preparative pyrolysis apparatus was used with two liquid N_2 traps, and at the end of the experiment the contents of the traps were allowed to expand into a gas cell for IR spectroscopy. Yields of products from **14** were as previously described,[13] except that traces of butatriene and ethylene were detected as well. In the preparative pyrolysis of **27** at 900 °C, 50% of the starting material was recovered unchanged. The liquid product showed strong signals at δ 95.7 and 170.9 (butatriene) and 128.3 (benzene) in the ^{13}C NMR. The gas-phase IR spectrum of the volatile product was due to a mixture of CO_2 and ethylene, identified by comparison with the spectra of authentic samples.

4-Cyclopentylidene-3-methylisoxazol-5(4*H*)-one (34)[25] (200 mg, 1.21 mmol) was sublimed at 85 °C and pyrolyzed at 800 °C (10^{-3} Torr), collecting the products at 77 K. The pyrolyzate was warmed to room temperature and analyzed by GC on two columns: (i) SE 52, 80 °C, programmed at 12 °C/min to 250 °C, 29 psi He; (ii) SE 30, isothermal, 180 °C, 30 psi He. The following products [retention time on column (i) and yield in parentheses] were identified by comparison of retention times and GC-MS with those of authentic samples: 4,5-dihydro-2-methylcyclopenta[*b*]pyrrole (**36**, R = H) (721 s, 71%), 4,5-dihydro-2-methyl-cyclopenta[*b*]pyrrole-3-carboxylic acid (**36**, R = COOH) (796 s, 17%), dodecahydrotriphenylene (**35**) (1597 s, ca. 2%). On column (ii) **35** had a retention time of 1038 s.

3-Methyl-4-(2-pyrrolidinylidene)-3-methylisoxazol-5(4*H*)-one (37). 3-Methylisoxazol-5(4*H*)-one (1.98 g, 20 mmol) and 2-methoxy-1-azacyclopent-1-ene[35] (1.98 g, 20 mmol) were dissolved in 50 mL of toluene, and 1.8 mL of acetic acid and 0.7 mL of piperidine were added. The mixture was stirred for 10 min at 50 °C, which caused a white solid to precipitate. The mixture was then heated at reflux for 20 min. The dark red to brown mixture was cooled and filtered and the solid recrystallized from either ethanol or water to give 1.5 g (45%) of long, white needles: mp 200-201 °C; IR (KBr) 3480 (m), 3230 (m), 2975 (w), 2930 (w), 1695 (s), 1595 (s), 1545 (s), 1415 (m), 1310 (s), 1145 (m), 1080 (m), 1010 (s), 960 (s), 870 (s), 830 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.20 (s, 3 H, CH$_3$), 2.21-2.28 (m, 2 H), 3.02 (t, 2 H), 3.76 (t, 2 H), 9.33 (br, NH); ^{13}C NMR (CDCl$_3$) δ 13.5 (CH$_3$), 86.9 (C-4), 158.4 (C-6), 168.7 (C-3), 175.3 (C-5); MS *m/z* (relative intensity) 167 ($[M + 1]^+$, 9), 166 ($[M]^{\cdot +}$, 100), 165 ($[M - 1]^+$, 65), 109 (15), 108 (37), 95 (22), 92 (15), 53 (12), 41 (12), 39 (13). Anal. Calcd for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 58.07; H, 6.04; N, 16.94.

Pyrolyses of this compound were carried out in the temperature range 680-790 °C as described fully in the text. For identification of the stable products, the pyrolysis was carried out at 700 °C in the preparative apparatus collecting the products in two liquid N_2 traps. The gaseous products were allowed to expand into a gas cell for IR spectroscopy. A strong spectrum due to CO_2 and ethylene resulted, and these were the only constituents (ratio ~1:1, i.e., 100% pyrolysis yield). The liquid product was taken up in CDCl$_3$ and determined by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy to consist of acetonitrile and acrylonitrile (1:0.9). No other products were detectable. Thus, the pyrolysis yield of acrylonitrile was 90%.

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Interrelationship between Carboxy(vinyl)ketenes, Methyleneketenes, Vinylketenes, and Hydroxyacetylenes

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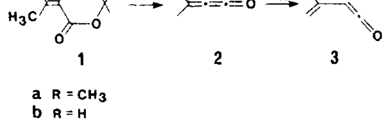
Abstract: Carboxy(vinyl)ketenes, alkylideneketenes, and vinylketenes have been obtained selectively, sequentially, and isomerically pure for the first time by flash vacuum pyrolysis of 2,2-dimethyl-5-alkylidene-1,3-dioxane-4,6-diones (Meldrum's acid derivatives) under controlled conditions. Each of the ketenes was directly observed by IR spectroscopy and trapped with methanol or aniline. Highly unstable compounds believed to be the hydroxyacetylene isomers of the alkylidene- and vinylketenes have been observed for the first time.

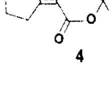
It was thought until recently that 5-alkylidene derivatives of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) **1** decompose thermally to alkylideneketenes **2** which then, given the presence of a δ-hydrogen atom, isomerize in a second step at higher temperatures to vinylketenes **3**. Photoelectron spectra of ketenes **2** and **3** were assigned on the basis of this assumption.[1] We have shown that the assumption is a vast oversimplification[2] and now report that the chemistry of simple Meldrum's acid derivatives is even more complicated than previously thought, involving no less than four different species: a carboxy(vinyl)ketene, a methyleneketene, a hydroxyacetylene, and a vinylketene.



1 **2** **3**

a R = CH$_3$
b R = H

The flash vacuum pyrolysis (FVP) of the 5-cyclopentylidene derivative **4** of Meldrum's acid to the three ketenes **5**-**7** was described previously.[2a] Carboxy(vinyl) ketenes had never been observed before, let alone isolated. Although all three ketenes could be observed, a completely sequential generation was not achieved, and their generic relationship therefore remained uncertain. We have now succeeded in a strictly sequential generation of such ketene triads and thus in establishing their exact relationships. The results are reported herein.



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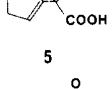

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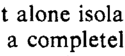

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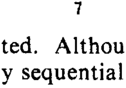

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Results

FVP of **1a** at 400 °C gave strong new bands at 2125 (C=C=O), 2500-3400 (COOH), 1770 (C=O), and 1630 (C=C)

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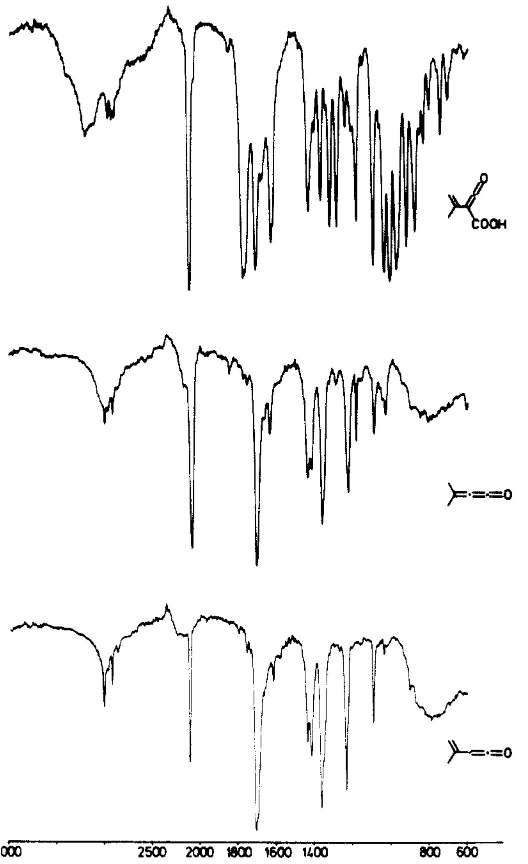
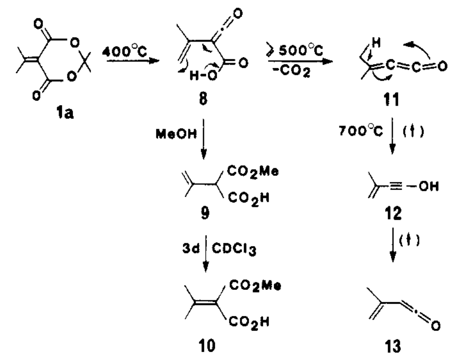


Figure 1. Top: carboxy(isopropenyl)ketene (**8**) produced from **1a** at 500 °C. Middle: isopropylideneketene (**11**) produced from **1a** at 700 °C. Bottom: isopropenylketene (**13**) produced from **1a** at 800 °C by pyrolysis through a packed tube. Bands at 1700 cm^{-1} are due to acetone.

Scheme I



cm^{-1} in the IR spectrum recorded at 77 K (Figure 1, top). Acetone was present (1710 cm^{-1}), but CO_2 was not. In these experiments, CO_2 is often not seen in the low-temperature spectra because it condenses on the colder metal parts of the cryostat. On subsequent warm-up, however, CO_2 sublimes from the heated metal surface to the cold sample disk, thus allowing its observation. For this reason, careful warm-up experiments were carried out for all the reactions described in this paper, and the gaseous products were furthermore assayed by gas-phase IR spectroscopy. Due to the nature of the spectrum, the absence of CO_2, and the subsequent chemistry, the species formed between 400 and 500 °C is assigned the carboxy(vinyl)ketene structure **8** (Scheme I). Cocondensation of the ketene with methanol followed by warm-up to room temperature resulted in the isolation of monomethyl isopropenylmalonate (**9**) is 95% yield (see the Experimental Section). After standing for 3 days in chloroform solution at room temperature, **9** has entirely isomerized to methyl isopropylidenemalonate (**10**).

As the FVP temperature was increased to 700 °C, less of **8** was being isolated, and a new ketene, absorbing strongly at 2088 cm^{-1} took its place. At 800 °C, the second ketene was virtually the only product (Figure 1, middle). Trapping of this ketene with methanol gave methyl isopropylideneacetate only, and the structure **11** is therefore secure.

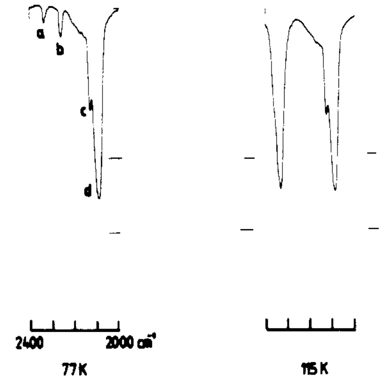


Figure 2. 2000–2400-cm^{-1} region of the IR spectrum of the pyrolyzate of **11** at 700 °C. Left: at 77 K; a = CO_2, b = 2260-cm^{-1} species, c = **13**, d = **11**. Right: same sample after warming to 115 K; b has disappeared, c and d are unchanged. CO_2 has increased due to sublimation from the cold end to the KBr disk (see text).

Further increase of the FVP temperture caused the appearance of a third ketene, absorbing strongly at 2109 cm^{-1}. However, **11** is so stable that drastic measures have to be employed in order to fully convert **11** to the third ketene **13**. The best results were obtained by filling the pyrolysis tube with loosely packed quartz chips. Under these conditions, **11** was fully converted to **13** at 800 °C. **13** absorbed at 2109 cm^{-1} (Figure 1, bottom) and was trapped with methanol to give methyl isopropenylacetate.

That these ketenes are really formed in a sequential manner, and not via competing fragmentation processes of the starting material **1a**, was shown with the aid of double-pyrolysis experiments. The technique is described in the accompanying publication.[3] At 500 °C, the starting material **1a** decomposes completely to **8** in a single 5-cm FVP tube. By using two such tubes in series, at 500 and 400 °C, respectively, a "1:1 mixture" (correctly, a 1:1 intensity ratio of the C=C=O stretching vibrations in the IR) of **8** and **11** was obtained. With both tubes at 500 °C only **11** was isolated. CO_2 was formed at the same time as **11**. Therefore, **8** decarboxylates via a six-center transition state as indicated in Scheme I. Very little **13** was formed under these conditions.

As the temperature was increased to 700–800 °C, **11** and **13** started to interconvert. Under conditions where both **11** and **13** were present, new bands at 2260 (w) and 3335 (s) cm^{-1} appeared as well (Figure 2). This new species disappeared on warm-up to 115 K, whereas the ketenes **11** and **13** were stable until 150–160 K, and **8** was stable until 210 K. Because trapping with methanol gave exclusively methyl isopropylidene- and/or isopropenylacetates (as well as the malonate **9** when **8** was present), the new species is assigned the vinylethynol structure **12**. This compound would be formed in a 1,5-shift of hydrogen in ketene **11**. The kinked structure established for propadienone by microwave spectroscopy[4] would be expected to pertain to **11** also, and this would facilitate the hydrogen shift depicted in Scheme I. The absorption maxima are in the regions expected for ethynol.[5] The same phenomenon is observed in the ethylidene series to be described below.

FVP of compound **1b** at 400 °C gave carboxy(vinyl)ketene **14**, absorbing at 2135 cm^{-1} and featuring strong bands due to the carboxylic acid function at 2500–3400 cm^{-1}, much as in the case of **8**. Pyrolysis of **1b** was complete at 500 °C, and **14** was the only product apart from acetone. Double pyrolysis of **14** at 500 °C gave ethylideneketene (**15**; 2093 cm^{-1}). By rapid sublimation of **1b** at 700 °C, **15** was obtained as the only product. Double pyrolysis above 600 °C gave increasing amounts of vinylketene[6]

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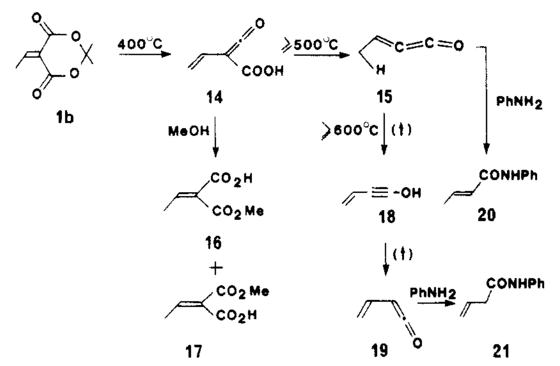
Scheme II



(**19**; 2118 cm^{-1}), and by maintaining the first tube at 600 °C and the second at 800 °C, **19** was the only product. Again, at intermediate temperatures, where both **15** and **19** were obtained, new peaks at 2250 (w) and 3350 (s) cm^{-1} were seen. When **15** had been completely consumed due to conversion to **19**, the new species also disappeared, and the bands are therefore assigned to vinylethynol (**18**; Scheme II). This species disappeared on warm-up to 100 K. Trapping experiments (see below) gave only products derived from **15** and/or **19**; **18** seemed to disappear, in conformity with its expected ready isomerization to **19** in the condensed phase.

14 was trapped with methanol to give a mixture of (*Z*)- and (*E*)-methyl ethylidenemalonates (**16**, **17**) in 94% yield. Ethylideneketene (**15**) was trapped with aniline, because it has been stated previously that this reaction gave in fact **21**.[7] By using conditions where only ketene **15** was formed, however, we obtained (*E*)-crotonanilide (**20**) in 82% isolated yield and free of any contamination by the isomeric **21**. At higher pyrolysis temperatures, where also vinylketene (**19**) was formed, 3-butenoic anilide (**21**) was obtained as well.

Discussion

The facts that we have succeeded in obtaining each of the ketenes **8**, **11**, **13–15**, and **19** free of each other and free of starting material and that each ketene can be converted to the next step in the series with the dual pyrolysis tube technique constitute rather compelling evidence that the generic relationships between the various species are in fact as illustrated in Schemes I and II. The first step in these reactions is believed to be tautomerization of the starting materials **1** to the 5-vinyl enols of Meldrum's acid as described earlier.[2a] The enol forms of **1a** and **1b** then cleanly eliminate acetone in a cycloreversion reaction, giving the remarkably stable carboxy(vinyl)ketenes **8** and **14**.

Also the alkylideneketenes **11** and **15** are remarkable stable thermally, especially isopropylideneketene (**11**), which requires pyrolysis through a packed 5-cm tube at 800 °C in order to isomerize fully to isopropenylketene (**13**), although this reaction will take place by using a longer, unpacked tube at 700 °C.

Furthermore, the observation of bands near 2250 and 3350 cm^{-1} belonging to a kintically unstable species in pyrolyzates containing **11** and **13** or **15** and **19** is strong indication for the existence of the hydroxyacetylenes **12** and **18**. This is of particular interest because no viable route to hydroxyacetylenes is known. These compounds have long been sought, especially because of their possible existence in interstellar space.[5,8,9] Although hydroxyacetylene is predicted to lie 36 kcal/mol above ketene, the gas-phase barrier to its tautomerization is equally predicted to be 73 kcal/mol.[10] Hydroxyacetylenes were not the primary objective of this work, and better conditions for their production can undoubtedly be found. We stress that, although the results are suggestive, they do not prove that hydroxyacetylenes lie on the paths from methyleneketenes (**11**, **15**) to vinylketenes (**13**, **19**); they could be side products reverting to the methyleneketenes. A theoretical investigation of the isomerization pathways and their energetics would be welcome.

The results also call for a reinvestigation of the photoelectron spectra of alkylideneketenes.[1] Since the carboxy(vinyl)ketenes **8** and **14** are quite stable thermally, and all six can be obtained selectively, it should also be possible to record their individual photoelectron spectra.

Conclusion. Flash vacuum pyrolysis can be employed as a highly selective synthetic tool, even in the preparation of compounds as unusual as carboxy(vinyl)ketenes and alkylideneketenes in preparatively useful yields and quantities.

Experimental Section

Apparatus. The pyrolysis apparatus and cryostats are described in the accompanying publication.[3] Trapping experiments with methanol or aniline were performed (i) by codeposition of the pyrolysis products with the trapping agent on the KBr window of the cryostat at 77 K, permitting IR spectroscopic observation of the ketenes, followed by warm-up to room temperature and characterization of the products by ^{1}H NMR; (ii) for quantitative measurements of yields the preparative apparatus[3] was used after having established the optimal temperature conditions with the analytical furnace. The temperature requried was usually 100 °C less in the preparative than in the analytical apparatus as established empirically. In the preparative apparatus the 20 × 2 cm quartz tube was fitted with a concentrical (5-mm-i.d. quartz tube passing through the sample inlet flask and terminating 5 cm before the exit of the pyrolysis oven. The trapping reagent was passed through the inner tube and collected together with the pyrolysis products on a cold finger cooled with liquid N_2. An NMR tube adapted below the cold finger allowed collection of the products in an N_2 atmosphere for NMR spectroscopy without opening the apparatus to the air. From the results of codeposition of ketenes with methanol, permitting IR spectroscopic observation of the ketenes, and from visual inspection of the cold finger in the preparative apparatus on warm-up, it appears that most of the actual trapping reaction takes place on the cold finger itself during warm-up.

Trapping of Carboxyisopropenylketene (8) with Methanol. 2,2-Dimethyl-5-isopropylidene-1,3-dioxane-4,6-dione[11] (**1a**; 100 mg, 0.543 mmol) was pyrolyzed at 400 °C (10^{-3} Torr) in the preparative apparatus, and the products were trapped with methanol as described above. Evaporation of excess methanol gave methyl isopropenylmalonate (**9**) (95%, determined by ^{1}H NMR): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 8.78 (s, 1 H, COOH), 5.14–4.96 (m, 2 H, CH_2), 4.13–4.09 (m, 1 H, CH), 3.73 (s, 3 H, OCH_3), 1.89–1.79 (m, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 172.3 (s, CO), 168.3 (s, CO), 136.8 (br s, C-3 quaternary), 117.6 (br t, ^1J = 159.6 Hz, $\mathit{C}H_2$ vinyl), 58.7 (br d, ^1J = 128.4 Hz, C-2), 52.6 (q, ^1J = 147.8 Hz, OCH_3), 20.7 (br q, ^1J = 128.4 Hz, $C\mathit{C}H_3$). There was no starting material in the sample and no other products were detectable.

Methyl Isopropylidenemalonate (10). The foregoing sample of **9** was allowed to stand in $CDCl_3$ solution at room temperature. NMR spectra were recorded each day to determine the progress of isomerization of **9** to **10**, which was quantitative after 3 days. **10**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.12 (br, 1 H, COOH), 3.78 (s, 3 H, OCH_3), 2.14 (s, 3 H, CH_3), 2.03 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 169.1 (s, CO), 166.6 (s, CO), 157.8 (br s, C-3 quaternary), 123.5 (s, C-2), 51.9 (q, ^1J = 147.8 Hz, OCH_3), 23.7 (br q, ^1J = 128.7 Hz, CH_3), 22.8 (br q, ^1J = 127.9 Hz, CH_3).

Trapping of isopropylideneketene (11) and isopropenylketene (13) with methanol was carried out on the cold end of the 77 K cryostat after establishing the reaction conditions necessary for the selective production of the individual ketenes (see general text). **11** gave methyl isopropylideneacetate, **10**, and **13** gave methyl isopropenylacetate as determined by ^{1}H NMR spectroscopic comparison with authentic samples. At intermediate pyrolysis temperatures where both **11** and **13** were present, mixtures were obtained accordingly. No starting material (**1a**) was detectable by ^{1}H NMR spectroscopy.

2,2-Dimethyl-5-ethylidene-1,3-dioxane-4,6-dione (1b). This compound was prepared previously by a condensation of Meldrum's acid with dimethylformamide dimethylacetal.[12,13] The high toxicity and sensitivity

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toward hydrolysis makes the use of the latter compound undesirable. We have developed a simpler and nontoxic method employing 5-piperidinomethylene Meldrum's acid, which itself is readily obtained in a one-pot reaction[14] between Meldrum's acid, piperidine, and triethyl orthoformate.

Dry ether (9 mL) was added to magnesium turnings (1.08 g, 45 mmol) in a three-necked flask under N_2. Methyl iodide (6.39 g, 45 mmol) dissolved in 5 mL of dry ether was added slowly with stirring. After the reaction had subsided, 2,2-dimethyl-5-(1-piperidinylmethylene)-1,3-dioxane-4,6-dione[14] (8.36 g, 35 mmol) dissolved in 100 mL of dry tetrahydrofuran was added in the course of 20 min, and the resulting mixture was stirred for a further 30 min and then poured into 200 mL of 2 N HCl. Extraction with methylene chloride (4 × 100 mL), drying over $MgSO_4$, filtering, and evaporation of the solvent gave a yellowish oil, which was "sublimed" at 30 °C (10^{-4} Torr) to furnish 5.47 g (92%) of **1b**: mp 58–59 °C (lit.[13] mp 58.5–60 °C); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 8.02 (q, J = 7.5 Hz, 1 H), 2.48 (d, J = 7.5 Hz, 3 H), 1.73 (s, 6 H); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 163.6 (d, C-H vinyl), 161.7 (s, CO), 159.8 (s, CO), 119.2 (s, C-5), 104.8 (s, C-2), 27.7 (q, $(CH_3)_2$), 17.7 (q, CH_3).

Trapping of Carboxy(vinyl)ketene 14 with Methanol. **1b** (100 mg, 0.588 mmol) was pyrolyzed at 400 °C in the preparative apparatus and the product trapped with methanol on the cold finger (see under Apparatus). Excess methanol was distilled in vacuum and the product dried in high vacuum and subjected to NMR analysis: yield 79 mg (94%) of a 1:1 mixture of (*Z*)- and (*E*)-methyl 2-ethylidenemalonate (**16**, **17**). **16**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.79 (s, 1 H, COOH), 7.66 (q, J = 7.4 Hz, 1 H), 3.88 (s, 3 H, OCH_3), 2.31 (d, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 172.4 (s, CO), 166.6 (s, CO), 154.7 (dq, ^1J = 157.4 Hz, ^3J = 6.9 Hz, C-3 vinyl), 124.4 (br s, C-2), 52.8 (q, ^1J = 148.3 Hz, OCH_3), 16.5 (qd, ^1J = 128.9 Hz, ^3J = 1.9 Hz, CH_3). **17**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.74 (s, 1 H, COOH), 7.69 (q, J = 7.4 Hz, 1 H), 3.85 (s, 3 H, OCH_3), 2.12 (d, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 25 MHz) δ 167.1 (s, CO), 166.3 (s, CO), 151.7 (dq, ^1J = 159.2 Hz, ^3J = 7.0 Hz, C-3 vinyl), 126.3 (br s, C-2), 52.4 (q, ^1J = 148.3 Hz, OCH_3), 16.2 (qd, ^1J = 29.0 Hz, ^3J = 2.6 Hz, CH_3); mass spectrum (field desorption) m/z 145 ($[M + 1]^+$, 100%).

Trapping of Ethylideneketene (15) to (*E*)-Crotonanilide (20). 2,2-Dimethyl-5-ethylidene-1,3-dioxane-4,6-dione (**1b**; 100 mg, 0.588 mmol) was pyrolyzed at 600 °C in the preparative apparatus, and the products were trapped with aniline on the cold finger as described above. After the end of the experiment, excess aniline was removed in high vacuum and the product taken up in chloroform and washed three times with 30 mL of 1.5 N HCl and then three times with 30 mL of H_2O. After drying, removal of the solvent in vacuum, and further drying in high vacuum, the white solid residue (77.6 mg, 82%) was identified as (*E*)-crotonanilide (**20**) by IR and ^{1}H NMR comparison with an authentic sample, prepared[15] from (*E*)-crotonyl chloride and aniline and itself verified by IR[16] and ^{1}H NMR spectroscopy. A trace of the *Z* isomer was apparent in the sample of **20** obtained from **15**, but none of the 3-butenoic anilide (**21**). Use of longer contact times (higher pressure) or higher pyrolysis temperature resulted in the formation of **21** as already reported.[7] **20**: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 8.05 (br s, 1 H, NH), 7.66–6.72 (m, 6 H, C_6H_5 + H(C-2)), 5.98 (dq, $^3J_{2,3}$ = 15.0 Hz, $^3J_{3,4}$ = 1.5 Hz, 1 H, H(C-3)), 1.81 (dd, $^3J_{2,4}$ = 6.6 Hz, $^3J_{3,4}$ = 1.5 Hz, 3 H, CH_3).

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Thermochemistry of the "Orthogonal" Butadienes (*Z*,*Z*)-3,4-Dimethylhexa-2,4-diene and 2,3-Di-*tert*-butylbuta-1,3-diene

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Abstract: The "orthogonal" dienes of the title, (*Z*,*Z*)-**1** and **6**, having the planes of their double bonds at a dihedral angle not far from 90°, serve as models for "conjugated" dienes lacking π-electron delocalization and for the transition state for interconversion of antiperiplanar (trans) and synperiplanar (cis or gauche) butadiene. Several effects on properties attributable to their nonplanar conformations are recorded. Structures are assigned to (*Z*)-3-methyl-4-methylenehex-2-ene ((*Z*)-**2**) and (*Z*)- and (*E*)-3,4-dimethylhexa-1,3-diene ((*Z*)-**3**, (*E*)-**3**) by application of the 1,5-dienyl hydrogen shift. The thermochemistries of (*E*,*E*)-**1**, (*E*,*Z*)-**1**, and (*Z*,*Z*)-**1**, the isomers of 3,4-dimethylhexa-2,4-diene (**1**), and of 2,3-di-*tert*-butylbutadiene (**6**) are established by base-catalyzed equilibration and catalytic hydrogenation. Discrepancies between experimental and modeled enthalpies of formation accord with the operation of planarity-demanding, π-electron delocalization.

An enduring interest in butadiene and its family of conjugated dienes has focused on the torsional energy profile, i.e., on change in enthalpy as the dihedral angle between planes of the two double bonds is varied from 0° (trans) to 180° (cis).[1,2] At the experimental and theoretical levels, most recently advanced (and reviewed) by Mui and Grunwald[1b] and Breulet, Lee, and Schaeffer,[2a] respectively, there is now general agreement that the antiperiplanar, trans conformation, long accepted as the global minimum, is separated by a transition state, higher by some 6–7 kcal/mol at a dihedral angle of 80–85°, from a gauche (<180°) or cis (180°) conformation, lying some 2.3–2.5 kcal/mol above trans.[1b,c,2a] The question of whether gauche or cis is the local minimum, if still unresolved, looks to be answered in favor of cis,[1a] or, if gauche, by a very small barrier of ~0.1 kcal/mol.[1c,2a]

At the time the work at Yale was started more than two decades ago, the existence of a trans–cis barrier had not been demonstrated

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