponding monoadduct **6** (k_1^{II}), bisadduct **7** (k_2^{II}), and trisadduct **8** (k_3^{II}) were expected to have rate constants of same order of magnitude. This is indeed the case for the first two reactions (Scheme 2) as one finds $k_1^{II}/k_2^{II} = 8.7$ at 25°C (statistically corrected: $k_1^c/k_2^c = 5.8$). Unexpectedly, however, the cycloaddition of the third equivalent of TCNE occurs much more slowly as given by $k_2^{II}/k_3^{II} = 312$ at 25°C (statistically corrected: $k_2^c/k_3^c = 156$). Noteworthy is the fact that cycloadditions **5** + TCNE \rightarrow **6** and **6** + TCNE \rightarrow **7** have, within experimental error limits, the same activation enthalpy ($\Delta H^\ddagger \approx 11 \text{ kcal mol}^{-1}$) whereas the addition **7** + TCNE \rightarrow **8** has a significantly higher activation enthalpy ($\Delta H^\ddagger \approx 15 \text{ kcal mol}^{-1}$)^[11].

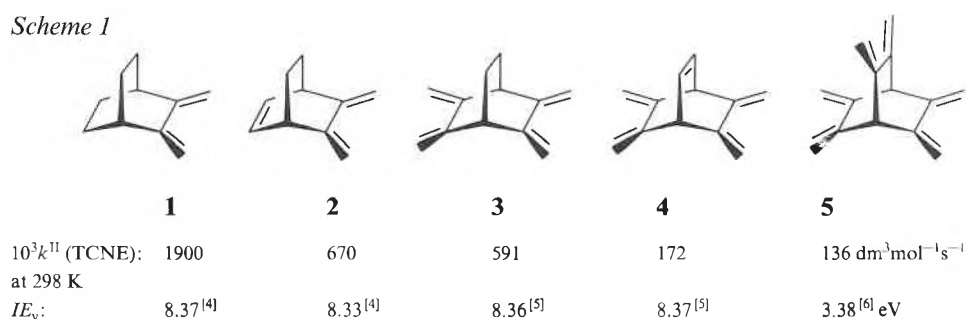
In the case of tetraene **3**, the two successive reactions **3** + TCNE \rightarrow **9** and **9** + TCNE \rightarrow **10** have similar rate constants ($k_1^c/k_2^c = 8.7$ at 25°C) and the same activation enthalpy ($\Delta H^\ddagger \approx 10.6 \pm 0.6 \text{ kcal mol}^{-1}$). In contrast, for pentaene **4**, a relatively

large difference in Diels-Alder reactivity was observed between the two successive reactions **4** + TCNE \rightarrow **11** and **11** + TCNE \rightarrow **12** (Scheme 2). A rate ratio $k_1^{II}/k_2^{II} = 282$ at 25°C (statistically corrected: $k_1^c/k_2^c = 141$) was measured and the activation enthalpy ($\Delta H^\ddagger = 13 \pm 0.3 \text{ kcal mol}^{-1}$) for **11** + TCNE \rightarrow **12** was significantly greater than that ($\Delta H^\ddagger = 11.3 \pm 0.8 \text{ kcal mol}^{-1}$) for **4** + TCNE \rightarrow **11**. Thus, tetraene **3** can be considered to model the tandem Diels-Alder properties of [2.2.2]hericene (**5**) while pentaene **4** models those of the monoadduct **6**.

In the case of the tandem Diels-Alder reactivity of **3**, **4**, and **5** to dimethyl acetylenedicarboxylate, the same reactivity trend was observed although the rate constant differences were strongly attenuated^[11,10]. These results were interpreted in terms of variations in the exothermicity (ΔH) of the successive cycloadditions. In the cases of TCNE additions to **1–5**, and of TCNE + **6** \rightarrow **7**, TCNE + **9** \rightarrow **10**, the exothermicities were all about the same, whereas, in the case of reactions TCNE + **7** \rightarrow **8** and TCNE + **11** \rightarrow **12**, a smaller exothermicity was expected because the latter cycloadditions generate barrelene derivatives that are known to be destabilized by π -electron repulsion^[11] arising from the specific arrangement of three-endocyclic double bonds^[12]. Thus, because of the Dimroth^[13] and Bell-Evans-Polanyi principle^[14], the less exothermic reactions TCNE + **7** \rightarrow **8** and TCNE + **11** \rightarrow **12** are expected to be less favoured than the other, more exothermic reactions. An exothermicity difference of 6–10 kcal mol⁻¹^[11] may cause a change of 2–3 kcal mol⁻¹ in the ΔH^\ddagger term, as observed. This interpretation assumes that all the cycloadditions under investigation have similar transition state geometries. In order to test this hypothesis, pentaenes less symmetrical than **4** or **6** should be made and their tandem Diels-Alder reactivity evaluated. We report the synthesis of such a system, i.e. 1,3-dimethoxy-5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (**13**).

Our starting material was the bisanhydride **14**^[15] which was esterified into **15** (57%) with EtOH in the presence of dicyclohexylcarbodiimide. Reduction with LiAlH₄ gave the corresponding tetrol **16** (51%) which, in turn, afforded the tetramethanesulfonate **17** (85%) on treatment with pyridine and CH₃SO₂Cl (Scheme 3). In

Scheme 1



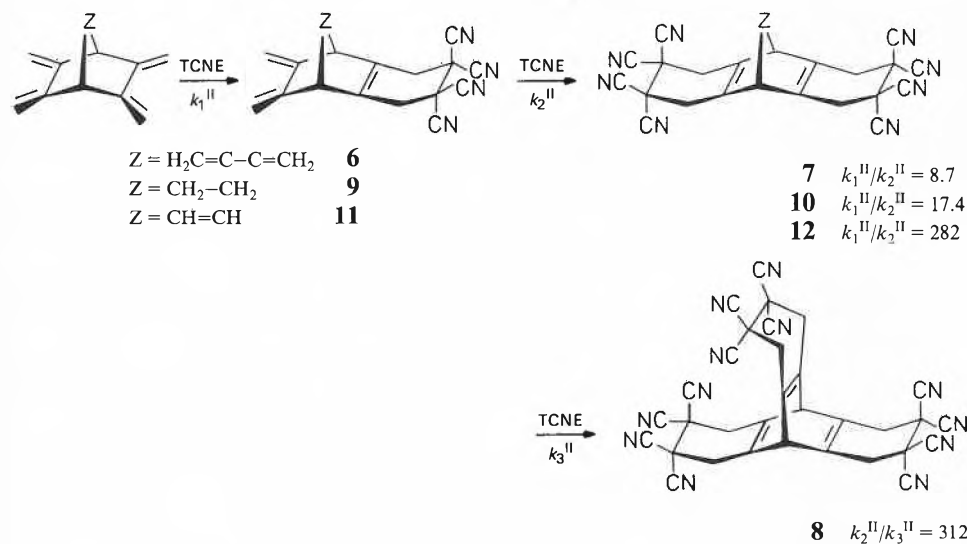
* Correspondence: Prof. Dr. P. Vogel
Institut de Chimie Organique
Université de Lausanne
Rue de la Barre 2
CH-1005 Lausanne

the presence of excess *t*-BuOK in dimethyl sulfoxide (DMSO), **17** eliminated four equivalents of CH₃SO₃H giving pentaene **13** in 94% yield. The structures of new compounds **13**, **15**–**17** were confirmed by their mode of formation, their elemental analysis, and their spectral data (see Expe-

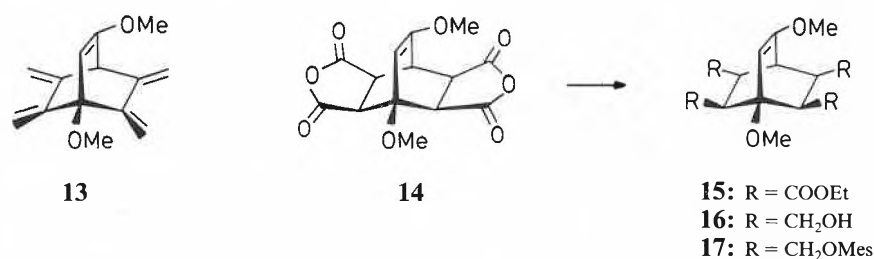
riental Part). The UV spectrum of **13** is very similar to that of **4**.

In the presence of one equivalent of TCNE (benzene, 20°C, 2 h), **13** gave adduct **18** in 86% yield. With an excess of TCNE, the bisadduct **19** was obtained in 90% yield (Scheme 4).

Scheme 2



Scheme 3



Scheme 4

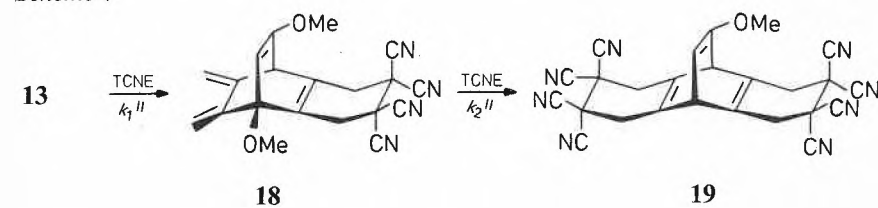


Table 1. Kinetic data of the cycloadditions of TCNE to **13** (k_1^{II} , ΔH_1^\ddagger , ΔS_1^\ddagger) and **18** (k_2^{II} , ΔH_2^\ddagger , ΔS_2^\ddagger) in toluene^{a)}.

k_1^{II} :	8.59×10^{-2}	0.15	0.267	0.462	$1.29 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
at	284.7	293.1	302.4	311.7	$323.8 \pm 0.05 \text{ K}$
	$k_1^{\text{II}} = 204 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K ^{b)}				
	$\Delta H_1^\ddagger = 10.7 \pm 0.5 \text{ kcal mol}^{-1}$; $\Delta S_1^\ddagger = -26 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$				
$10^3 \times k_2^{\text{II}}$:	1.87	3.85	8.18	20.4	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
at	312.5	322.4	333.4	347.8	$\pm 0.05 \text{ K}$
	$k_2^{\text{II}} = 0.6 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 298 K ^{b)}				
	$\Delta H_2^\ddagger = 14 \pm 1 \text{ kcal mol}^{-1}$; $\Delta S_2^\ddagger = -26 \pm 4 \text{ cal K}^{-1} \text{ mol}^{-1}$				

^{a)} Statistical standard deviations for 4–6 independent measurements with different solutions of polyenes and TCNE were found to be within 2–3%; for instrumentations and technical details, see reference¹⁶⁾.

^{b)} Inter- or extrapolated to 298 K.

The second-order rate constants of the TCNE Diels-Alder additions to **13** (k_1^{II}) and **18** (k_2^{II}) measured in toluene at various temperatures provided a means to evaluate the activation parameters reported in Table 1.

The disubstituted pentaene **13** has the same tandem Diels-Alder reactivity towards TCNE than the parent pentaene **4**. It presents the «record» value for the rate constant ratio $k_1^{\text{II}}/k_2^{\text{II}} = 340$ at 25°C (282 for **4**, 312 for **6**). As in the case of the TCNE additions to **4** and **6**, the reactivity difference between the two successive cycloadditions **13** + TCNE → **18** and **18** + TCNE → **19** is due to a change in the ΔH^\ddagger term. The methoxy groups in **13** and **18** do not affect their Diels-Alder reactivity compared with that of **4** and **11**, respectively. The activation entropies ΔS_1^\ddagger and ΔS_2^\ddagger (Table 1) are practically identical with those measured for the TCNE tandem Diels-Alder additions to **3–5**¹¹⁾, suggesting similar transition-state geometries and solvation effects for all the cycloadditions under study.

Our results are in agreement with the interpretation that the higher reactivity of pentaenes **4**, **6**, and **13** towards strong dienophiles compared with that of adducts **11**, **7**, and **18**, respectively, is associated with a change in the exothermicity of the two successive Diels-Alder additions. Because the cycloadditions of the monoadducts **11**, **7**, and **18** are generating the barrelene derivatives **12**, **8**, and **19**, respectively, they are slower than the cycloadditions of pentaene **4**, **6**, and **13**, respectively. The destabilizing «barrelene effect» is not present in the tandem Diels-Alder additions of tetraene **3** and in the case of the additions of the first two equivalents of dienophiles to [2.2.2]hericene¹¹⁾.

Experimental

General remarks, see Ref.¹⁷⁾

(5*R*,6*R*,7*S*,8*S*)-Tetraethyl 1,3-dimethoxybicyclo-[2.2.2]oct-2-ene-5,6,7,8-tetracarboxylate (**15**): A mixture of bisanhydride **14**¹⁵⁾ (2.5 g, 8.1 mmol) and dicyclohexylcarbodiimide (3.7 g, 18 mmol) in abs. EtOH (40 mL) was stirred at 50°C for 4 d. After filtration, the precipitate was washed with EtOH until discoloration. The filtrate was evaporated and the residue dissolved in CHCl₃ (100 mL) and washed with H₂O (100 mL, 5 times). After drying (MgSO₄), the solvent was evaporated and the residue recrystallized from EtOH. Yield: 2.11 g (57%), colourless crystals, *m.p.* 214–215°C. – UV (CH₂CN): $\epsilon_{200} = 5400$, final absorption. IR (KBr): 3000, 2950, 2920, 2840, 1800, 1650, 1270, 1230, 1140, 1070, 1040, 970, 910. ¹H-NMR (360 MHz, CDCl₃): 4.75 (d, ⁴*J* = 2.1, H–C(2)); 3.75, 3.55 (2m, ³*J* = 7, 4 COOCH₂); 3.64, 3.48 (2s, 2 OMe); 3.30 (m, ³*J* = 9.6, H–C(6), H–C(7)); 3.16 (dtd, ³*J* = 2.6, ⁴*J* = 2.1, H–C(4)); 2.68 (m, *J* = 9.6, 2.6, H–C(5), H–C(8)); 1.23, 1.21 (2t, ³*J* = 7, 4 CH₃–CH₂). ¹³C-NMR (90.55 MHz, CDCl₃): 169.7, 157.8 (2s, 4 CO); 119.0 (s, C(3)); 94.9 (d, ¹*J*(C,H) = 172, C(2)); 78.9 (s, C(1)); 60.0, 58.6 (2t, ¹*J*(C,H) = 145, 4 COOCH₂); 54.7 (q, ¹*J*(C,H) = 143, CH₃O–C(3)); 51.1 (q, ¹*J*(C,H) = 143, CH₃O–C(1)); 46.5, 45.8 (2d, ¹*J*(C,H) = 137, C(5), C(6), C(7), C(8)); 34.8 (d, ¹*J*(C,H) = 146, C(4)); 14.9, 14.8 (2q, ¹*J*(C,H) = 128, 4 CH₃CH₂O). MS (70 eV): 457 (0.3), 456 (1.9, *M*⁺), 411

(6), 383 (12), 368 (2), 355 (2), 339 (4), 309 (4), 295 (5), 247 (8), 237 (5), 211 (17), 139 (22), 138 (100).

(5R,6R,7S,8S)-1,3-Dimethoxybicyclo[2.2.2]oct-2-ene-5,6,7,8-tetramethanol (**16**): A suspension of **15** (4 g, 8.8 mmol) in anhydrous THF (40 mL) was added dropwise to a stirred suspension of LiAlH_4 (1.45 g, 38 mmol) in anhydrous THF (25 mL). The mixture was heated to reflux for 70 h. After cooling to 20°C H_2O (2.9 mL) was added dropwise. The mixture was heated to reflux and filtered through silica gel (20 g). The salts were taken with EtOH (60 mL, 3 times) and heated under reflux for 45 min. The filtrates were united and evaporated. The residue was recrystallized from acetone. Yield: 1.29 g (51%), *m.p.* 155–156°C. – IR (KBr): 3390, 3290, 3010, 2960, 2940, 2920, 2870, 2840, 1650, 1210, 1080, 1050, 1030. $^1\text{H-NMR}$ (360 MHz, D_2O): 4.6 (s, 4 OH), 4.45 (d, $^4J = 2.5$, H–C(2)); 3.65 (dd, $^2J = 11.5$, $^3J = 6.5$), 3.54 (dd, $^2J = 11.5$, $^3J = 2.5$, $\text{CH}_2\text{–C}(6)$, $\text{CH}_2\text{–C}(7)$); 3.37, 3.18 (2s, 2 OMe); 3.22 (m, $\text{CH}_2\text{–C}(5)$, $\text{CH}_2\text{–C}(8)$); 2.42 (m, $^3J = 2.5$, $^4J = 2.5$, H–C(4)); 2.42, 2.10 (2m, H–C(5), H–C(6), H–C(7), H–C(8)). $^{13}\text{C-NMR}$ (90.55 MHz, D_2O): 158.9 (s, C(3)); 96.9 (d, $^1J(\text{C,H}) = 166$, C(2)); 82.5 (s, C(1)); 63.4, 60.3, (2t, $^1J(\text{C,H}) = 142$, 4 CH_2OH); 56.3 (q, $^1J(\text{C,H}) = 146$, $\text{CH}_3\text{O–C}(3)$); 50.4 (q, $^1J(\text{C,H}) = 144$, $\text{CH}_3\text{O–C}(1)$); 45.4, 44.1 (2d, $^1J(\text{C,H}) = 131$, C(5), C(6), C(7), C(8)); 40.6 (d, $^1J(\text{C,H}) = 137$, C(4)). MS (70 eV): 288 (2, M^+), 270 (1), 257 (13), 240 (14), 225 (14), 207 (30), 179 (16), 177 (17), 149 (21), 135 (22), 129 (31), 119 (34), 99 (100).

(5R,6R,7S,8S)-1,3-Dimethoxybicyclo[2.2.2]oct-2-ene-5,6,7,8-tetramethyl methanesulfonate (**17**): Methanesulfonyl chloride (1.35 mL, 17.3 mmol) was added dropwise to a solution of **16** (0.5 g, 1.73 mmol) in anhydrous pyridine cooled to 0°C. After 16 h at 3°C, the mixture was poured into ice (10 g) under vigorous stirring. The mixture was extracted with CH_2Cl_2 (20 mL, 5 times). The extract was washed with H_2O (100 mL, 3 times) and dried (MgSO_4). After solvent evaporation, the residue was washed with a little acetone. Yield: 1.04 g (85%), colourless powder, *m.p.* 155–156°C (dec.). – IR (KBr): 3030, 3000, 2950, 2930, 2840, 1650, 1360, 1335, 1170, 1095, 985, 960, 940, 870, 850, 820. $^1\text{H-NMR}$ (360 MHz, CD_3CN): 4.66 (d, $^4J = 2.5$, H–C(2)); 4.38, 3.94 (2m, 4 CH_2OMes); 3.55, 3.33 (2s, 2 OMe); 3.03 (s, 4 CH_3SO_3); 2.83 (td, $^3J = 9.5$, 2.5), 2.48 (td, $^3J = 9.5$, 4.5, 2.5, H–C(5), H–C(6), H–C(7), H–C(8)); 2.72 (td, $^3J = 2.5$, $^4J = 2.5$, H–C(4)). $^{13}\text{C-NMR}$ (90.55 MHz, CD_3CN): 158.0 (s, C(3)); 97.0 (d, $^1J(\text{C,H}) = 167$, C(2)); 80.5 (s, C(1)); 70.6, 68.8 (2t, $^1J(\text{C,H}) = 155$, 4 CH_2OMes); 55.8, 50.4 (2q, $^1J(\text{C,H}) = 145$, 2 OCH_3); 42.3, 40.3 (2d, $^1J(\text{C,H}) = 134$, C(5), C(6), C(7), C(8)); 39.7 (d, $^1J(\text{C,H}) = 140$, C(4)); 37.7, 37.4 (2q, $^1J(\text{C,H}) = 140$, 4 SO_2CH_3). MS (70 eV): 409 (0.3), 359 (0.9), 314 (1), 298 (9), 285 (13), 270 (1), 257 (1), 252 (3), 235 (2), 219 (7), 203 (5), 191 (3), 189 (3), 173 (2), 171 (2), 151 (3), 121 (13), 101 (10), 95 (14), 91 (8), 79 (100).

1,3-Dimethoxy-5,6,7,8-tetramethylidenebicyclo[2.2.2]oct-2-ene (**13**): Potassium *tert*-butanolate (1.5 g, 13.9 mmol) freshly sublimed was added portionwise to

a stirred solution of **17** (744 mg, 1.27 mmol) in anhydrous DMSO (20 mL). After stirring at 20°C for 3.5 h, ice (40 g) was added and the mixture extracted with CH_2Cl_2 (60 mL, 5 times). The organic phases were united and washed with H_2O (300 mL, 5 times). After the solvent evaporation, the residue was purified by column chromatography on silica gel (10 g, AcOEt/petroleum ether 1:9) yielding 253 mg (94%), colourless crystals, *m.p.* 99.5–100°C. – UV (95% EtOH): 254 (S, 8330), 245 (S, 9520), 235 (11750), 228 (12180), 220 (S, 11380), 206 (12400). UV (isooctane): 254 (S, 8400), 246 (S, 9450), 235 (11900), 228 (12400), 220 (S, 11500), 205 (12400). IR (KBr): 3090, 3030, 2970, 2950, 2840, 1640, 1340, 1200, 1160, 1100, 1020, 1000, 900, 890. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 5.38, 5.33, 5.19, 5.02 (4s, 8H); 5.06 (d, $^4J = 2.5$, H–C(2)); 3.71 (d, $^4J = 2.5$, H–C(4)); 3.69, 3.64 (2s, 2 MeO). $^{13}\text{C-NMR}$ (90.55 MHz, CDCl_3): 160.3 (s, C(3)); 145.6, 142.4 (2s, C(5), C(6), C(7), C(8)); 104.5, 101.2 (2t, $^1J(\text{C,H}) = 158$, $\text{H}_2\text{C}=\text{C}(5)$, $\text{H}_2\text{C}=\text{C}(6)$, $\text{H}_2\text{C}=\text{C}(7)$, $\text{H}_2\text{C}=\text{C}(8)$); 92.8 (d, $^1J(\text{C,H}) = 169$, C(2)); 83.2 (s, C(1)); 55.5 (q, $^1J(\text{C,H}) = 144$), 53.4 (q, $^1J(\text{C,H}) = 142$, 2 OMe); 55.3 (d, $^1J(\text{C,H}) = 144$, C(4)). MS (70 eV): 216 (7, M^+), 215 (5), 201 (27), 188 (36), 185 (38), 173 (19), 164 (58), 163 (34), 141 (32), 135 (30), 128 (35), 121 (40), 115 (52), 91 (72), 78 (47), 77 (68), 69 (37), 65 (64), 63 (48), 52 (73), 51 (100).

1,12-Dimethoxy-9,10-dimethylidenetricyclo[6.2.2.0^{2,7}]dodeca-2(7),11-diene-4,4,5,5-tetracarboxitrile (**18**): A mixture of **13** (111 mg, 0.51 mmol) and TCNE (66 mg, 0.51 mmol) in benzene (7 mL) was stirred at 20°C for 2 h. After solvent evaporation, the residue was purified by column chromatography on silica gel (5 g, AcOEt/petroleum ether 1:9). Yield: 140 mg (86%), colourless powder, *m.p.* 172–173°C. – IR (KBr): 3100, 3000, 2960, 2930, 2840, 1640, 1325, 1290, 1205, 1100, 1005, 900. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 5.40, 5.34, 5.17, 5.06, (4s, 2 $\text{H}_2\text{C}=\text{C}$); 5.25 (d, $^4J = 2.3$, H–C(11)); 3.67 (d, $^4J = 2.3$, H–C(8)); 3.65, 3.62 (2s, 2 OMe); 3.29 (m, $\text{H}_2\text{C}(3)$, $\text{H}_2\text{C}(6)$). MS (70 eV): 344 (4, M^+), 313 (4), 292 (14), 238 (14), 201 (5), 185 (5), 165 (20), 164 (100).

1,16-Dimethoxytetracyclo[6.6.2.0^{2,7}.0^{9,14}]hexadeca-2(7),9(14),15-triene-4,4,5,5,11,11,12,12-octacarboxitrile (**19**): A mixture of **13** (10 mg, 0.046 mmol) and TCNE (12 mg, 0.092 mmol) in benzene (1 mL) was stirred at 20°C for 8 d. After solvent evaporation, the residue was recrystallized from CHCl_3 . Yield: 22 mg (90%), colourless crystals, *m.p.* 252–253°C (dec.). – IR (KBr): 3130, 3030, 3000, 2980, 2940, 2840, 1635, 1430, 1300, 1270, 1100, 990, 750. $^1\text{H-NMR}$ (80 MHz, CDCl_3): 5.65 (d, $^4J = 2$, H–C(15)); 3.92 (d, $^4J = 2$, H–C(8)); 3.72, 3.55 (2s, 2 MeO); 3.35 (br.s., $\text{H}_2\text{C}(3)$, $\text{H}_2\text{C}(6)$, $\text{H}_2\text{C}(10)$, $\text{H}_2\text{C}(13)$). MS (70 eV): 473 (17), 472 (48, M^+), 457 (14), 441 (51), 430 (68), 368 (98), 344 (28), 329 (42), 315 (59), 292 (100), 277 (33), 240 (51), 164 (79).

- [1] O. Pilet, J.-L. Birbaum, P. Vogel, *Helv. Chim. Acta* 66 (1983) 19.
- [2] K. Fukui, *Acc. Chem. Res.* 4 (1971) 57; *Bull. Chem. Soc. Jpn.* 39 (1966) 498; N. D. Epiotis: *Theory of Organic Reactions*, Springer-Verlag, Berlin (1978); N. D. Epiotis, *Pure Appl. Chem.* 51 (1979) 203; R. Sustmann, *Tetrahedron Lett.* 12 (1971) 2721; R. Sustmann, R. Schubert, *Angew. Chem. Int. Ed. Engl.* 11 (1972) 840; J. Sauer, R. Sustmann, *ibid.* 19 (1980) 779; C. Rücker, D. Lang, J. Sauer, H. Friege, R. Sustmann, *Chem. Ber.* 113 (1980) 1663; G. Klopman, *J. Am. Chem. Soc.* 90 (1968) 223; L. Salem, *ibid.* 90 (1968) 543, 553; K. N. Houk, in A. P. Marchand, R. E. Lehr (Ed.): *Pericyclic Reactions*, Vol. 2, Academic Press, New York (1977), p. 181–271 and ref. cit. therein.
- [3] H. D. Scharf, H. Plum, J. Fleischhauer, W. Schlerker, *Chem. Ber.* 112 (1979) 862; R. Sustmann, M. Böhm, J. Sauer, *ibid.* 112 (1979) 883.
- [4] P. Asmus, M. Klessinger, *Tetrahedron* 30 (1974) 2477.
- [5] M. Mohraz, C. Batich, E. Heilbronner, P. Vogel, P.-A. Carrupt, *Recl. Trav. Chim. Pays-Bas* 98 (1979) 361.
- [6] M. Mohraz, W. Jian-qi, E. Heilbronner, P. Vogel, O. Pilet, *Helv. Chim. Acta* 63 (1980) 568.
- [7] O. Pilet, P. Vogel, *Angew. Chem. Int. Ed. Engl.* 19 (1980) 1003; A. Chollet, M. Wismer, P. Vogel, *Tetrahedron Lett.* 17 (1976) 4271.
- [8] P. Mercier, C. Sandorfy, O. Pilet, P. Vogel, *Can. J. Spectrosc.* 28 (1983) 184.
- [9] R. Hoffmann, *Acc. Chem. Res.* 4 (1971) 1; R. Hoffmann, A. Imamura, W. J. Hehre, *J. Am. Chem. Soc.* 90 (1968) 1499; R. Gleiter, *Angew. Chem. Int. Ed. Engl.* 13 (1974) 696; E. Heilbronner, A. Schmelzer, *Helv. Chim. Acta* 58 (1975) 936.
- [10] In the case of tandem Diels-Alder additions of 2,3,5,6-tetramethylidenebicyclo[2.2.1]heptane derivatives, large values for rate constant ratio k_1^1/k_2^1 were also found: L. de Piccioto, P.-A. Carrupt, P. Vogel, *J. Org. Chem.* 47 (1982) 3796; O. Pilet, P. Vogel, *Helv. Chim. Acta* 64 (1981) 2563.
- [11] R. B. Turner, *J. Am. Chem. Soc.* 86 (1964) 3586; R. B. Turner, W. R. Meador, R. E. Winkler, *ibid.* 79 (1957) 4116; J. L. Jensen, *Prog. Phys. Org. Chem.* 12 (1976) 189.
- [12] E. Haselbach, E. Heilbronner, G. Schröder, *Helv. Chim. Acta* 54 (1971) 153.
- [13] O. Dimroth, *Angew. Chem.* 46 (1933) 571.
- [14] M. G. Evans, M. Polanyi, *Trans. Faraday Soc.* 32 (1936) 1340; 34 (1938) 11; R. P. Bell, *Proc. R. Soc. London A* 154 (1936) 414; M. J. S. Dewar, *J. Am. Chem. Soc.* 106 (1984) 209.
- [15] A. P. Kozikowski, R. Schmiesing, *Tetrahedron Lett.* 19 (1978) 4241.
- [16] O. Pilet, A. Chollet, P. Vogel, *Helv. Chim. Acta* 62 (1979) 2341.
- [17] K. A. Black, P. Vogel, *J. Org. Chem.* 51 (1986) 5341.

Received: September 21, 1987 [FC 120]