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Formation of Two Heterocyclic Dimers From Dimethyl Diazomalonate and Bis(methoxycarbonyl)carbene. Preparation and Trapping of Methoxy(methoxycarbonyl)ketene with Cyclopentadiene

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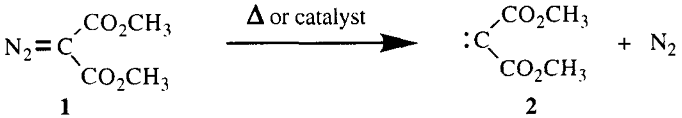
Abstract: Thermal decomposition of dimethyl diazomalonate (**1**) gives two dimers **9** and **10**, in varying ratio and yield, depending on the reactant / solvent. It is suggested that the ketene **11**, formed by Wolff rearrangement, reacts by two different pathways to produce the dimers; a mechanism which seems more reasonable than several alternatives. Independent preparation of **11** in the presence of **1** did not produce either dimer but with cyclopentadiene the 4-membered ring adduct 7-methoxy-7-(methoxycarbonyl)bicyclo[3.2.0]hept-2-en-6-one (**13**) was produced. The structure of **13** was obtained by X-ray crystallography. *Ab initio calculations (6-31G*) indicated* that the observed product **13** was more thermodynamically stable than the isomeric adduct **16**.

INTRODUCTION

For a number of years we have been studying the reactions of dimethyl diazomalonate (**1**) and the carbene, bis(methoxycarbonyl)carbene (**2**), derived from it by thermal and catalyzed decomposition (equation 1).[1,2] We found that the azine **3** was frequently a product and, under the proper catalytic conditions, could be made the major product.[2]

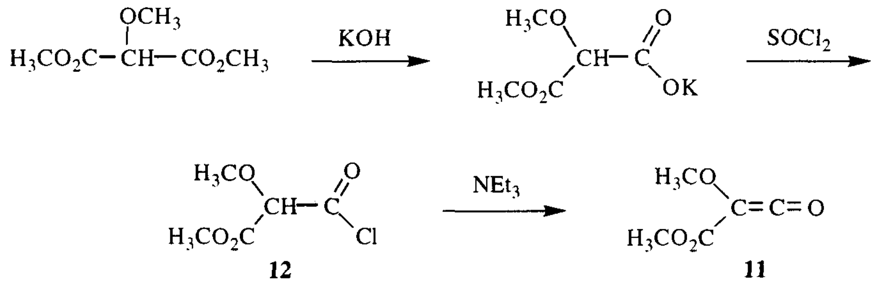


$$N_2{=}C(CO_2CH_3)_2 \xrightarrow{\Delta \text{ or catalyst}} :C(CO_2CH_3)_2 + N_2 \qquad (1)$$

1 **2**

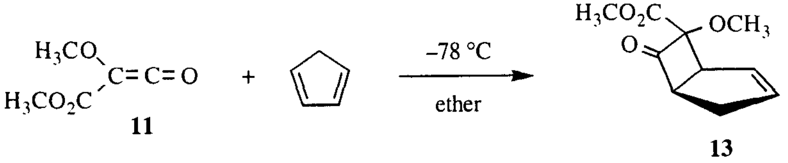
Thermal (140-160 °C) reaction of **1** with naphthalene produced about 5-10% of the azine **3**, a small amount of the "normal" carbene dimer **4**, 30-40% of the carbene addition product **5**, 5-10% of dimethyl (1-naphthyl)malonate (**6**), about 10% of the bis-addition product **7** and 5-10% of the carbene addition product to the 2,3-bond of naphthalene, namely 7,7-bis(methoxycarbonyl)-3,4-benzotropilidene (**8**). There were also additional dimers, **9** and **10**, in a total yield of 30% and a ratio of 5 : 1.[2] This is shown in Scheme 1.

Dimer **9** was previously obtained by Regitz and Maas[3,4] upon photochemical decomposition of **1** in molten *p*-dichlorobenzene (equation 2). They postulated that carbene **2** underwent a photochemical Wolff rearrangement (equation 3) followed by a [3+2]-cycloaddition of another carbene **2** to the resulting ketene, methoxy(methoxycarbonyl)ketene (**11**). They did not observe **10** which they expected to be the major elimination from an acid chloride. The synthetic sequence to produce the acid chloride, methyl (chloroformyl)-methoxyacetate (**12**) is shown in Scheme 4 and is a slight modification of the literature preparation.[10] The ketene **11** was formed from **12** in the standard way by dehydrochlorination using triethylamine.[9]



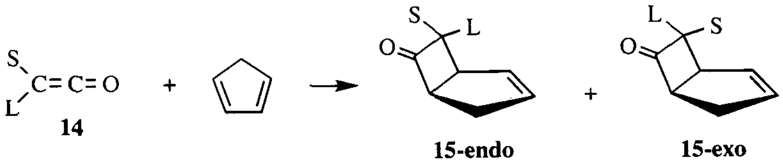
Scheme 4

When methyl (chloroformyl)methoxyacetate (**12**, 1.2 mmol) was allowed to react with triethylamine (1.2 mmol) in the presence of dimethyl diazomalonate (**1**, 1.2 mmol) in 10 mL of solvent, neither dimer was observed under a variety of conditions, by gas chromatography or ^{1}H NMR spectroscopy. The conditions included using ether, THF and CH_2Cl_2 at –78 and 0 °C, benzene at 0 °C and benzene and toluene at room temperature and under reflux. Not observing either dimer must be the result of either the ketene **11** not reacting with the diazo compound **1** under these particular conditions, or the ketene not being formed. To demonstrate that methoxy(methoxycarbonyl)ketene (**11**) was formed, **12** was treated with triethylamine in the presence of an excess of cyclopentadiene, a typical trapping agent for ketenes,[9] at –78 °C in ether solution. A product **13** was produced in 46% isolated yield, mp 57-58 °C. The spectral properties and the combustion analysis was consistent with the [2+2]-cycloadduct, 7-methoxy-7-(methoxycarbonyl)bicyclo[3.2.0]hept-2-en-6-one (**13**, equation 4). The stereochemistry was obtained by single crystal X-ray analysis. Figure 1 shows the ORTEP structure.



(4)

The structure of the adduct **13** revealed by the X-ray determination is quite interesting. Table 2 gives the bond lengths. Cycloaddition of ketenes with cyclopentadiene (equation 5) frequently give the product where the larger group, L, on the ketene **14**, is in the endo-position (**15-endo**) and this isomer is also the



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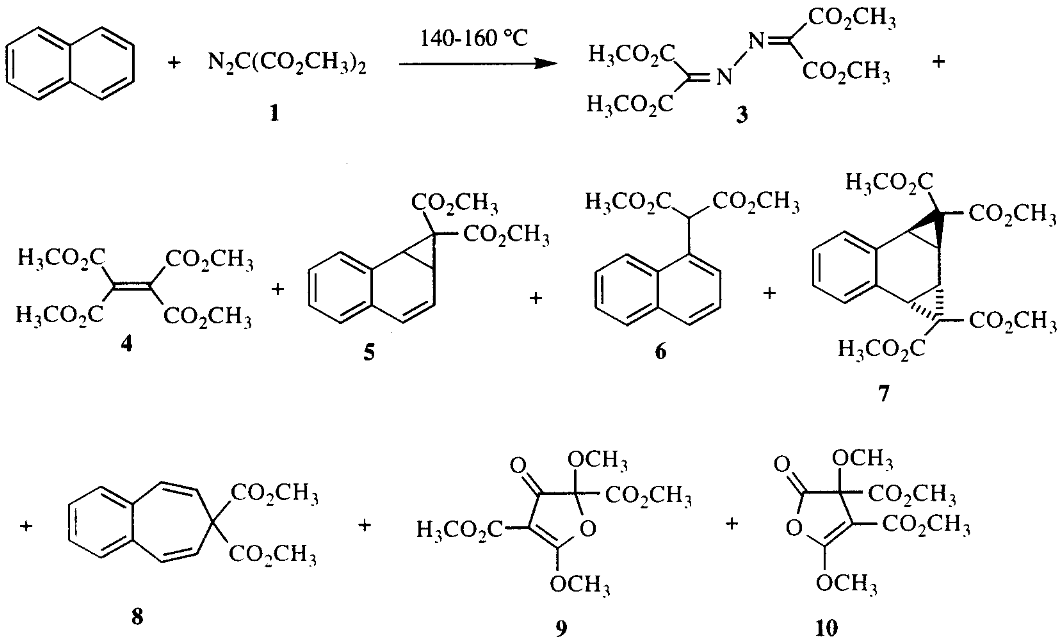
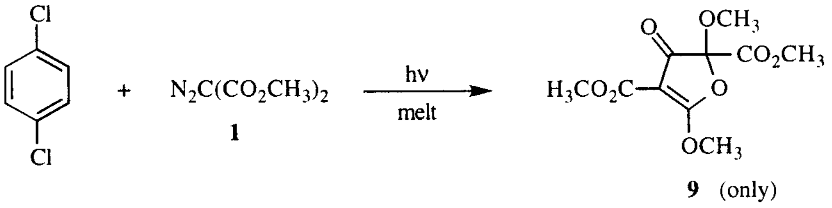


Scheme 1

cycloadduct. A photochemical Wolff rearrangement of the carbene was postulated since Jones had reported earlier[5] that, in the gas phase, the thermal Wolff rearrangement did not occur at temperatures below 280 °C. This was then followed by reaction of the ketene **11** with the carbene **2**.[3,4]

In our work, mentioned above, we observed both products in the thermal decomposition of **1** in naphthalene although dimer **9** was the major product (5:1 ratio), indicating the Wolff rearrangement was occurring, even at temperatures as low as about 120 °C.[2]



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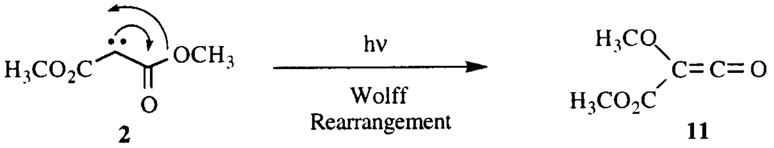


(3)

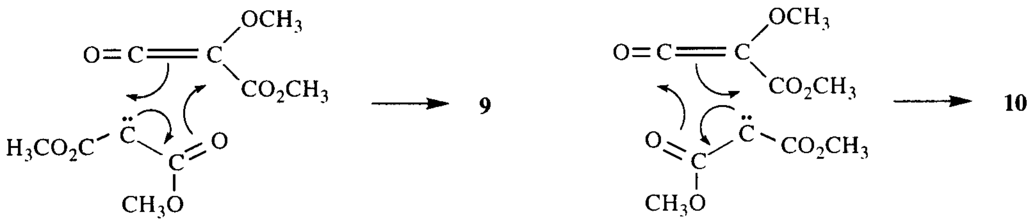
RESULTS AND DISCUSSION

We have now studied the yield and the ratio of the two dimers (**9** and **10**) while varying the reactant/solvent [5:1 ratio of the reactant/solvent : dimethyl diazomalonate (**1**) / 140 °C / 5 hours]. Table 1 shows the results. There are a number of notable entries and comparisons in the Table. First, while the ratio of **9** to **10** with naphthalene was 5:1, *only **10*** was observed with anthracene and phenanthrene, a seemingly large effect for a relatively modest change in reactant / solvent. Benzene, surprisingly, did not produce either dimer. With *p*-dichlorobenzene and chlorobenzene the **9**:**10** ratio was 7:1 and 6.5:1 respectively. However, with 1-chloronaphthalene the ratio was again *reversed* to 1:1.8. The methyl groups in 2,3-dimethylnaphthalene had only a small effect on the product distribution but the yield decreased substantially. Xylene, like benzene, did not give these products. Finally, bromobenzene gave a rather good yield of an equal mixture of **9** and **10** while *p*-dimethoxybenzene produced neither. To see if there was a heavy atom effect CH_2I_2 was used as the solvent but again neither dimer was produced. Isooctane gave neither dimer and only **10** was produced in the neat decomposition of **1**.

Table 1. Ratio of **9** : **10** and Yield in the Thermal Decomposition of **1** (140 °C / 5 h)

Solvent / Reactant	**9**	**10**	Approx. Yield (%)
Naphthalene	5	1	30
Anthracene	–	only	20
Phenanthrene	–	only	10
Benzene	–	–	–
2,3-Dimethylnaphthalene	only	–	<3
p-Xylene	–	–	–
p-Dichlorobenzene	7	1	50
Chlorobenzene	6.5	1	30
1-Chloronaphthalene	1	1.8	30
Bromobenzene	1	1	50
p-Dimethoxybenzene	–	–	–
CH_2I_2	–	–	–
Isooctane (120 °C)	–	–	–
Neat **1**	–	only	20

There are a number of mechanistic possibilities to explain how the two products **9** and **10** might be formed. The first would be that the carbene **2** approaches the ketene **11**, in a [3+2]-cycloaddition reaction, with both possible orientations relative to **11** as shown in Scheme 2. We think this is relatively unlikely since minor changes in the solvent / reactant produce quite substantial changes in the product ratio, as shown, for example, in the reactions of the chlorinated benzenes, naphthalene and 1-chloronaphthalene. Further, it must be remembered that the photochemical production of carbene **2** in molten *p*-dichlorobenzene resulted in the exclusive formation of adduct **9** and the alternate (expected) adduct **10** was not found.[3,4] One would have expected to find some of

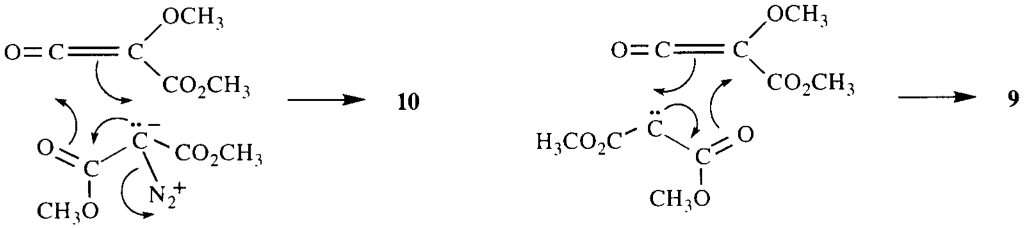


Scheme 2

adduct **10** if this were the mechanism (Scheme 2) since the photochemical reaction was carried out in molten *p*-dichlorobenzene (mp 53 °C).

A second mechanistic possibility might involve electron transfer, however, the product variation does not correlate with the ionization potentials of the solvent / reactant. This of course assumes the electron would be transferred from the solvent / reactant to the carbene **2** which would stabilize the negative charge.

A third mechanistic possibility to account for these results involves two different reactions which produce the dimers, namely, reaction of methoxy(methoxycarbonyl)ketene (**11**) with the diazo compound **1** to give the butenolide **10** and with the carbene **2** to produce the other dimer **9** (Scheme 3). There are examples in the literature of stable ketenes reacting with diazo compounds to give butenolides,[4,6-8] hence the suggestion that **10** results from reaction of **11** with **1**. These butenolide products were shown to arise by direct reaction of ketenes with diazo compounds at temperatures below that required for carbene formation.[7,8] Also, [3+2]-cycloaddition of the carbene **2** to ketene **11** was originally postulated by Regitz and coworkers.[4] Thus it is reasonable to assume that **10** is formed from the diazo compound and **9** from the carbene (Scheme 3). This appears to be a more reasonable mechanistic possibility than the other two mechanisms discussed above. In this case it is still difficult to account for the dramatic changes in the product ratios, but one would expect very different solvent effects on the two reactions. Dimethyl diazomalonate (**1**) is quite polar and is reacting with a polar ketene. On the other hand, bis(methoxycarbonyl)carbene (**2**) is expected to be substantially less polar and is reacting with the same ketene.



Scheme 3

In order to test this hypothesis, or at least the one involving the formation of the butenolide **10**, it was decided to independently prepare methoxy(methoxycarbonyl)ketene (**11**) in the presence of dimethyl diazomalonate (**1**) and to look for these dimers. There are a number of different ways to prepare ketenes using conditions which presumably would not cause **1** to react.[9] The method chosen here was the base induced HCl

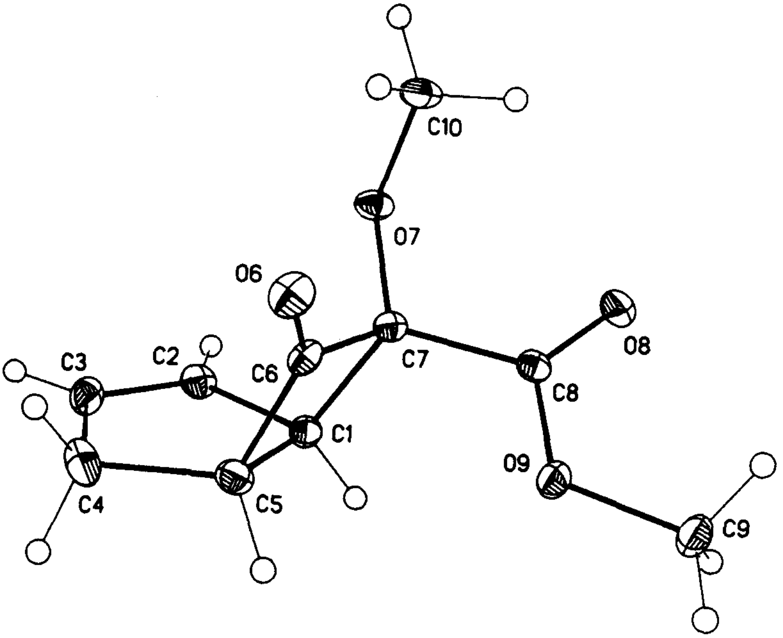


Figure 1. X-ray crystal structure of 7-methoxy-7-(methoxycarbonyl)bicyclo[3.2.0]hept-2-en-6-one (**13**).

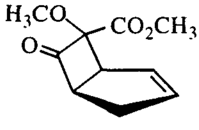
thermodynamically more stable.[9,11] The percent of **15-endo** relative to **15-exo** is, in the cases where S is always H, 89% for L = F, 76 % for L = CH_3, 64% for L = Et, 57% for L = *i*-Pr, 67 % for L = Ph but only 10% for L = *t*-Bu.[9-11]

Table 2. X-ray Determined and Ab initio Calculated (6-31G*) Bond Lengths in **13***

Bond	X-ray Bond Length (Å)	Ab initio 6-31G* Bond Length (Å)	Bond	X-ray Bond Length (Å)	Ab initio 6-31G* Bond Length (Å)
C1–C5	1.560 (3)	1.556	C1–C7	1.565 (3)	1.565
C4–C5	1.534 (3)	1.537	C2–C3	1.314 (3)	1.320
C5–C6	1.507 (4)	1.523	C3–C4	1.489 (4)	1.511
C6–C7	1.559 (3)	1.553	C6–O6	1.200 (2)	1.181
C7–C8	1.521 (2)	1.527	C7–O7	1.402 (2)	1.373
C8–O8	1.202 (3)	1.184	O7–C10	1.439 (2)	1.411
O9–C9	1.449 (2)	1.420	C8–O9	1.331 (2)	1.325
C1–C2	1.497 (3)	1.506			

* See Figure 1 for the numbering scheme.

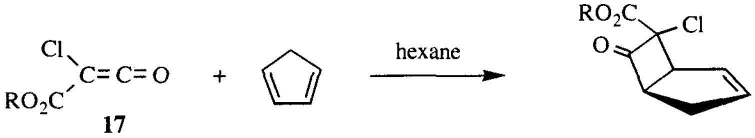
In the case of ketene **11**, the ester group is presumably larger (L) than the methoxy group (S) based on conformational A-values,[12] and so one might have anticipated the other isomer **16** to be the major product. This



16

situation is more complicated, however, since the endo/exo ratio is also solvent dependent. Thus, for example, chloro(methyl)ketene **14**, S = Cl, L = CH_3, gives 81% **15-endo** in hexane solvent, 69% in Et_3N, 62% in $CHCl_3$ and only 37% in acetonitrile.[9,13] Further, when bromo(methyl)ketene **14**, S = Br, L = CH_3, was used, the amount of **15-endo** produced was 42% in hexane, 22% in Et_3N and 12% in acetonitrile.[10,14] According to the standard A-values,[12] Cl and Br are similar in steric bulk and are both smaller than CH_3. Thus it would be difficult to come to any conclusions concerning the intimate mechanistic details of the ketene cycloaddition to produce **13**. It should be noted, however, that the OCH_3 group has an A-value similar to those of Cl and Br. It is thus interesting to note that ketene **17**, R = CH_3, with a chlorine and a methyl ester, produces a cycloadduct with the same stereochemistry as observed here, that is with the chlorine in the endo position, in 70% isolated yield (equation 6).[14] Furthermore, when the *t*-butyl ester group was used **17**, R = *t*-Bu, the same stereochemistry, with the Cl in the endo position, was observed exclusively (equation 6).[14]

In order to understand why the adduct **13** was formed and not its epimer **16**, ab initio calculations were performed on both adducts with geometry optimization, at both the 3-21G and 6-31G* levels.[18] The bond



(6)

lengths thus obtained (from the 6-31G* level; the corresponding bond lengths from the 3-21G calculation are similar) are shown in Table 2. The agreement in most bond lengths is quite good, with only a few deviating more than 0.02Å. These are O9-C9, C3-C4, C7-O7 and O7-C10 and all but C3-C4 involve polar C–O bonds and could be the result of crystal packing forces. What is interesting is the energy differences between **13** and **16**. At the 3-21G ab initio level **13** is more stable than **16** by 5.6 kcal/mol and at the 6-31G* level **13** is more stable than **16** by 2.2 kcal/mol. This result shows that in this particular cycloaddition (as is generally true with ketene cycloaddition reactions with cyclopentadiene)[9] the more thermodynamically stable product is formed.

CONCLUSION

The yield and ratio of the two heterocyclic dimers **9** and **10** produced in the thermal decomposition of dimethyl diazomalonate (**1**) have been studied as a function of the reactant / solvent. Either **9** (nearly exclusively) or **10** (exclusively), or mixtures, could be produced depending on the reactant/solvent. There are several mechanistic possibilities for these results, and the one which seems more reasonable than the others is that **9** and **10** are produced by different mechanistic pathways, both involving Wolff rearrangement of carbene **2** to produce methoxy(methoxycarbonyl)ketene (**11**) (Scheme 4). According to this, dimer **9** would result from reaction of **11** with **2** while **10** would result from reaction of **11** with **1**. To test this hypothesis the ketene **11** was independently prepared in the presence of dimethyl diazomalonate (**1**) but no dimers were observed under a variety of conditions. That ketene **11** was produced in this latter reaction was shown by trapping as the [2+2]-cycloadduct with cyclopentadiene which produced 7-methoxy-7-(methoxycarbonyl)bicyclo[3.2.0]hept-2-en-6-one (**13**; equation 4). The structure of **13** was obtained by X-ray crystallography. Ab initio calculations at the 3-21G and 6-31G* levels showed that **13** was more thermodynamically stable than the other possible cycloadduct **16**.

EXPERIMENTAL SECTION

General Procedures

NMR spectra were recorded at 300 MHz for ^{1}H and 75 MHz for ^{13}C in $CDCl_3$, unless indicated otherwise, and TMS or $^{13}CDCl_3$ ($\delta = 77.00$ ppm) were used as internal reference. FTIR spectra were recorded as either a liquid film between NaCl plates or, for solids, as a mixture with KBr powder in a diffuse reflectance cell. Gas chromatography was done with a DB-5 capillary column (30 m x 0.32 mm I.D., 0.25 μm coating) using a flame ionization detector. HPLC was performed using an Econosil C18 10U (10 μm) reverse-phase column (250 mm x 4.6 mm) and a UV detector at 254 nm. X-ray crystallography was done on a Siemens P4 X-ray diffractometer. The mass spectrum was obtained on a Finnigan Mat TSQ-70 instrument. Elemental analyses were obtained on a Perkin-Elmer 2400 CHN analyzer. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and were uncorrected.

Thermal Decomposition of Dimethyl Diazomalonate (1) in the Presence of the Reactants / Solvents in Table 1

A ratio of 5 : 1 by weight of the reactant/solvent listed in Table 1 to dimethyl diazomalonate (**1**)[7] was heated at 130-140 °C for 5-6 hours in a round-bottomed flask equipped with a reflux condenser and a bubbler to monitor the nitrogen evolution. The reaction using benzene was done in a sealed tube. The ratios of dimers **9** and **10** were obtained by gas chromatography.

Methyl (Chloroformyl)methoxyacetate (12)[10]

40.54 g (0.25 mol) of dimethyl methoxymalonate was dissolved in 100 mL of methanol, and 15.92 g (0.41 mol) of KOH was dissolved in 100 mL of methanol. The KOH solution was then added to the dimethyl methoxymalonate solution very slowly to prevent complete hydrolysis. After the addition was complete, the reaction mixture was allowed to stir at room temperature for 24 hours. No precipitate formed as described in literature.[13] The methanol was removed in vacuum and the residue was vacuum dried (0.1mm Hg) overnight. The sticky product was pure enough for further reactions as shown in the NMR spectra. ^{1}H NMR (D_2O): δ 4.25 (s), 3.66 (s), 3.26 (s). ^{13}C NMR (D_2O): δ 174.7, 173.6, 84.9, 59.9, 55.5. Thionyl chloride (18 mL) was added to the product above at 0 °C and the mixture was stirred at room temperature for 18 hours. Vacuum distillation three times gave a pure sample (ca. 20.8 g) of **12**. Overall yield 50%; b.p. 34-36 °C (0.50 mm Hg).

^{1}H NMR: δ 4.65 (s, 1H), 3.88 (s, 3H), 3.58 (s, 3H); ^{13}C NMR: δ 168.9, 164.2, 86.7, 59.1, 53.5; [lit.[16,17] ^{1}H NMR: δ 4.65 (s, 1H), 3.85 (s, 3H), 3.58 (s, 3H)].

Attempted reaction of Methoxy(methoxycarbonyl)ketene (11) with Dimethyl Diazomalonate (1)

Dimethyl diazomalonate (**1**), 190 mg (1.2 mmol) of and 122 mg of triethylamine were put in a 25 mL three-necked reaction flask and mixed with 10 mL of solvent. The mixture was kept under nitrogen maintaining strictly dry conditions. Then 200 mg (1.3 mmol) of methyl (chloroformyl)methoxyacetate (**12**) in 5 mL of solvent was slowly added to the reaction mixture. The progress of the reaction was monitored by GC. After the disappearance of the acid chloride peak (about half an hour), the reaction mixture was filtered to remove the $Et_3N{\cdot}HCl$, the solvent was removed under reduced pressure and the residue was vacuum dried (0.01 mm Hg) overnight. The reactions were run in the indicated solvents under the following sets of conditions: benzene at 0 °C, room temperature and reflux, CH_2Cl_2 at 0 and –78 °C, THF at 0 and –78 °C, ether at 0 and –78 °C, and toluene at room temperature and reflux. In no case was either dimer **9** or **10** observed by GC or NMR spectral analysis.[2]

7-Methoxy-7-(methoxycarbonyl)bicyclo[3.2.0]hept-2-en-6-one (13)

Cyclopentadiene was distilled, by cracking dicyclopentadiene under a N_2 atmosphere, into a Dry-Ice cooled bath right before use. An excess of cyclopentadiene (1.73 g) was mixed with 0.40 g (3.95 mmol) of Et_3N in 20 mL of dry ether. Then 0.56 g (3.36 mmol) of methyl (chloroformyl)methoxyacetate (**12**) in 5 mL of dry ether was slowly injected into the cold mixture under a N_2 atmosphere, at –78 °C. A white salt precipitated immediately. The reaction mixture was kept at –78 °C under N_2 for an additional half hour and was then warmed to room temperature. The white salt was filtered and washed with 5 mL of cold ether. The liquid was then concentrated under reduced pressure and the residue was distilled at 61-63 °C (0.01 mm Hg) to give 0.30 g (46%) of adduct **13**. An analytical sample, m.p. 57-58 °C, was prepared by recrystallizing the distilled sample at –78 °C from hexanes. ^{1}H NMR: δ 5.99-5.97 (m, 1H), 5.77-5.75 (m, 1H), 3.95-3.86 (m, 2H), 3.85 (s, 3H), 3.55 (s, 3H), 2.83-2.75 (m, 1H), 2.58-2.44 (m, 1H); ^{13}C NMR: δ: 205.9, 169.3, 135.9, 127.1, 98.1, 58.1, 55.9, 52.7, 49.8, 35.2; MS: m/z 196 (M^+), 181 (M–Me), 168 (M–CO), 153 (M–CO–Me), 137, 130, 125 (M–Me–2CO), 121, 109 (M–Me–CO–CO_2), 105, 102, 94, 93, 91, 79, 77, 66, 65; IR: $\bar{\nu}$ 3072, 3003, 2954, 2923, 2848, 1774 (cyclobutanone CO), 1737 (ester CO), 1702 (sh), 1611, 1462, 1443, 1348, 1280, 1248, 1212, 1177, 1054, 1019, 988, 976, 926, 891, 833, 794, 775, 734, 666, 618, 579, 507 cm^{-1}. Anal. Calcd. for $C_{10}H_{21}O_4$: C, 61.22; H, 6.16. Found: C, 60.92; H, 5.86.

X-ray Structure Determination of 13[19]

A colorless single crystal of **13** was mounted on a glass fiber using 5-minute epoxy and immediately placed in the low temperature nitrogen stream. Data collection was carried out at –40 °C on a Siemens P4 diffractometer equipped with a LT-2A device for low temperature work and graphite monchromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Cell parameters were determined using 28 reflections. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods followed by successive cycles of full-matrix least-squares refinement and difference Fourier analysis using Siemens SHELXTL (PC version 5) software package.[20] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions and refined isotropically using a riding model with 1.2 or 1.5 times the equivalent isotropic temperature factors of the atoms to which they are attached.

Supplementary Material

Tables of crystal data and structure refinement, atom parameters, thermal parameters, bond lengths and bond angles are available upon request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge CB2 1EW, U.K.

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18. The MacSpartan software package, Wavefunction, Inc., Irvine, CA, was used. The geometries were first optimized by molecular mechanics using Sybyl, the structure thus obtained was optimized three more times, first using AM1 semi-empirical, then 3-21G ab initio and finally 6-31G* ab initio calculations.
19. Crystal data for **13**: $C_{10}H_{14}O_4$, triclinic, space group $P\bar{1}$ with a = 6.2342(6) Å, b = 7.1747(7) Å, c = 12.031(1) Å, α = 76.189(5)°, β = 87.288(7)°, γ = 68.252(8)°, V = 484.89(8) Å^3, Z = 2, D_c = 1.344 g/cm^3, T = –40 °C, μ (Mo Kα) = 0.104 mm^{-1}, R1 [I > 2σ(I)] = 0.0365, wR2 = 0.0979 (all data).
20. *Siemens SHELXTL (PC version 5)*; Siemens Industrial Automation, Inc.: Madison, WI, USA.

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