Ketene-Ketene Interconversion. 6-Carbonylcyclohexa-2,4-dienone - Hepta-1,2,4,6-tetraen-1,7-dione - 6-Oxocyclohexa-2,4-dienylidene and Wolff Rearrangement to Fulven-6-one.

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Ketene−Ketene Interconversion. 6-Carbonylcyclohexa-2,4-dienone−Hepta-1,2,4,6-tetraene-1,7-dione−6-Oxocyclohexa-2,4-dienylidene and Wolff Rearrangement to Fulven-6-one

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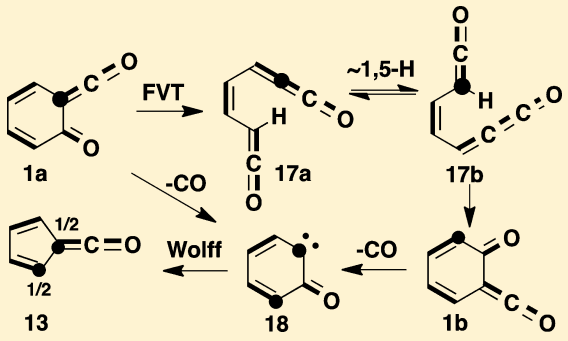
Supporting Information

ABSTRACT: 6-Carbonylcyclohexa-2,4-dienone (**1**) has been generated by flash vacuum thermolysis (FVT) with Ar-matrix isolation of methyl salicylate (**7**), 2-phenylbenzo-1,3-dioxan-4-one (**8**), phthalic peranhydride (**9**), and benzofuran-2,3-dione (**11**) and also by matrix photolysis of **9**, **11**, and 2-diazocyclohepta-4,6-dien-1,3-dione (**12**). In each case, FVT above 600 °C results in decarbonylation of **1** and Wolff rearrangement to fulven-6-one (**13**) either concertedly or via open-shell singlet 6-oxocyclohexa-2,4-dienylidene (**18**). Ketenes **1** and **13** were characterized by IR spectroscopy. Photolysis of matrix-isolated **1** at 254 nm also results in the slow formation of **13**. The sequential formation of ketenes **1** and **13** from **7** has also been monitored by FVT-mass spectrometry, and **13** has been trapped with MeOH to afford methyl 1,3-cyclopentadiene-1- and -2-carboxylates **15** and **16**. FVT of methyl salicylate-1-^{13}C **7a** revealed a deep-seated rearrangement of the ^{13}C-labeled **1a** to hepta-1,2,4,6-tetraen-1,7-dione (**17a**) by means of electrocyclic ring opening followed by a facile 1,5-H shift and recyclization prior to CO-elimination and ring contraction to ^{13}C-labeled **13**. The rearrangement mechanism is supported by M06-2X/6-311++G(d,p) calculations, which predict feasible barriers for the FVT rearrangements and confirm the observed labeling pattern in the isolated methyl salicylate **7a**/**7b** and methyl cyclopentadienecarboxylates **20** and **21** resulting from trapping of **13** with MeOH.



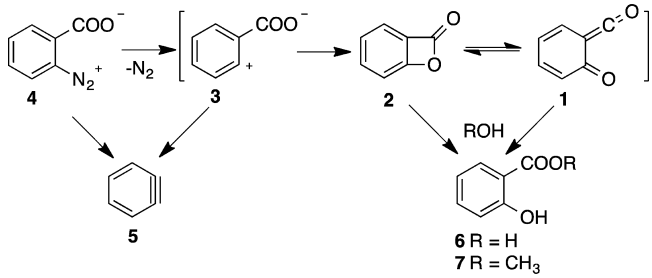
INTRODUCTION

Ketenes, RR′C═C═O, are usually thermodynamically stable but kinetically highly reactive compounds useful in cycloaddition and electrocyclization reactions and nucleophilic addition chemistry.[1] Several rearrangements involving ketenes are known, e.g., the Wolff[2] and retro-Wolff[3] rearrangements, the α-oxoketene−α-oxoketene rearrangement, and similar rearrangements of imidoylketenes, acylthioketenes, and vinylketenes.[4] Ketenes can eliminate CO on flash vacuum thermolysis (FVT), thereby generating carbenes, which may undergo further rearrangements.[5]

In an investigation of the mechanism of benzyne formation by thermolysis of benzenediazonium carboxylate (**4**), Gompper et al. demonstrated on the basis of kinetic measurements the intermediacy of species that could be trapped with water and methanol to generate salicylic acid (**6**) and methyl salicylate (**7**) together with the main products derived from benzyne (**5**).[6] Logically, the formation of 6-oxocyclohexa-2,4-dienylideneketene (**1**) via benzoxetone (**2**) and carboxylate **3** was postulated (Scheme 1), but other work suggests that this is only a minor route to **1** and **2**.[7]

The photolysis of 2-phenylbenzo-1,3-dioxin-4-one (**8**) at 77 K afforded an IR spectrum ascribed to **1** (2118 cm^{-1}) (Scheme 2).[8] Photolysis of an Ar matrix of **9** at λ > 315 nm also gave a ketene, presumably **1**, now absorbing at 2139 and 1650 cm^{-1}.[9] Further photolysis of this species at λ > 340 nm converted it into benzoxet-2-one **2** in a photochemically reversible process, and continued photolysis yielded benzyne **5**.[9] Calculations at the QCISD//MP2 level indicate a very small free energy difference between **1** and **2**, the ketene **1** being more stable by ca. 2.8 kcal/mol.[10] Ketene **1** was trapped with MeOH to afford

Scheme 1. Gompper's Proposal



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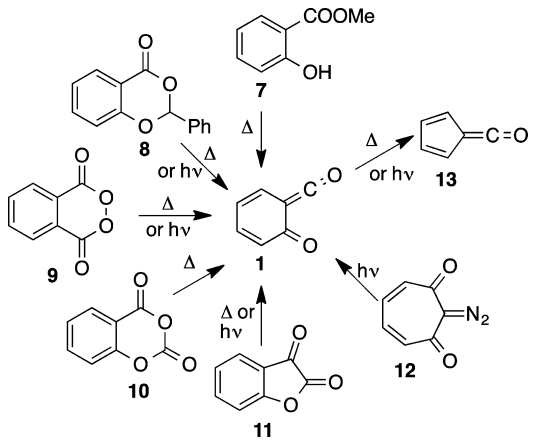
Scheme 2. Precursors for α-Oxoketene (1) and Carbonylcyclopentadiene (13)



methyl salicylate (7).[9] Formation of **1** by treatment of salicyloyl chloride with Hünig's base and by solid-state thermolysis of **10** at 130 °C was also postulated,[11] but the reported IR frequencies of **1** and **2** (2070, 2050, and 1930 cm^{-1}) are not in good agreement with current values (2134−2145 and 1904 cm^{-1}, respectively; see below). Similarly, the thermolysis of phenyl salicylate (salol) was postulated to proceed via oxoketene (**1**).[12] The photolysis of **11** in the presence of water and carboxylic acids gave salicylic acid **6** and mixed anhydrides thereof, and the intermediacy of **1** was postulated.[13] A UV spectrum ascribed to **1** was obtained on photolysis of **8**, **9**, and **10**, but IR spectra were not observed.[14]

The IR spectrum of **1** in Ar matrix was obtained by flash vacuum thermolysis (FVT) of methyl salicylate **7** in 1994, and the same IR spectrum was obtained by FVT of **9** and **11** and also by matrix photolysis of **9**, **11**, and **12**.[15] Four years later, an IR absorption at 2135 cm^{-1} was ascribed to **1** in acetonitrile solution by means of time-resolved IR spectroscopy.[10a] This study permitted the evaluation of the rates of reaction of **1** with H_2O, MeOH, and Et_2NH at room temperature as ca. 1.5, 3.0, and 100 × 10^7 M^{-1} s^{-1}, respectively. No barrier was found for the addition of H_2O at the MP2 computational level.[10a,16]

Gas-phase pyrolysis of methyl salicylate (**7**) and benzofurandione (**11**) yields fulven-6-one (carbonylcyclopentadiene) (**13**). Both ketenes **1** and **13** were observed by photoelectron spectroscopy,[17] but pyrolysis−mass spectrometry failed to detect ketene **1**.[18] Our work, detailed below, has provided clear evidence for the sequential formation of **1** and **13** by FVT as evidenced by IR and mass spectrometry as well as trapping with MeOH. Moreover, we report a cascade rearrangement of α-oxoketene **1** involving electrocyclic ring opening, 1,5-H shift, CO elimination, and finally Wolff rearrangement to **13**. This new rearrangement mechanism is supported by ^{13}C labeling as well as computational studies.

RESULTS AND DISCUSSION

1. Generation of α-Oxoketene (1). Argon matrices of **1** were prepared from five different precursors. FVT of **7**, **8**, **9**, and **11** resulted in elimination of MeOH, benzaldehyde, CO_2, and CO, respectively. Ketene **1** was also obtained by matrix photolysis of **9**, **11**, and **12**. Identical IR spectra of α-oxoketene (**1**) were obtained in each case and dominated by the very strong C═C═O absorption at 2134 cm^{-1}, which is flanked by a strong absorption at 2145 cm^{-1} and a weaker one at 2114 cm^{-1}. Examples are shown in Figure 1 and in Figure S1 (Supporting Information). The observed IR spectra are in very good agreement with the calculated harmonic vibrational spectrum at the B3LYP/6-31G(d) level (see Figure S2, Supporting Information). It is well established that α-oxoketenes can exhibit multiple IR absorption bands in the cumulene region.[19] When the matrices are slowly warmed to remove the argon, the multiple absorptions coalesce to a single peak at 2143 cm^{-1}. The neat ketene is observable at temperatures up to 150 K.

In each case, the photochemical interconversion[9a] of α-oxoketene (**1**) and benzoxetone (**2**) was used as a diagnostic tool to confirm the correct assignment of spectra due to **1**. An example is shown in Figure 2.

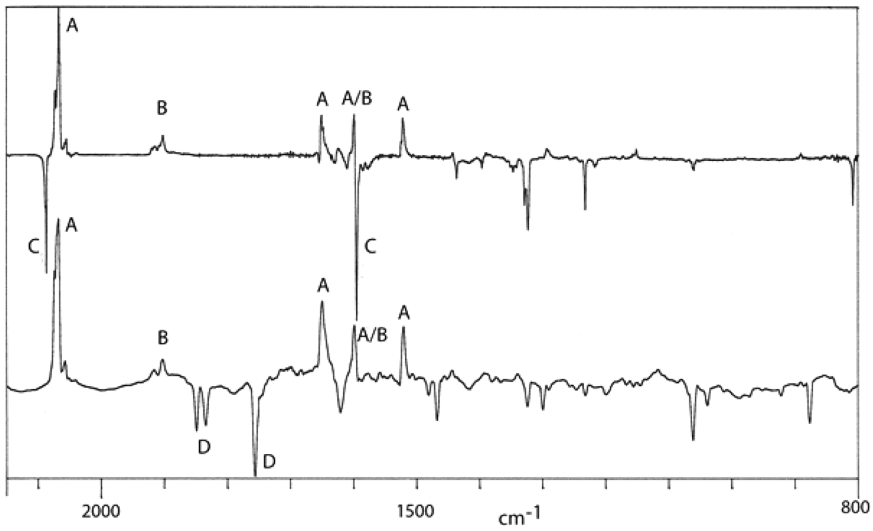


Figure 1. IR difference spectrum resulting from irradiation at λ > 360 nm of (top) diazocycloheptadienedione (**12**); (bottom) benzofurandione **11**. A = ketene **1**; B = benzoxetone **2**; C = **12**; D = **11** (products are shown as positive peaks and precursors as negative peaks in both spectra). All spectra in Ar matrix at 10 K.

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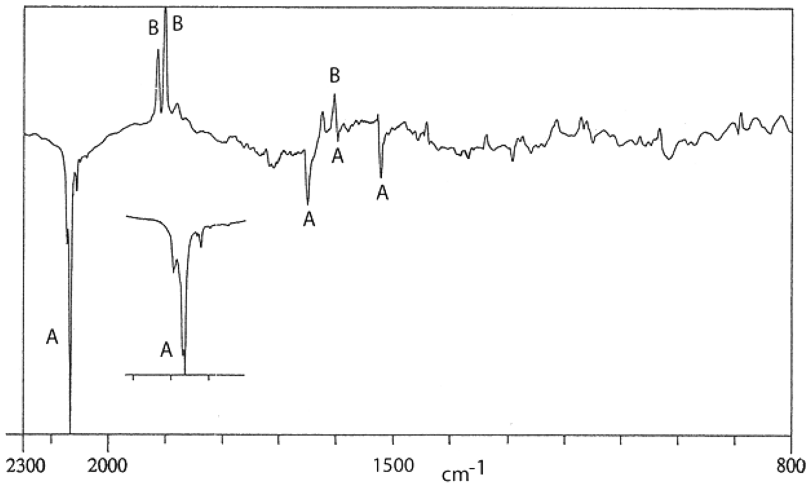
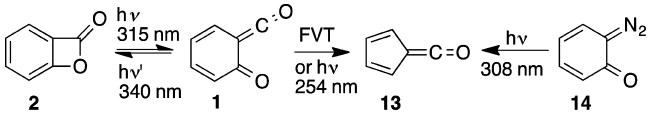


Figure 2. IR difference spectrum showing ketene **1** (A) formed by FVT of methyl salicylate (**7**) at 800 °C and condensed in Ar matrix at 10 K (negative peaks). Positive peaks are due to benzoxetone **2** (B) formed on irradiation of the matrix at $\lambda > 340$ nm. A: 2145 (m), 2134 (vs) and 2114 (w), 1650, 1521, 1292 cm^{-1}. B: 1916, 1904, 1624, 1604, 1443, 1340 cm^{-1}. Inset: expansion of the ketene peaks A (2145, 2134, 2114 cm^{-1}).

2. Generation of Carbonylcyclopentadiene (13). The formation of α-oxoketene (**1**) starts at 300 °C in the FVT of methyl salicylate (**7**) and reaches a maximum at 650−700 °C. At temperatures around 700 °C, a new ketene starts appearing, which absorbs at 2135 (vvs) and 2131 (vs) cm^{-1} in the Ar matrix. This compound was identified as fulven-6-one (carbonylcyclopentadiene) (**13**) by comparison with an authentic sample prepared by matrix photolysis of 2-diazo-3,5-cyclohexadienone **14**[20] (Scheme 3 and Figures S3 and S4, Supporting Information) and with the calculated vibrational spectrum (Figure S2, Supporting Information). Other examples of Wolff-type ring contraction to fulvenones on FVT of oxet-2-ones, thiet-2-ones, and azet-2-ones have been reported.[21] Moreover, photolysis of the matrix-isolated ketene **1** at 254 nm also resulted in decarbonylation and formation of **13**. After gentle warming of matrices of **13** to allow the Ar to evaporate, this ketene was observable at temperatures up to 180 K. This is important, because it will allow us to isolate **13** on a coldfinger at 77 K in order to trap it with MeOH as described below.

Scheme 3. Formation of Carbonylcyclopentadiene (13)



The thermal decarbonylation of **1** with formation of **13** was monitored by online mass spectrometry.[22] The molecular ion of methyl salicylate $\mathbf{7}^{\bullet+}$ (m/z 152) disappears at FVT temperatures above 700 °C (Figure 3). The ion corresponding to $\mathbf{1}^{\bullet+}$ (m/z 120) is both a fragment peak in the mass spectrum of **7**[23] and a thermal reaction product. This ion, $\mathbf{1}^{\bullet+}$ (m/z 120), reaches maximum intensity at ca. 680 °C (Figure 4) when $\mathbf{7}^{\bullet+}$ has almost disappeared (Figure 4). At higher temperatures, m/z 120 decreases rapidly, as fulven-6-one **13** is formed thermally above ca. 700 °C (m/z 92, Figure 4). All the while, m/z 64 (formally cyclopentadienylidene) keeps increasing because it is a fragment ion of both $\mathbf{7}^{\bullet+}$ and $\mathbf{13}^{\bullet+}$, but especially of $\mathbf{13}^{\bullet+}$. A further increase in the intensity of m/z 64 at the highest temperature suggests that thermal decarbonylation of ketene **13** to form cyclopentadienylidene may be taking place. In agreement with this, a trace of naphthalene was isolated from the preparative FVT reactions, but not seen in the matrix isolation experiments, where the lower pressure and presence of Ar gas would disfavor dimerization. Naphthalene is the known thermal rearrangement product of the dimer of cyclopentadienylidene, fulvalene.[20a,18]

Thermal elimination of CO from ketenes has been observed in several other instances.[5] Thus, high-temperature elimination of CO from ketenes **1** and **13** is not surprising. In the case of **13**, CO elimination will be facilitated by the fact that this ketene is born with an excess energy of more than 60 kcal/mol (see the Computational Details).

In summary, and in contrast to the unsuccessful FVT-MS experiments of Mamer et al.,[18] the sequential formation of **1** and **13** on FVT of **7** is clearly established by the IR and MS investigations reported here (Scheme 4).

3. Trapping of the Ketenes with MeOH. Preparative FVT reactions[22] of methyl salicylate were carried out with trapping of the product on a liquid N_2-cooled coldfinger (77 K). The yields of products were determined by GC−MS. When the FVT reaction was carried out at 600 °C, subsequent warming of the coldfinger afforded methyl salicylate **7** (92%) together with cyclopentadienecarboxylates **15** and **16** (4%) as a result of trapping of ketenes **1** and **13** with methanol (Scheme 5). The corresponding FVT reaction at 780 °C afforded methyl salicylate **7** (52%) and cyclopentadienecarboxylates **15** and **16** (41%) in accord with the thermal processes described in Sections 1 and 2 (Figure S5, Supporting Information). The combined yields of these products were increased to 100% when excess methanol was present. Two methods were used for trapping with excess methanol: (i) A layer of MeOH is deposited on the coldfinger prior to the FVT reaction. The FVT product is deposited on top of this layer, and finally a new layer of MeOH is deposited on top of the pyrolyzate. This methanol matrix melts on warming and is allowed to flow into a receiving flask. (ii) The gaseous thermolysis product can be mixed with MeOH vapor, which is passed through a concentric tube terminating shortly before the exit of the FVT tube. The FVT product is thus collected in a methanol matrix on the coldfinger.[22,24]

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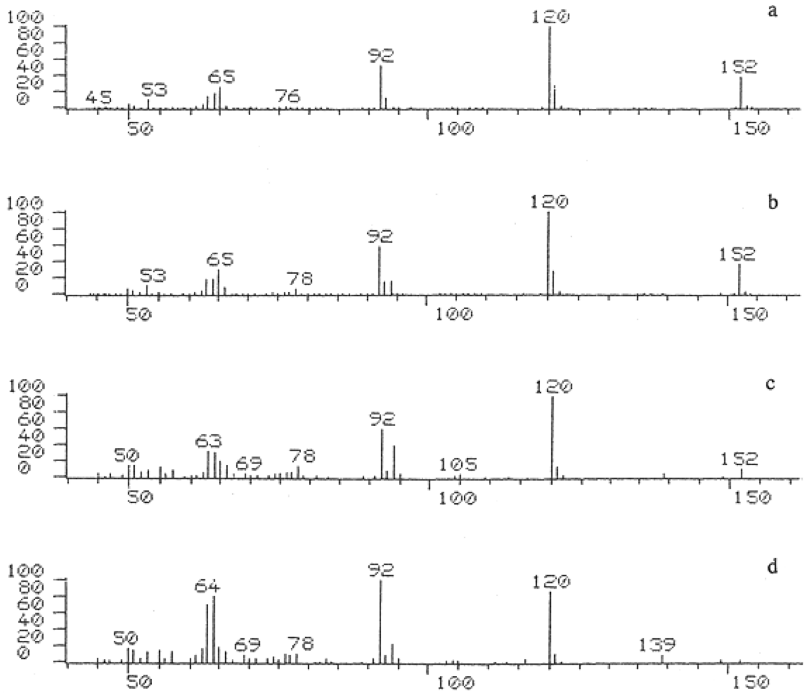


Figure 3. EI mass spectra of the products of online FVT of methyl salicylate **7** (m/z 152) at various temperatures: (a) 200 °C; (b) 500 °C; (c) 600 °C; (d) 800 °C. **1** = m/z 120. **13** = m/z 92.

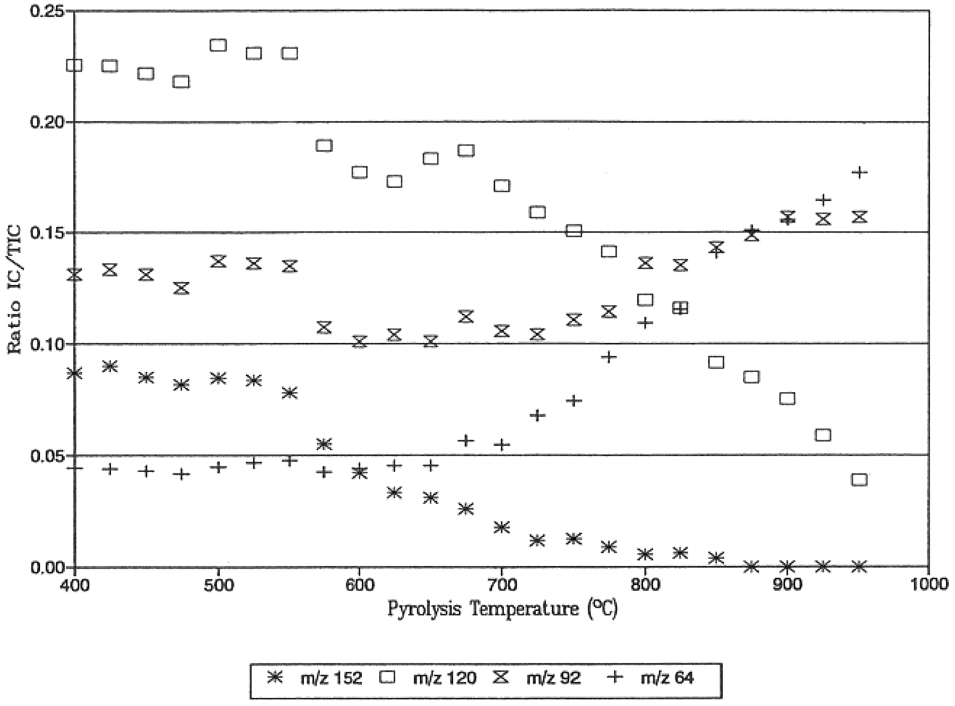
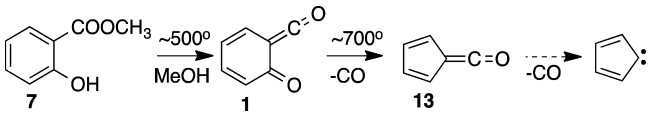


Figure 4. Ion intensities as ion current (IC) versus total ion current (TIC) in the online FVT of **7** (m/z 152) at various temperatures. **1** = m/z 120. **13** = m/z 92. C_5H_4 = m/z 64.

Scheme 4



4. FVT of Methyl 1-^{13}C-Salicylate 15 Establishing Ketene Rearrangements. Methyl 1-^{13}C-salicylate (**7a**) (95 atom -% ^{13}C) was synthesized from 1-^{13}C-benzoic acid as indicated in Scheme 6.

FVT of compound **7a** at 800 °C with trapping of the ketene products with MeOH on the coldfinger afforded a mixture of recovered but rearranged ^{13}C-labeled methyl salicylate (**7b**) together with a mixture of ^{13}C-labeled methyl cyclopentadienecarboxylates **20** and **21** (ratio 7:5:1). After thawing of the MeOH matrix, the sample was kept at −40 °C in order to avoid

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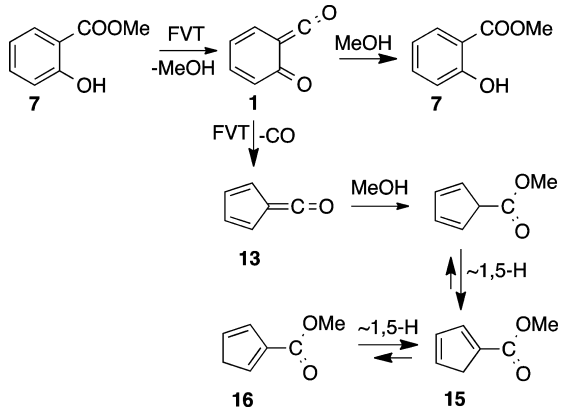
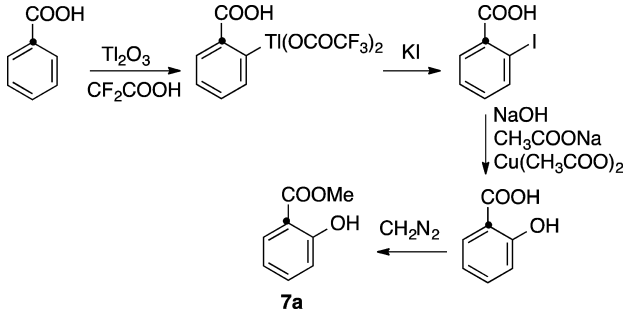
Scheme 5. Trapping of Ketenes 1 and 13



Scheme 6. Synthesis of Methyl 1-^{13}C-Salicylate 7a

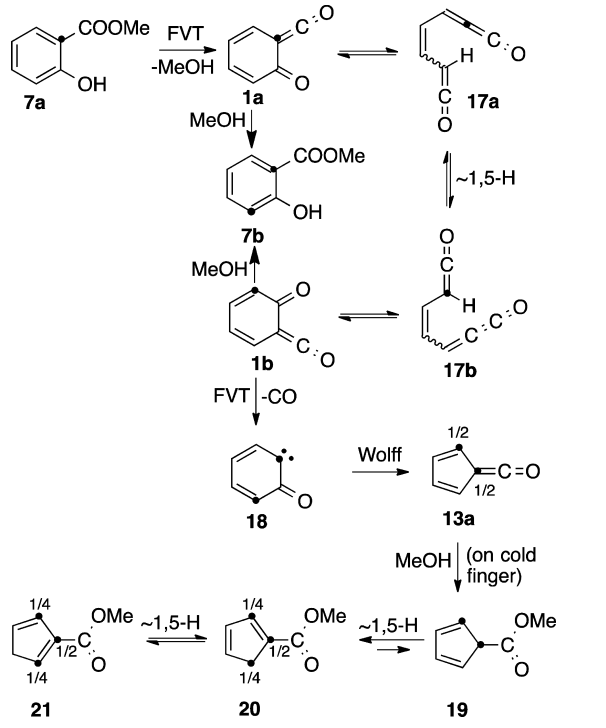


dimerization of the cyclopentadienes, and NMR spectroscopy was performed at −40 °C. The composition of the mixture and the distribution of the ^{13}C label were determined by comparison of the ^{13}C NMR spectrum with those of the previously analyzed unlabeled compounds (Figures S7−S9, Supporting Information). The surprising outcome was that the label in the methyl salicylate (**7b**) was now distributed evenly between carbons 1 and 3 (47% each; see Scheme 7) with only natural abundance of ^{13}C on all other carbon atoms. In the methyl cyclopentadiene-1-carboxylate (**20**) 47% of the label resided at the *ipso* carbon C1, and the remaining 47% was distributed almost evenly between C2 and C5 as indicated in Scheme 7. Only a natural abundance of ^{13}C was found at all other carbon atoms. Similar results were obtained for the minor isomer **21** (Scheme 7 and Figure S9, Supporting Information).

The label distribution in **7b**, **20**, and **21** demonstrates that a profound but specific rearrangement is taking place. We explain this in terms of an electrocyclic ring opening in the initial ^{13}C-labeled *α*-oxoketene (**1a**), which generates the bis-ketene **17a** (Scheme 7). Recyclization will now generate equal amounts of **1a** and **1b**, which are trapped with MeOH to give the observed compound **7b**. Loss of CO from the equilibrated ketenes **1a** and **1b** with Wolff-type rearrangement (concerted or stepwise via carbene **18**) affords the labeled ketene **13a** and hence the isolated cyclopentadienecarboxylates **20** and **21**.

The ring-opened ketene **17** is a high energy species lying ca. 44 kcal/mol above ketene **1**, and it has only a very small barrier for the electrocyclization back to **1** and a ca. 10 kcal/mol barrier for a 1,5-hydrogen shift (see the Calculations). Therefore, the experimental characterization of **17** is not straightforward. Ketene **17** is predicted to absorb strongly at 2147, 2105, and 1546 cm^{-1} (see Figure S2, Supporting Information; wavenumbers scaled by 0.9614), but the complex IR absorptions in

Scheme 7. Interpretation of the ^{13}C-Labeling Results[a]

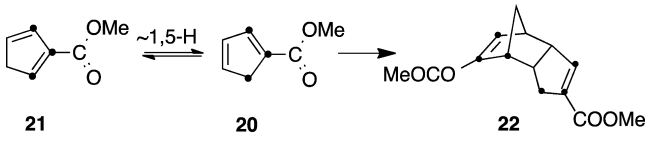


[a]Note: the thermal interconversions of **1a** and **1b** with ^{13}C-labeled benzoxet-2-one **2** are omitted for clarity.

the ketene region around 2100 cm^{-1} due to **1**, **13**, and CO (Figures 1, 2, and S1, Supporting Information) make it impossible to identify the presence of potential absorptions due to **17** in this region. However, an otherwise unassigned weak absorption at 1550 cm^{-1} seen in some spectra resulting from the photolyses of **11** and **12** may be due to **17**. This peak disappears on further photolysis (see Figures S10 and S11, Supporting Information).

The cyclopentadienecarboxylates dimerize at room temperature. For further proof of the labeling pattern, the labeled dimer **22** was isolated and examined by ^{13}C NMR spectroscopy, which clearly shows that only the carbon atoms expected from Scheme 7 are labeled (see Scheme 8 and Figure S12, Supporting Information). The structure of **22** and the assignment of the ^{13}C NMR data have been established unequivocally.[25]

Scheme 8. Dimerization of the ^{13}C-Labeled Methyl Cyclopentadienecarboxylates to 22 (Only One Enantiomer of the Racemate Is Shown)



It is interesting to note that benzoxirene (**23**) is not involved in the rearrangements. Had it been, then labeling of the carboxylate carbon would have occurred, and this was not detectable (Scheme 9). This is in contrast to the case of the corresponding iminocarbene, where ^{13}C-labeling demonstrated the interconversion with 1*H*-benzazirene prior to ring contraction to cyclopentadienecarbonitrile.[26]

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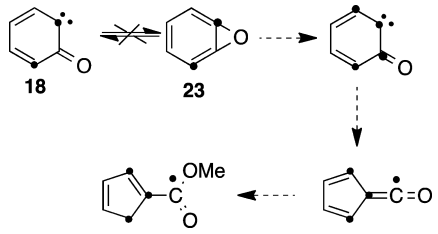
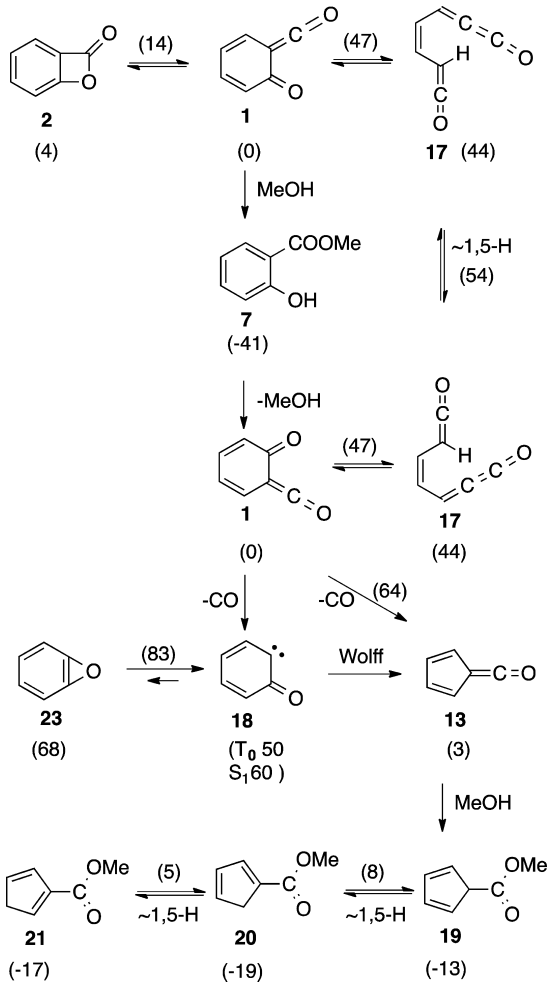
Scheme 9. Absence of Benzoxirene 23



5. Calculations. To shed some light on the observed rearrangements in Schemes 4 and 7, we performed DFT calculations with the relatively new and reliable[27] M06-2X hybrid functional together with a triple-ξ quality basis set (6-311++G(d,p)). The computed free energies (relative to **1**) are given in Scheme 10.

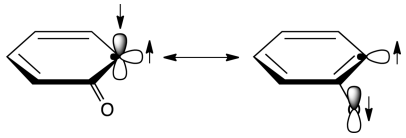
In agreement with previous studies,[10] benzoxetone (**2**) is formed with relative ease from ketene **1**, requiring only a free energy of activation of ~14 kcal/mol. Bisketene **17**, which is formed by electrocyclic ring opening, lies 44 kcal/mol above the cyclic ketene **1**, and an activation barrier of 47 kcal/mol is required for its formation. The recyclization of **17** to **1** and the degenerate 1,5-H shift (**17** ⇄ **17**) have calculated barriers of 3 and 10 kcal/mol, respectively. The triplet ground state (T_0) of the α-oxocarbene, 2-oxocyclohexa-3,5-dienylidene (**18**), is predicted to lie 50 kcal/mol above **1**. A singlet state of **18** could not be optimized at the present DFT level, not surprisingly, because the lowest singlet state (S_1) is an open shell, as was also found for the isomeric 4-oxocyclohexadienylidene.[28] Calculations on **18** at the CASSCF(8,8)/6-311++G(d,p) level afforded a singlet−triplet splitting (S_1-T_0) of 10 kcal/mol, with the closed-shell singlet S_2 lying 21 kcal/mol above T_0 (Scheme 10). The corresponding numbers at the CASSCF(8,8)/6-31G(d) level are 5 and 13 kcal/mol. Usually, the lowest singlet state of carbenes is closed-shell, but the different energy ordering for **18** can be understood by noting that the open-shell singlet S_1 can acquire aromaticity by moving a p electron from the carbene center to the oxygen (Scheme 11). This is not possible for the closed-shell S_2 singlet.

Scheme 10. M06-2X/6-311++G(d,p)-Calculated Free Energies (Numbers in Parentheses) of Ground and Transition States (kcal/mol) Relative to 1[a]



[a]The T_0-S_1 (open-shell singlet) energy splitting in carbene **18** is from a CASSCF(8,8)/6-311++G(d,p) calculation.

Scheme 11. Resonance Structures of the Open-Shell Singlet Carbene S_1-18



Similarly to diazoketone **14**[20d] and 2-diazo-1-naphthoquinone,[29] ketene **1** may undergo CO elimination and Wolff rearrangement to **13** via carbene **18** or in a concerted manner. The concerted singlet-state reaction has a calculated barrier of 64 kcal/mol (Scheme 10); the stepwise carbene reaction is expected to be competitive: the S_1 state of **18** lies about 60 kcal/mol above **1**, and the Wolff rearrangement barrier[29b] is about 7 kcal/mol.

The ring-contracted ketene **13** + CO are more stable than **18** by 47 kcal/mol at the M06-2X computational level. Quenching of **13** leads to the methyl cyclopentadienecarboxylates **19**−**21**. The initially formed but unobserved 2,4-cyclopentadiene isomer **19** is the least stable of the three (but only by a few kcal/mol), and it interconverts with the methyl 1,3-cyclopentadiene-1-carboxylate (**20**) with a barrier of 21 kcal/mol. The subsequent 1,5-H shift to give **21** requires 24 kcal/mol. The energetics of the three isomers and their interconversions are in good agreement with the finding that the major product **20** is also the most stable. The rearrangement to the minor product **21** is slightly more feasible than the conversion to the least stable **19**. The trapping product of **1** with MeOH, methyl salicylate **7**, is the global minimum in the investigated sequence, mostly due to its aromatic character, with a free energy of −41 kcal/mol relative to **1**.

The observed labeling of **7b** (Scheme 7) and the interpretation given in Scheme 7 are confirmed by the calculations. Ketene **1a** can rearrange to **1b**, giving the labeling pattern shown in **7b**, before it loses CO to form **13**. The latter process has a barrier of ca. 64 kcal/mol, which is significantly higher than the energies required for the rearrangements interconverting **1a** and **1b**.

The transition state for the formation of the unobserved benzoxirene **23** is predicted to lie at 83 kcal/mol relative to **1**, i.e., well above the transition state for the ring contraction reaction **1** → **13** (Schemes 9 and 10). Thus, the formation of

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benzoxirene **23** is not intrinsically impossible, but its formation is not going to be likely under any reaction conditions, since its ring opening and Wolff rearrangement will always be very facile reactions.

CONCLUSION

The α-oxoketene **1** is formed by FVT of methyl salicylate **7** and characterized by matrix-isolation IR spectroscopy as well as online mass spectrometry. Compound **1** is also formed by FVT of 2-phenylbenzo-1,3-dioxan-4-one (**8**), phthalic peranhydride (**9**), and benzofuran-2,3-dione (**11**) and by matrix photolysis of **9**, **11**, and 2-diazocyclohepta-4,6-dien-1,3-dione (**12**). α-Oxoketene (**1**) undergoes elimination of CO at FVT temperatures above 600 °C with Wolff rearrangement to fulven-6-one (**13**) either concertedly or via the α-oxocarbene **18**. FVT of methyl 1-^{13}C-salicylate **1a** revealed a complex rearrangement by electrocyclic ring opening to bisketene **17a**, 1,5-H shift to **17b**, recyclization to **1b**, and Wolff rearrangement to **13a**. The resulting ketenes **1a**/**1b** and **13a** were trapped with MeOH to generate the corresponding methyl esters **7b**, **20**, and **21** (Scheme 7). The ^{13}C labeling results demonstrate that benzoxirene **23** is not involved.

M06-2X/6-311++G(d,p) calculations confirm the feasibility of the reaction mechanism. The calculated activation energies for the reactions of α-oxoketene **1** and the ring-opened bisketene **17** allow the preferential formation of the major product **7** before ketene **13** is formed in a Wolff-type rearrangement. CASSCF calculations indicate that the lowest singlet state of 6-oxacyclohexa-2,4-dienylidene (**18**) is open-shell. The reaction sequence (Scheme 10) confirms the observed ^{13}C labeling pattern in the trapped products and the absence of formation of benzoxirene **23**.

EXPERIMENTAL SECTION

General Methods. The apparatus used for FVT-matrix isolation and FVT-MS has been described in detail.[22] For FVT-matrix isolation, in order to avoid unwanted formation of CO by back-streaming of gaseous pyrolysis products onto the hot filament, an externally heated quartz tube (10 × 0.9 cm i.d.) was flanged directly to the cryostat head, the so-called "brick-pyrolyzer".[22] Preparative FVT was usually performed in vacuo of ∼10^{-3} hPa in 32 × 2 cm i.d. electrically heated quartz tubes. Two methods were used for trapping of ketenes with methanol: (i) in "cold trapping" a layer of MeOH is condensed on a coldfinger cooled in liquid N_2, the pyrolysis product is then condensed on top of it, and at the end a fresh layer of MeOH is deposited, so that the pyrolysis product is sandwiched between methanol layers. After thawing, excess MeOH is removed in vacuo, and the resulting methyl 1,3-cyclopentadienecarboxylates are dissolved in cold $CDCl_3$ for immediate low-temperature NMR spectroscopy or allowed to dimerize at room temperature. (ii) In "hot trapping" a stream of MeOH vapor in N_2 gas is passed through a concentric tube through the FVT tube, terminating 5 cm from the exit of the FVT tube, so that the gaseous pyrolysis product will mix with the MeOH vapor before isolation on the liquid N_2-cooled coldfinger. In this case, a vacuum of 0.5−0.8 hPa is maintained during the pyrolysis. Drawings and photographs of the apparatus have been published.[22] Matrix photolyses were performed using a 1000 W high-pressure Hg/Xe lamp equipped with a monochromator, appropriate cutoff filters, and a water filter to eliminate infrared irradiation, or a 75 W low-pressure Hg lamp (254 nm).

Methyl Salicylate-1-^{13}C (7a). The following procedures for preparation of ^{13}C-labeled methyl salicylate were optimized in several trial runs with unlabeled materials, and the identities of the products were ascertained by comparison with authentic samples. **Warning**: Thallium derivatives are highly poisonous.

(a) A solution of thallium trifluoroacetate[30] was prepared by adding 50 g of Tl(III) oxide to 200 mL of TFA in a 500 mL flask. The suspension was vigorously stirred and refluxed for 12 h under exclusion of light. The solution thus obtained was filtered to yield a 0.88 M solution of Tl trifluoroacetate, which was then diluted to 0.69 M with trifluoroacetic acid. (b) A 5.9 mL portion of this solution was added to 500.5 mg (4.07 mmol) of benzoic-1-^{13}C acid (95 atom % ^{13}C). The mixture was stirred magnetically at 73 °C for 24 h and then cooled to rt. A 5 mL portion of 2.3 N aqueous KI solution was added, and the mixture was stirred for 15 min. Sodium thiosulfate (250 mg) was added, and stirring was continued for another 15 min. The resulting solution was cooled in ice, made alkaline with 4 N NaOH, filtered, reacidified, and extracted with diethyl ether. The extract was concentrated and purified by column chromatography on silica gel, eluting with $CHCl_3$−MeOH 97:3 (R_f = 0.3) to yield 568 mg (57%) *o*-iodobenzoic-1-^{13}C acid, mp 162 °C (lit.[31] for the unlabeled material 162 °C). (c) The foregoing compound (565 mg; 2.26 mmol) was mixed with 2.3 mL of 1 N NaOH and heated at reflux for 5 min. Sodium acetate (900 mg), Cu(II) acetate (74 mg), and water (7 mL) were then added, and the resulting mixture was refluxed for 1 h. After cooling, the solution was filtered and the filtrate acidified. The product was extracted with ether and purified by column chromatography on silica gel, eluting with $CHCl_3$−MeOH 9:1, thus affording 245 mg (78%) of a white powder with an R_f value identical to that of salicylic acid and mp 158.5−159 °C (159 °C for the unlabeled material). (d) This sample (245 mg; 1.77 mmol) of salicylic-1-^{13}C acid was dissolved in 5 mL of anhydrous ether, and 3.6 mL (1.98 mmol) of a previously titrated 0.55 M solution of diazomethane in ether was added at 0 °C. This mixture was stirred magnetically at 0 °C for 5 min. The ether was then removed in vacuo at 0 °C, leaving 260 mg (97%) of the desired ester, having R_f identical with that of unlabeled methyl salicylate prepared in the same manner: ^{1}H NMR ($CDCl_3$) δ 8.3 (br s, 1H), 7.82 (d, 1H), 7.44 (t, 1H), 6.97 (d, 1H), 6.86 (t, 1H), 3.93 (s, 3H) (see Figure S6, Supporting Information); ^{13}C NMR ($CDCl_3$) δ 170.6, 161.5, 135.6, 129.8, 119.1, 117.5, 112.3 (^{13}C-labeled carbon, C1), 52.2 (see Figure S7, Supporting Information). For the assignment of peaks, see the literature.[32]

FVT-Matrix Isolation of Methyl Salicylate (7). This compound was introduced into the FVT apparatus from a sample reservoir held at 0 °C with Ar passing over the sample at a pressure of 10^{-4} hPa. Pyrolysis started at ∼300 °C with a very low degree of conversion. Conversion was complete at temperatures of 750 °C and above. Carbonylcyclohexadienone (**1**) was best observed at temperatures of 600−700 °C. Fulven-6-one (**13**) is formed above 700 °C and became the main product at and above 800 °C.

IR spectrum of **7** (Ar, 10 K): 3372 m, 3040 w, 2966 w, 1750 m, 1625 vs, 1610 vs, 1446 m, 1360 w, 1350 w, 1330 m, 1310 s, 1257 m, 1217 s, 1197 m, 1160 m, 1094 w, 1034 w, 850 w.

IR spectrum of **1** obtained at 600 °C (Ar, 10 K): 2145 s, 2134 vs, 2114 w, 1655 m, 1600 w, 1521 m, 1420 w, 1292 vw, 1262 vw, 1253 vw, 835 w, 806 w cm^{-1}. When ketene **1** is deposited as a neat substance, it survives heating until 150 K.

IR spectrum of **13** obtained at 800 °C (Ar, 10 K): 2135 vvs, 2131 vs, 1624 vw, 1594 vw, 1457 m, 1403 m, 1327 m, 1076 w, 1072 vw, 896 m cm^{-1}. When ketene **13** is deposited as a neat substance, it survives heating until 180 K.

Matrix Photolysis of 1. Photochemical conversion of **1** to **2** was achieved by photolysis of the matrix-isolated **1** at λ> 340 nm, and this process was reversed on photolysis of **2** at λ>310 nm. Cycling between **1** and **2** was performed at least 6 times without any significant differences between initial and final spectra.

IR spectrum of **2** (Ar, 10 K): 1916 m, 1904 s, 1624 w, 1604 m, 1443 vw, 1340 w, 1173 w, 1162 w, 892 m, 977 w, 824 m.

Photolysis of the matrix-isolated **1** at 254 nm for 2 h resulted in decreased absorbances due to **1** and increased absorbances ascribed to fulvene-6-one **13** and CO.

FVT-Matrix Isolation and Photolysis of 2-Phenylbenzodioxin-4-one (8). Compound **8** was sublimed into the FVT apparatus at 50 °C with Ar passing over the sample. Pyrolysis commenced at ca.

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400 °C with formation of ketene **1** and benzaldehyde, and above 600 °C ketene **13** was also formed (IR spectra as above).

Photolysis of matrix-isolated **8** at λ>300 nm for 1 h caused nearly complete conversion to ketene **1** (see Figure S1, Supporting Information). Subsequent irradiation at λ > 340 nm resulted in the usual interconversion of **1** and **2**.

FVT-Matrix Isolation and Photolysis of Phthalic Peranhydride 9. CAUTION: This compound is highly explosive.[33]

Peroxide **9** was sublimed into the FVT tube at 25 °C with Ar passing over the sample. Pyrolysis commenced at an oven temperature of 450 °C with formation of ketene **1** (IR spectrum as above), and the additional formation of ketene **13** took place at temperatures above 650 °C.

IR spectrum of **9** (Ar, 10 K): 1780 vs, 1760 m, 1620 m, 1604 m, 1477 m, 1312 s, 1301 vs, 1246 m, 1108 w, 1102 m, 1048 s, 912 w, 853 w cm^{-1}.

Photolysis of the matrix-isolated **9** at λ > 310 nm afforded ketene **1**. At λ > 345 nm, a mixture of **1** and **2** was obtained, and it was possible to cycle between these two substances (IR spectra as above).

FVT-Matrix Isolation and Photolysis of Benzofurandione (11). Compound **11** was sublimed into the FVT apparatus in a stream of Ar at RT. Elimination of CO and formation of ketene **1** was observable from FVT temperatures of ca. 400 °C. At temperatures of 700 °C and above, ketene **13** was also formed. Compound **2** was not observed as a product of FVT.

A matrix containing **1** and **13** was obtained by FVT at 800 °C and then photolyzed at λ > 340 nm. This resulted in the familiar conversion of **1** to **2**, but ketene **13** remained unchanged.

Benzofurandione (**11**) was also deposited with Ar without pyrolysis: IR (Ar, 10 K) 1848 m, 1834 m, 1757 s, 1624 m, 1480 w, 1667 m, 1323 m, 1246 w, 1156 vw, 1026 s, 1037 w, 876 m cm^{-1}.

Photolysis of this matrix at λ = 310 ± 10 or λ > 310 nm resulted in the formation of CO and ketene **1** (IR spectrum as above). Photolysis λ > 345 or at 380 ± 10 nm caused conversion of **1** to **2** as described above. Broadband UV−vis photolysis caused the formation of CO, ketene **1**, and a small amount of ketene **13** (IR spectrum as above).

Matrix Isolation and Photolysis of Diazocycloheptadienedione (12). Compound **12**[34] was sublimed at rt and deposited with Ar: IR (Ar, 10 K) 2175 s, 1703 w, 1692 vs, 1437 w, 1347 w, 1323 s, 1223 m, 1217 w, 1061 w, 809 m cm^{-1}. Photolysis of the matrix at λ > 295 nm resulted in the elimination of N_2 and formation of ketene **1** (IR as above). Photolysis above 360 nm resulted in the usual mixture of **1** and **2** (see Figure 1 and Figure S10, Supporting Information). Further photolysis at >300 nm resulted in reversion of **2** to **1**. Photolysis at 254 nm caused slow loss of CO and formation of ketene **13**.

FVT of Methyl Salicylate (7). Trapping with MeOH. Formation of Methyl Cyclopentadienecarboxylates 15 and 16. A 100 mg sample of methyl salicylate (**7**) was distilled into the pyrolysis tube of the preparative FVT apparatus at rt and pyrolyzed at 800 °C. The pyrolysis products were trapped with MeOH using either the "hot trapping" or "cold trapping" method (see the General Methods). After the end of the pyrolysis, the product−methanol mixture was allowed to warm to −60 °C, and excess MeOH was removed by bulb-to-bulb distillation in vacuo at −60 to −40 °C. The sample was then cooled to −70 °C, and ice-cold $CDCl_3$ was injected to dissolve the sample, which was then transferred rapidly to an NMR tube at −78 °C. ^{1}H and ^{13}C NMR spectra were recorded at −40 °C (see Figure S8, Supporting Information). For methyl salicylate (**7**) thus reformed: ^{1}H NMR ($CDCl_3$) δ 10.89 (s, 1H), 7.9−7.3 (m, 4H), 3.93 (s, 3H), ^{13}C NMR ($CDCl_3$) δ 170.6 (COO), 161.9 (C2), 135.8 (C4), 129.9 (C6), 119.2 (C5), 117.4 (C3), 112.0 (C1), 52.5 (CH_3).[34] Methyl 1,3-cyclopentadiene-1-carboxylate (**15**): ^{1}H NMR ($CDCl_3$) δ 6.98−6.83 (m, 1H), 6.70 (m, 1H), 6.57 (m, 1H), 3.76 (s, 3H), 3.28 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 161.9 (COO), 143.1 (C2), 140.2 (C3), 139.9 (C1), 132.2 (C4), 51.6 (CH_3), 41.3 (C5). Methyl 1,3-cyclopentadiene-2-carboxylate (**16**): ^{1}H NMR ($CDCl_3$) δ 7.30 (br s, 1H), 6.76 (m, 1H), 6.46 (m, 1H), 3.82 (s, 3H), 3.18 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 164.7 (COO), 143.2 (C1), 138.4 (C2), 134.3 (C4), 130.4 (C3), 42.7 (C5), 51.8 (CH_3). The spectra were identical with those of authentic materials, and peak assignments for **7**,[32,35] **15**, and **16**[36] were made in accord with the literature.

FVT of Methyl Salicylate-1-^{13}C (7a). Trapping with MeOH. Formation of 7b and Methyl Cyclopentadienecarboxylates 20 and 21. An 80 mg sample of methyl salicylate-1-^{13}C was pyrolyzed as above at 800 °C, and the products were trapped on the coldfinger with MeOH ("cold trapping"). After workup as above, NMR spectra were recorded at −40 °C (see Figure S9, Supporting Information). The ratio of products **7b**:**20**:**21** was 7:4.5:1. ^{13}C NMR of **7** (unlabeled) and **7b** (labeled) ($CDCl_3$) δ (integrals for unlabeled/^{13}C labeled compound): 170.6 (0.47/0), 161.9 (0.68/0), 135.8 (1.09/1.11), 129.9 (1.17/1.15), 119.2 (1.09/1.11), 117.4 (C3, 0.14/51.48), 112.0 (C1, 0.56/25.56), 52.5 (1/1).

^{13}C NMR of **15** (unlabeled) and **20** (labeled) ($CDCl_3$) δ (integrals for unlabeled/^{13}C labeled compound): 161.9 (0.1/0), 143.1 (C2, 1.0/25.0), 140.2 (C3, 0.8/0.9), 139.9 (C1, 0.6/28.3), 132.2 (C4, 0.8/0.8), 51.6 (CH_3, 1/1), 41.3 (C5, 1.3/28.6). Peak assignments were made in accord with the literature.[32,35,36]

^{13}C NMR of **16** (unlabeled) and **21** (labeled) ($CDCl_3$) δ (integrals for unlabeled/^{13}C labeled compound): 164.7 (0.1/0), 143.2 (C1, 0.7/20.4), 138.4 (C2, 1.3/22.7), 134.3 (C4, 1.1/0), 130.4 (C3, 1.3/22.7), 51.8 (CH_3, 1/1), 42.7 (C5, 1.2/0.5). Peak assignments were made in accord with the literature.[32,35,36]

Dimethyl Dicyclopentadienedicarboxylate (22). The product of FVT of 100 mg of **7a** at 800 °C was trapped with MeOH in the gas phase ("hot trapping", see the General Methods). After removal of excess MeOH in vacuo, the residue was purified by chromatography on silica gel, eluting with $CHCl_3$. A trace of naphthalene was detected but not examined further. The main fraction was the dimer **22**, identical with the authentic (unlabeled) dimer[25] except for the presence of ^{13}C-labeled carbon atoms: ^{13}C NMR ($CDCl_3$) δ 165.1, 164.9, 146.9, 142.2, 138.8, 137.7, 54.0, 51.0, 50.9, 50.5, 46.9, 46.3, 40.7, 32.7 (see Figure S12, Supporting Information). For peak assignments, see ref 25b.

Computational Details. Calculations were performed with the program package Gaussian 09.[37] Structures are optimized using the global hybrid functional M06-2X[38] with the 6-311++G(d,p)[39] basis set. The nature of all stationary points as true minima or as first-order transition states was confirmed by calculating harmonic frequencies. Gibbs free energies are obtained at 298.15 K under inclusion of zero-point vibrational energy corrections.[40] The wave function stability of selected transition states and their open-shell character has been examined; however, no instability or diradical character could be found. Vibrational spectra are simulated using the B3LYP/6-31G(d) level of theory[41] and scaled by 0.9614 to correct for anharmonicity. The CASSCF(8,8)/6-31G(d) and CASSCF(8,8)/6-311++G(d,p) calculations[42] on **18** used an active space consisting of 8 electrons and 8 orbitals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional IR and NMR spectra (Figures S1−S12) and calculated structures of carbene **18** (Figure S13). Absolute energies and Cartesian coordinates for all calculated compounds and imaginary frequencies for transition states. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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