

Thermal [2 + 2]Cycloaddition of 1,1-Dimethoxyalkenes to Acetylenic Esters

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[2 + 2]Cycloaddition of the 1,1-dimethoxyalkenes **1** to acetylenic esters, such as dimethyl acetylenedicarboxylate **2a** and methyl propiolate **2b**, occurs *via* 1,4-dipolar intermediates which, trapped by methyl propiolate and *tert*-butyl alcohol, give functionalized 3,3-dimethoxycyclobutenes **3**, synthetic precursors to naturally occurring products and biologically active compounds.

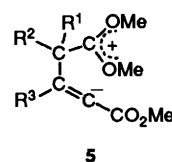
Because of their importance,¹ in recent years, a great number of syntheses of four-membered carbocycles have been developed.² Of these, [2 + 2]cycloaddition of alkenes to alkynes provides a simple route to functionalized cyclobutenes.³ In an extension of this work, we have investigated the reaction of 1,1-dialkoxyalkenes and acetylenic esters to form dialkyl acetals of functionalized cyclobutenones. The latter compounds which, other than the halogen derivatives,⁴ had been prepared in only a very few cases,⁵ can be considered as synthetic precursors to naturally occurring products and biologically active compounds.⁶ However, it is reported that acetylenic esters lead easily to cyclobutenes only by reaction with enamines.^{7,8} With the other alkenes used, such as mono- or 1,1-di-alkyl substituted alkenes,⁹ silyl enol ethers¹⁰ and ketene alkyl silyl acetals¹¹ (which are less nucleophilic than enamines) the reaction occurs in the presence of a Lewis acid. So, the mechanism of the cycloaddition of 1,1-dialkoxyalkenes to acetylenic esters also appeared interesting since the nucleophilicity of the former is intermediate between that of enamines and enol ethers.¹²

The alkenes **1a–c** and the acetylenic esters **2a,b** were allowed to react in dry acetonitrile (Scheme 1) at the reaction temperatures and for the times reported in Table 1 (entries 1–6). The reaction mixtures were analysed by ¹H NMR spectroscopy. Inspection of the ¹H NMR spectra of the mixtures of **1a–c** with

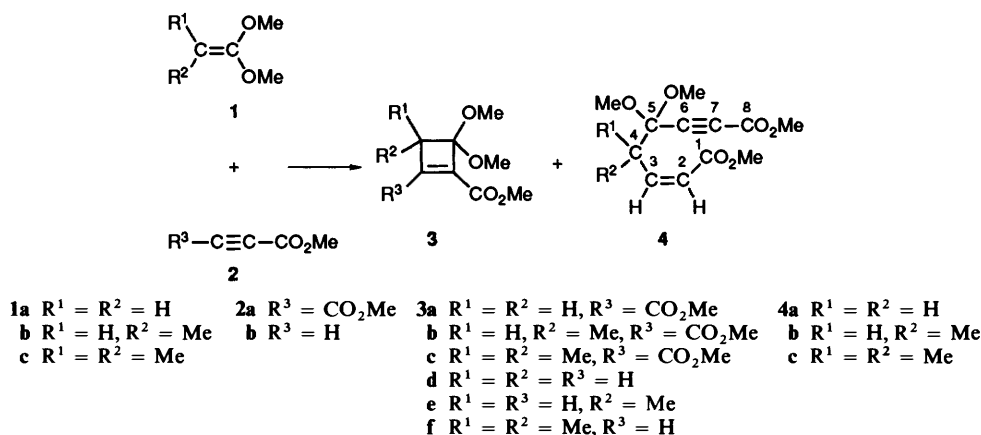
dimethyl acetylenedicarboxylate (DMAD) **2a** showed the cyclobutenes **3a–c** as the sole products. In contrast, in the reaction mixtures of the alkenes **1a–c** with methyl propiolate (MP) **2b** the enynes **4a–c** in addition to the cyclobutenes **3d–f** were also present. Compounds **3a–f** and **4a–c** were isolated by silica gel chromatography with the yields† reported in Table 1; their structures were assigned on the basis of analytical and spectral data (Table 2). In particular the *cis* configuration of the enynes **4a–c** was assigned on the basis of the coupling constant of the vinyl protons (J_{cis} 11.5 Hz for **4a** and **4b**, 13.0 Hz for **4c**) and by comparison of the chemical shifts of the same protons with those of the products **6b**, **7b** and **8b** (see below). Neither spectroscopic nor chromatographic evidence was obtained for the presence of the *trans*-isomers of the enynes **4a–c** in the reaction mixtures. Control experiments showed that the cyclobutenes **3** were stable under the reaction conditions, so excluding the possibility that the enynes **4** were formed through a ring-opening of the cyclobutenes **3** by MP.

1,4-Dipolar intermediates have been suggested or evidenced in the reactions between DMAD and enamines⁷ or imino ethers¹⁶ respectively. We therefore examined the possibility that the reaction of the alkenes **1** and acetylenic esters **2** could occur *via* an ionic mechanism through the formation of 1,4-dipolar intermediates such as **5**, and that the enynes **4** were trapping products of the intermediates from reaction with MP.

† As observed in other cycloadditions^{13,14} the reactivity of the alkene **1c** disubstituted at C-2 is lower than those of the mono- and un-substituted ones **1a,b** in that the first, even if it has the largest highest occupied molecular orbital (HOMO) energy, has a more symmetric π -electron distribution.¹⁵ Therefore polymerization¹³ of **1c** occurs to a great extent and the yields of the reaction products **4c** and/or **3c,f** are the lowest.



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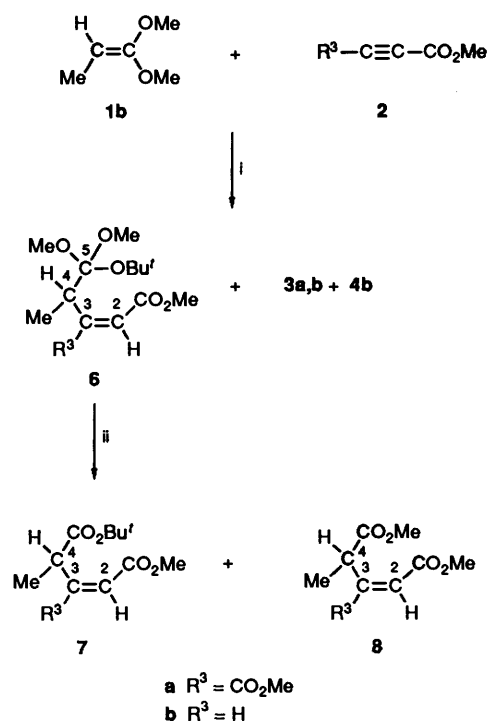
Scheme 1‡

‡ The numeration on the structure **4** is used to simplify the reading of the NMR data. Product **4** occurs only for R³ = H.

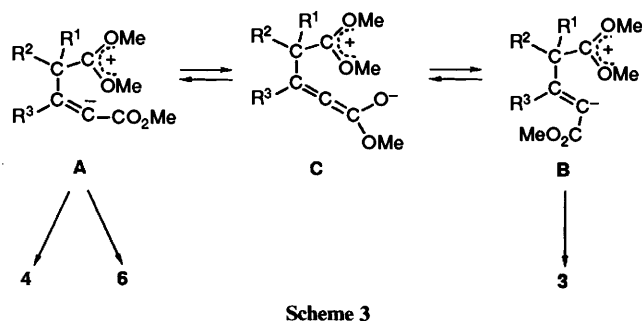
Table 1 Reaction of the 1,1-dialkoxyalkenes **1** with the acetylenic esters **2**

| Entry | Reagents ^a | | Reaction conditions | | | Product distribution [yields (%)] ^d |
|-------|-----------------------|-----------|---------------------|------------------|---------------------------------|---|
| | Alkene | Ester | T/°C | t/h ^b | Solvent ^c | |
| 1 | 1a | 2a | 18–22 | 3 | MeCN | 3a (53) |
| 2 | 1b | 2a | 18–22 | 3 | MeCN | 3b (58) |
| 3 | 1c | 2a | 60 | 24 | MeCN | 3c (30) |
| 4 | 1a | 2b | 50 | 7 | MeCN | 3d (20) 4a (28) |
| 5 | 1b | 2b | 50 | 7 | MeCN | 3e (28) 4b (23) |
| 6 | 1c | 2b | 60 | 96 | MeCN | 3f (20) 4c (8) |
| 7 | 1b | 2b | 50 | 24 | CH ₂ Cl ₂ | 3e (35) 4b (14) |
| 8 | 1b | 2b | 50 | 96 ^e | CCl ₄ | 3e (20) 4b (trace) |
| 9 | 1b | 2a | 18–22 | 4 | Bu ^t OH | 3b (55) 6a (16) ^f |
| 10 | 1b | 2b | 50 | 8 | Bu ^t OH | 3e (14) 4b (20) 6b (21) ^g |

^a Molar ratio **1**:**2** = 1.5:1. ^b Time required for the completion of the reaction (TLC or IR). ^c Solution of **2** (1 mol dm⁻³). ^d Deduced on the basis of the ¹H NMR spectrum of the reaction mixture, confirmed by silica gel chromatography (except for **6**) and calculated with respect to the ester **2**. ^e At this time the ester **2b** was also present in the reaction mixture, but the alkene **1b** was polymerized to a large degree (¹H NMR). ^f Obtained by the sum of the yields of the esters **7a** and **8a** (see Experimental section). ^g Obtained by the sum of the yields of the esters **7b** and **8b** (see Experimental section).

**Scheme 2*** Reagents: i, Bu^tOH (solvent); ii, SiO₂ chromatography

* The numeration on the structures **6**–**8** is used to simplify the reading of the NMR data.



Thus, **1b** and MP were allowed to react in apolar solvents such as dichloromethane and carbon tetrachloride under conditions identical with those used with acetonitrile as the polar solvent. The results obtained (Table 1, entries 7 and 8)

show a correlation between solvent polarity and both reaction time and product distribution.[†] In fact in contrast to the reaction in acetonitrile (entry 5), in dichloromethane the reaction was complete after 24 h and the cyclobutene **3e** and the enyne **4b** were formed in *ca.* 5:1 molar ratio (*ca.* 2.5:1 in acetonitrile). In carbon tetrachloride the reaction was so slow that it was not run to completion and, in addition to the cyclobutene **3e**, only traces of the enyne **4b** were formed.

These results support the occurrence of an ionic mechanism which was confirmed by suitable trapping experiments. In fact, the alkene **1b** reacted with DMAD or MP in *tert*-butyl alcohol,[‡] to give the ortho esters **6a,b** as trapping products of 1,4-dipolar intermediates (such as **5**) by the alcohol, in addition to the products obtained with acetonitrile as the solvent (Scheme 2). Temperatures, times§ and percentage yields of the reaction products are reported in Table 1 (entries 9 and 10). Quantification was made on the basis of the ¹H NMR spectra of the reaction mixtures and confirmed by chromatography on silica gel (except for the ortho esters **6a,b**). The latter were not isolated by chromatography since they underwent quantitative hydrolysis partly to *tert*-butyl esters **7a,b** and partly to methyl esters **8a,b** on contact with the adsorbents. Therefore, the structures of the ortho esters **6a,b** were assigned on the basis of the spectral data (Table 2) obtained by ¹H NMR spectra of the reaction mixtures, the signals of the known products being subtracted. The yields of **6a,b**, deduced from these spectra, were confirmed from the sum of those of the esters **7a,b** and **8a,b**, the latter being obtained by chromatography of the crude reaction mixtures. The spectral and analytical data for the esters **7a,b** and **8a,b**¶ are reported in Table 2. The *trans* configuration of the

[†] An accurate study of the solvent effect is very difficult since the alkenes **1** are sensitive to hydrolysis and also tend to polymerize at room temperature.¹³

[‡] Control experiments showed that *tert*-butyl alcohol combines neither with the reagents nor with the reaction products. Only the cyclobutene **3e** undergoes partial polymerization after long reaction times. However, in the time required for the completion of the reaction, the polymerization of **3e** occurs to only a small extent.

[§] It is to be noted that the rate of the reactions of **1b** with **2** in *tert*-butyl alcohol is very similar to that in more polar acetonitrile¹⁷ (Table 1), suggesting that the 1,4-dipolar intermediates are stabilized by hydrogen bonding with the protic solvent. Nevertheless, the trapping ability of *tert*-butyl alcohol is smaller than that of MP (Table 1), probably because the steric hindrance of the *tert*-butoxy group makes the formation of the C–O bond at the cationic site of the intermediates difficult.

[¶] Compound **8b** is known,¹⁸ but its analytical and spectral data are not reported.

Table 2 Physical, spectral and analytical data for the products derived from the reaction between the alkenes **1** and the acetylenic esters **2**

| Compound ^a | $\nu_{\max}(\text{CDCl}_3)/\text{cm}^{-1}$ | $\delta_{\text{H}}(\text{CDCl}_3)(\text{J}/\text{Hz})$ | $\delta_{\text{C}}(\text{CDCl}_3)$ |
|------------------------|--|--|---|
| 3a ^b | 1723, 1651 | 2.77 (2 H, s, CH ₂), 3.37 (6 H, s, 2 × OMe), 3.77 (6 H, s, 2 × CO ₂ Me) | 40.7 (t, C-4), 51.4 and 51.8 (2 × q, 4 × OMe) 101.1 (s, C-3), 141.4 and 143.5 (2 × s, C-1, C-2), 160.7 and 162.0 (2 × s, 2 × CO ₂) |
| 3b ^c | 1735, 1651 | 1.24 (3 H, d, <i>J</i> 7.1, Me), 3.20 (1 H, q, <i>J</i> 7.1, CH), 3.36 and 3.46 (6 H, 2 × s, 2 × OMe), 3.82 (6 H, s, 2 × CO ₂ Me) | 12.3 (q, 4-Me), 48.0 (d, C-4), 51.4, 51.7, 51.8 and 51.9 (4 × q, 4 × OMe), 102.0 (s, C-3), 139.9 and 148.1 (2 × s, C-1, C-2), 161.1 and 162.1 (2 × s, 2 × CO ₂) |
| 3c ^d | 1735, 1653 | 1.31 (6 H, s, 2 × Me), 3.40 (6 H, s, 2 × OMe), 3.80 (6 H, s, 2 × CO ₂ Me) | |
| 3d ^e | 1719, 1610 | 2.65 (2 H, d, <i>J</i> 1.2, CH ₂), 3.43 (6 H, s, 2 × OMe), 3.76 (3 H, s, CO ₂ Me), 7.16 (1 H, t, <i>J</i> 1.2, CH) | 40.8 (t, C-4), 50.6, 51.4 and 51.7 (3 × q, 3 × OMe), 103.7 (s, C-3), 140.6 (s, C-2), 149.3 (d, C-1), 161.1 (s, CO ₂) |
| 3e ^f | 1719, 1607 | 1.15 (3 H, d, <i>J</i> 7.3, Me), 2.99 (1 H, dq, <i>J</i> 7.3, 1.4, CH), 3.37 and 3.48 (6 H, 2 × s, 2 × OMe), 3.76 (3 H, s, CO ₂ Me), 7.11 (1 H, d, <i>J</i> 1.4, CH) | 13.1 (q, 4-Me), 46.9 (d, C-4), 50.9, 51.1 and 51.4 (3 × q, 3 × OMe), 103.7 (s, C-3), 138.7 (s, C-2), 153.9 (d, C-1), 161.3 (s, CO ₂) |
| 3f ^g | 1719, 1623 | 1.22 (6 H, s, 2 × Me), 3.41 (6 H, s, 2 × OMe), 3.75 (3 H, s, CO ₂ Me), 7.05 (1 H, s, CH) | |
| 4a ^h | 2243, 1720, 1645 | 3.32 (2 H, dd, <i>J</i> 6.8, 1.9, 4-H ₂), 3.36 (6 H, s, 2 × OMe), 3.72 and 3.79 (6 H, 2 × s, 2 × CO ₂ Me), 5.94 (1 H, dt, <i>J</i> 11.7, 1.9, 2-H), 6.37 (1 H, dt, <i>J</i> 11.7, 6.8, 3-H) | 38.6 (t, C-4), 51.2, 51.7, 51.9 and 52.9 (4 × q, 4 × OMe), 82.2 and 90.4 (2 × s, C-6 and C-7), 98.3 (s, C-5), 121.8 (d, C-2), 142.0 (d, C-3), 153.1 (s, C-8), 164.4 (s, C-1) |
| 4b ⁱ | 2243, 1718, 1647 | 1.03 (3 H, d, <i>J</i> 6.9, 4-Me), 3.32 and 3.36 (6 H, 2 × s, 2 × OMe), 3.72 and 3.81 (6 H, 2 × s, 2 × CO ₂ Me), 4.10 (1 H, ddq, <i>J</i> 6.9, 10.1, 1.1, 4-H), 5.85 (1 H, dd, <i>J</i> 11.5, 1.1, 2-H), 6.34 (1 H, dd, <i>J</i> 11.5, 10.1, 3-H) | 15.5 (q, 4-Me), 38.4 (d, C-4), 50.6, 50.7, 51.1 and 52.9 (4 × q, 4 × OMe), 81.4 (s, C-6, C-7), 101.6 (s, C-5), 119.7 (d, C-2), 148.8 (d, C-3), 153.2 (s, C-8), 166.4 (s, C-1) |
| 4c ^j | 2240, 1719, 1638 | 1.37 (6 H, s, 2 × Me), 3.56 (6 H, s, 2 × OMe), 3.71 and 3.83 (6 H, 2 × s, 2 × CO ₂ Me), 5.77 (1 H, d, <i>J</i> 13.3, 2-H), 6.45 (1 H, d, <i>J</i> 13.3, 3-H) | 21.0 (q, 4-Me ₂), 48.4 (s, C-4), 51.3 and 53.0 (2 × q, 2 × OMe), 55.1 (q, 2 × OMe), 80.1 and 81.0 (2 × s, C-6, C-7), 105.1 (s, C-5), 119.3 (d, C-2), 149.4 (d, C-3), 152.9 (s, C-8), 166.9 (s, C-1) |
| 6a | | 1.34 (s, CMe ₃), 1.33, (d, <i>J</i> 7.3, 4-Me), 3.26 and 3.34 (2 × s, 2 × OMe), 3.74 (s, 2 × CO ₂ Me), 4.45 (q, <i>J</i> 7.3, 4-H), 6.22 (s, 2-H) ^k | |
| 6b | | 1.13 (d, <i>J</i> 7.1, 4-Me), 1.33 (s, CMe ₃), 3.28 and 3.33 (2 × s, 2 × OMe), 3.70 (s, CO ₂ Me), 4.25 (ddq, <i>J</i> 7.1, 1.1, 10.1, 4-H), 5.73 (dd, <i>J</i> , 11.5, 1.1, 2-H), 6.46 (dd, <i>J</i> 11.5, 10.1, 3-H) ^k | |
| 7a ^l | 1724, 1646 | 1.39 (d, <i>J</i> 7.1, 4-Me) and 1.41 (s, CMe ₃) (together 12 H), 3.79 and 3.80 (6 H, 2 × s, 2 × CO ₂ Me), 4.65 (1 H, q, <i>J</i> 7.1, 4-H), 6.78 (1 H, s, 2-H) | 15.7 (q, 4-Me), 27.8 (q, CMe ₃) 39.1 (d, C-4), 51.8 and 52.3 (2 × q, 2 × OMe), 84.8 (s, CMe ₃), 126.4 (d, C-2), 147.1 (s, C-3), 165.7, 166.2 and 171.5 (3 × s, 3 × CO ₂) |
| 7b ^m | 1719, 1650 | 1.29 (3 H, d, <i>J</i> 7.3, 4-Me) 1.44 (9 H, s, CMe ₃) 3.72 (3 H, s, OMe), 4.36 (1 H, ddq, <i>J</i> 7.3, 9.6, 1.1, 4-H), 5.83 (1 H, dd, <i>J</i> 11.6, 1.1, 2-H), 6.35 (1 H, dd, <i>J</i> 11.6, 9.6, 3-H) | 17.8 (q, 4-Me), 27.9 (q, CMe ₃) 39.8 (d, C-4), 51.1 (q, OMe), 80.6 (s, CMe ₃), 119.5 (d, C-2), 147.9 (d, C-3), 166.2 and 173.2 (2 × s, 2 × CO ₂) |
| 8a ⁿ | 1724, 1646 | 1.42 (3 H, d, <i>J</i> 7.1, 4-Me), 3.66, 3.79 and 3.81 (9 H, 3 × s, 3 × OMe), 4.74 (1 H, q, <i>J</i> 7.1, 4-H), 6.85 (1 H, s, 2-H) | 15.6 (q, 4-Me), 37.9 (d, C-4) 51.8, 51.9 and 52.5 (3 × q, 3 × OMe), 127.0 (d, C-2), 146.2 (s, C-3), 165.5, 165.8 and 172.9 (3 × s, 3 × CO ₂) |
| 8b ^o | 1719, 1647 | 1.33 (3 H, d, <i>J</i> 7.1, 4-Me), 3.70 and 3.73 (6 H, 2 × s, 2 × OMe), 4.53 (1 H, ddq, <i>J</i> 7.1, 9.7, 1.1, 4-H), 5.86 (1 H, dd, <i>J</i> 11.4, 1.1, 2-H), 6.35 (1 H, dd, <i>J</i> 11.4, 9.7, 3-H) | 17.7 (q, 4-Me), 38.6 (d, C-4), 51.2 and 51.9 (2 × q, 2 × OMe), 120.0 (d, C-2), 147.1 (d, C-3), 166.1 and 174.4 (2 × s, 2 × CO ₂) |

^a All compounds were obtained as oils. ^b (Found: C, 52.3; H, 6.2. C₁₀H₁₄O₆ requires C, 52.17; H, 6.13%). ^c (Found: C, 54.2; H, 6.5. C₁₁H₁₆O₆ requires C, 54.09; H, 6.60%). ^d (Found: C, 56.6; H, 5.5. C₁₂H₁₄O₆ requires C, 56.69; H, 5.55%). ^e (Found: C, 55.9; H, 7.1. C₈H₁₂O₄ requires C, 55.80; H, 7.03%). ^f (Found: C, 58.1; H, 7.6. C₉H₁₄O₄ requires C, 58.05; H, 7.58%). ^g (Found: C, 61.3; H, 6.2. C₁₀H₁₂O₄ requires C, 61.21; H, 6.17%). ^h (Found: C, 56.3; H, 6.2. C₁₂H₁₆O₆ requires C, 56.24; H, 6.29%). ⁱ (Found: C, 57.9; H, 6.7. C₁₃H₁₈O₆ requires C, 57.77; H, 6.71%). ^j (Found: C, 59.2; H, 7.1. C₁₄H₂₀O₆ requires C, 59.14; H, 7.09%). ^k It was not possible to integrate the signals since the product was mixed with other compounds. ^l (Found: C, 57.4; H, 7.3. C₁₃H₂₀O₆ requires C, 57.34; H, 7.40%). ^m (Found: C, 61.7; H, 8.4. C₁₁H₁₈O₄ requires C, 61.66; H, 8.47%). ⁿ (Found: C, 52.2; H, 6.2. C₁₀H₁₄O₆ requires C, 52.17; H, 6.13%). ^o Known product,¹⁸ but analytical and spectral data are unreported (Found: C, 55.7; H, 7.1. C₈H₁₂O₄ requires C, 55.80; H, 7.03%).

products **6a**, **7a** and **8a** was assigned on the basis of the chemical shifts of the vinyl protons which experience a large deshielding effect due to the methoxycarbonyl group linked at the adjacent unsaturated carbon on the same side.¹⁹ The *cis* configuration of **6b**, **7b** and **8b** was assigned on the basis of the coupling constant of the vinyl protons (J_{cis} 11.7 Hz) and confirmed by comparison of the ¹H NMR spectrum of **8b** with that of its *trans*-isomer.²⁰ Neither spectroscopic nor chromatographic evidence was obtained for the presence, in either reaction mixture, of the stereoisomers of the ortho esters **6a,b** and the esters **7a,b** and **8a,b**.

All the results obtained can be rationalized in terms of the generally accepted mechanism for thermal cycloaddition of an electron-rich to electron-poor alkene.^{21*} Thus, 1,1-dialkoxyalkenes **1** react with the alkynes **2**, to give the cyclobutenes **3**, via 1,4-dipolar intermediates such as **5**. These 1,4-dipoles, in which the negative charge is delocalized on the methoxycarbonyl

* In the thermal [2 + 2]cycloadditions the experimental and theoretical criteria used for double bonds are the same for triple bonds.³

group, may be represented as a mixture of the two geometric isomers **A** and **B** in equilibrium *via* the allenic structure **C**²² (Scheme 3). Although cyclobutene **3** formation may only occur *via* **B**, the stereochemistry of the trapping products **4** and **6** shows that only **A** is intercepted. In fact, since **B** is well orientated²³ for cyclization this occurs faster than the trapping reactions, and since **A** into **B** isomerization is slow the lifetime of **A** is long enough for it to be trapped. The polarity of the solvent in which the reaction is performed influences the lifetime of **A** and, consequently, the ratio of cyclobutene to enyne, **3**:**4**. Thus, the ratio of cyclobutene to enyne **3e**:**4b** in apolar dichloromethane is higher than in polar acetonitrile (Table 1), showing that in the former solvent the lifetime of **A** decreases owing to its poor solvation.

Experimental

IR spectra were recorded on a Perkin-Elmer 1760 X-FT spectrophotometer using chloroform as solvent. ¹H and ¹³C NMR spectra were recorded with a Varian XL-200 spectrometer using deuteriochloroform as solvent and tetramethylsilane as internal standard. The solvents used in the reactions were dried. Silica gel [0.005–0.20 (Merck)] and light petroleum (b.p. 40–70 °C) were used for column chromatography. TLC was carried out on silica gel K6F (Whatman).

1,1-Dimethoxyethene **1a**,²⁴ 1,1-dimethoxyprop-1-ene **1b**²⁵ and 1,1-dimethoxy-2-methylprop-1-ene **1c**²⁶ were prepared as reported.

Reaction of 1,1-Dimethoxyalkenes 1 with DMAD 2a.—Solutions of DMAD (1 mol dm⁻³; 5 mmol) in acetonitrile were added to the alkenes **1** (7.5 mmol) and the resulting mixtures were kept at the temperatures reported in Table 1 (entries 1–3) under strictly anhydrous conditions. The solutions were monitored for the disappearance of DMAD by TLC (UV, chloroform). When the reactions were complete (Table 1), the solvent was removed at reduced pressure and the ¹H NMR spectra of the residues showed only the presence of the *dimethyl 3,3-dimethoxycyclobutene-1,2-dicarboxylates 3a–c* in addition to polymeric material derived from the alkenes **1**. The mixtures were chromatographed on silica gel (30 g). Elution with light petroleum–diethyl ether (9:1, v/v) and diethyl ether gave the cyclobutenes **3a–c** and polymeric material successively. The yields of **3a–c** are reported in Table 1 and the physical, analytical and spectral data in Table 2.

Solutions of the cyclobutenes **3a–c** (1 mol dm⁻³; 2 mmol) in acetonitrile when kept at the temperatures and for the times used for the parent alkenes **1a–c** (Table 1, entries 1–3) were recovered quantitatively.

Reactions of the Alkenes 1 with MP 2b.—Solutions of MP (1 mol dm⁻³; 5 mmol) in acetonitrile were added to the alkenes **1** (7.5 mmol) and the resulting mixtures were kept at the temperatures reported in Table 1 (entries 4–6) under strictly anhydrous conditions. Periodically the solutions were monitored by IR spectroscopy for the disappearance of MP (CH stretching at 3300 cm⁻¹). When the reactions were complete (Table 1), the solvent was removed under reduced pressure and the ¹H NMR spectrum of the residues showed the presence of the *methyl 3,3-dimethoxycyclobutene-2-carboxylates 3d–f* and the *dimethyl 5,5-dimethoxyoct-2-en-6-yne-1,8-dioates 4a–c* (in *ca.* molar ratio 1.5:1 for **1a**; 2.5:1 for **1b**; 5:1 for **1c**), in addition to polymeric material derived from the alkenes **1**. The mixtures were chromatographed on silica gel (30 g). Elution with benzene and diethyl ether gave the enynes **4a–c**, the cyclobutenes **3d–f** and polymeric material successively. The yields of **3d–f** and **4a–c** are reported in Table 1 and the physical, analytical and spectral data in Table 2.

When solutions of MP (1 mol dm⁻³; 1 mmol) in acetonitrile were added to the cyclobutenes **3d–f** (1 mmol) and the resulting mixtures were kept at the temperatures and for the times used for the related alkenes **1a–c** (Table 1, entries 4–6), the cyclobutenes **3d–f** were recovered quantitatively.

Reaction of the Alkene 1b with MP 2b in Apolar Solvents.—The reactions of **1b** with MP in dichloromethane and in carbon tetrachloride were carried out following the conditions used when acetonitrile was the solvent. When the reaction in dichloromethane was complete (Table 1, entry 7), the solvent was removed under reduced pressure and the ¹H NMR spectrum of the residue showed the presence of the cyclobutene **3e** and the enyne **4b** in *ca.* 5:1 molar ratio in addition to polymeric material derived from the alkene **1b**. Silica gel chromatography carried out as previously described gave **3e** and **4b** with the yields reported in Table 1 (entry 7).

The reaction in carbon tetrachloride was stopped after 4 days (entry 8). The ¹H NMR spectrum of the mixture recorded with a Varian EM-360 spectrometer in carbon tetrachloride showed the presence of MP, small amounts of the alkene **1b**, the cyclobutene **3e**, trace amounts of the enyne **4b** and polymeric material derived from the alkene **1b**. The products **1b**, **2b**, **3e** and **4b** were identified by comparison of the ¹H NMR spectrum of this mixture with those of the pure products recorded in carbon tetrachloride. Thus, silica gel chromatography carried out as above described gave the cyclobutene **3e** with the yields reported in Table 1 (entry 8), in addition to some amounts of the enyne **4b** and polymeric material.

Reaction of the Alkene 1b with DMAD 2a in tert-Butyl Alcohol.—The reaction between **1b** and DMAD in *tert*-butyl alcohol was performed under the conditions used when acetonitrile was the solvent. When the reaction was complete (Table 1, entry 9), the solvent was removed under reduced pressure and the ¹H NMR spectrum of the residue showed the presence of the cyclobutene **3b** and methyl 5-*tert*-butoxy-5,5-dimethoxy-3-methoxycarbonyl-4-methylpent-2-enoate **6a** in addition to polymeric material derived from the alkene **1b**. All attempts to isolate the ortho ester **6a** by chromatography failed since it underwent hydrolysis to the esters 5-*tert*-butyl 1-methyl 3-methoxycarbonyl-4-methylpent-2-ene-1,5-dioate **7a** and *dimethyl 3-methoxycarbonyl-4-methylpent-2-ene-1,5-dioate 8a* on contact with the adsorbents. The ¹H NMR data of **6a** reported in Table 2 were obtained from those of the reaction mixture, the signals of **3b** being subtracted. Slow chromatography of this mixture on silica gel (30 g) (eluent benzene) gave the *tert*-butyl ester **7a** (4%), methyl ester **8a** (12%) (both derived from the hydrolysis of **6a**) and cyclobutene **3b** successively. Subsequent elution with diethyl ether gave polymeric material. The yields of **3b** and **6a** (the latter obtained by the sum of the esters **7a** and **8a**) are reported in Table 1 (entry 9). The physical, spectral and analytical data of **7a** and **8a** are reported in Table 2.

When a solution of the cyclobutene **3b** (1 mol dm⁻³; 1 mmol) in *tert*-butyl alcohol was kept at room temp, after 4 h it was recovered quantitatively.

Reaction of the Alkene 1b with MP 2b in tert-Butyl Alcohol.—The reaction of the alkene **1b** and MP in *tert*-butyl alcohol was carried out under the conditions used when acetonitrile was the solvent. When the reaction was complete (Table 1, entry 10), the solvent was removed immediately under reduced pressure and the ¹H NMR spectrum showed the presence of the methyl 5-*tert*-butoxy-5,5-dimethoxy-4-methylpent-2-enoate **6b**, enyne **4b** and cyclobutene **3e**, in addition to polymeric material derived from the alkene **1b**. All attempts to isolate the ortho ester **6b** by chromatography failed since it underwent hydrolysis to 5-*tert*-

butyl 1-methyl 4-methylpent-2-ene-1,5-dioate **7b** and dimethyl 4-methylpent-2-ene-1,5-dioate **8b** on contact with the adsorbents. The ¹H NMR data of **6b** (Table 2) were deduced from those of the reaction mixture, the signals of **3e** and **4b** being subtracted. Slow chromatography of this mixture on silica gel (30 g) (eluent benzene) gave the *tert*-butyl ester **7b** (9%), the methyl ester **8b** (12%), the enyne **4b** and the cyclobutene **3e**. Subsequent elution with diethyl ether gave polymeric material. The yields of **3e**, **4b** and **6b** (the latter obtained by the sum of those of the esters **7b** and **8b**) are reported in Table 1. The physical, spectral and analytical data of esters **7b** and **8b** are reported in Table 2.

A solution of the cyclobutene **3e** (1 mol dm⁻³; 1 mmol) in *tert*-butyl alcohol was kept at 50 °C for 8 h after which solvent was removed under reduced pressure; the ¹H NMR spectrum of the residue showed only the presence of **3e** in addition to polymeric material. Chromatography on silica gel (eluent benzene and diethyl ether) gave **3e** (80%) and polymeric material successively. When the same treatment was performed on the enyne **4b**, the latter was recovered quantitatively.

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