

Ketenylidene-1,4-cyclohexadiene: preparation of a divinylketene and reaction with the aminoxyl radical TEMPO

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Dedicated to Professor Oswald S. Tee on the occasion of his 60th birthday, and in recognition of his contributions to chemistry in Canada

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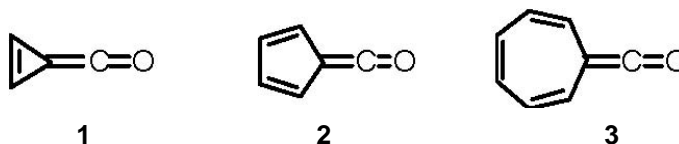
Abstract

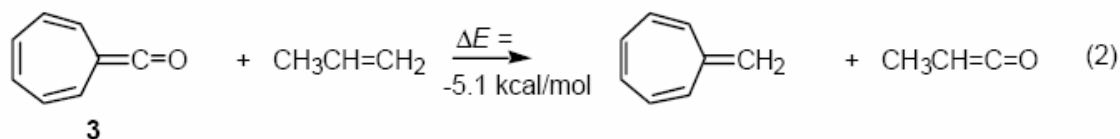
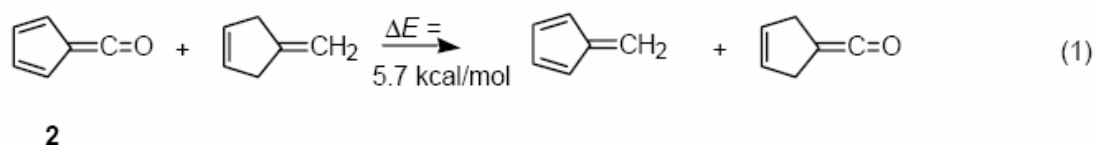
Reaction of 1,4-cyclohexadienyl-3-carbonyl chloride **17** with 1,8-bis(dimethylamino) naphthalene **6** gave the divinylketene ketenylidene-1,4-cyclohexadiene **14** as identified by the IR band at 2101 cm⁻¹. Reaction of **14** with tetramethylpiperidinyloxy (TEMPO, TO•) gives N-2,2,6,6-tetramethylpiperidinyloxy benzoate **18** formed from the radical **19** resulting from TEMPO attack on the carbonyl carbon of **14**.

Keywords: Divinylketene, aminoxyl radical, TEMPO, ketenylidene-1,4-cyclohexadiene

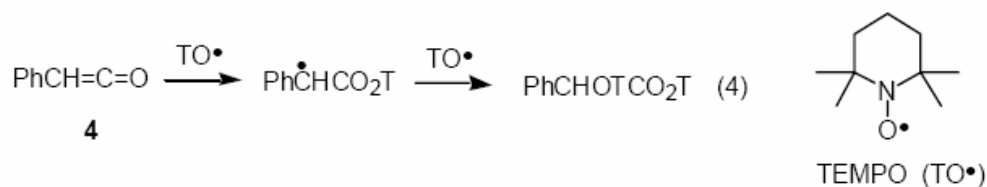
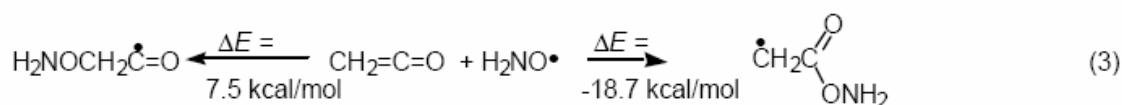
Introduction

In 1992 we reported a computational study of the fulvenones **1-3**.^{1a} On the basis of isodesmic comparisons **1** was found to be destabilized by 17.1 kcal/mol, and as illustrated by the comparison of eq 1 pentafulvenone **2** is stabilized by 5.7 kcal/mol, whereas heptafulvenone **3** is destabilized by 5.1 kcal/mol (eq 2).¹ These effects were attributed¹ to the high electron density at C β of the the ketenyl group, which gives **2** the character of a 6 π -electron aromatic system, whereas **1** has the character of an 4 π -antiaromatic system, and **3** has the character of an 8 π -electron antiaromatic ring.

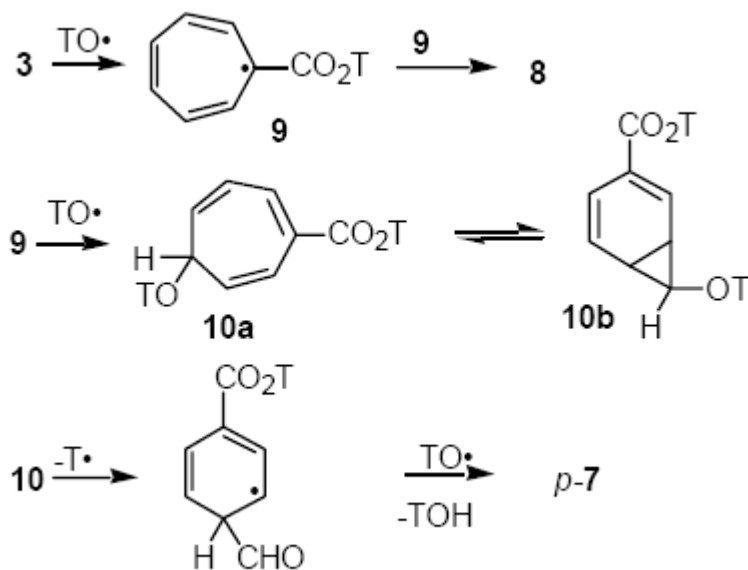
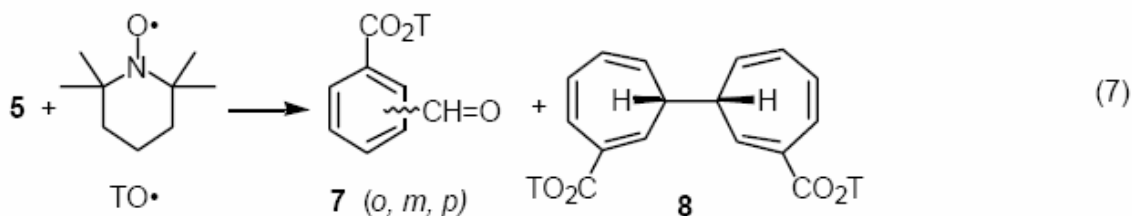
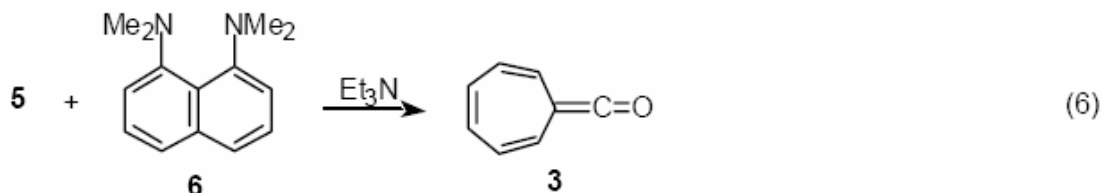
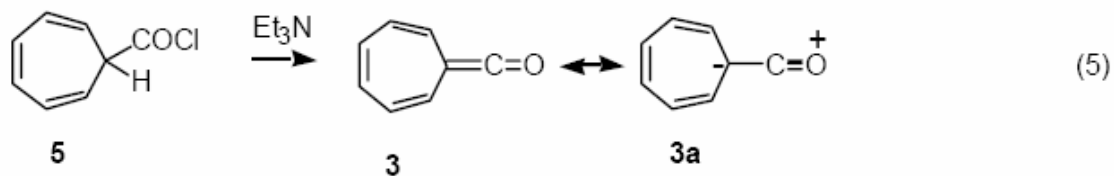




Recently we have undertaken the study of radical reactions of ketenes,² and predicted on the basis of B3LYP/6-31G* calculations that the reaction of H₂NO• with CH₂=C=O at the α-carbon would be exothermic by 18.7 kcal/mol (eq 3).^{2a} This prediction was confirmed experimentally by the discovery that ketenes such as phenylketene **4** undergo facile reaction with the aminoxyl radical tetramethylpiperidinyloxyl (TEMPO) forming 1,2 bis(addition) products (eq 4), or in some cases products resulting from allylic rearrangements, cyclizations, or free radical rearrangements.² These reactions were all interpreted as involving rate limiting attack of TEMPO on the carbonyl carbon as shown in eq 4, and in the case of **4** this was followed by fast capture of the resulting radical by a second TEMPO.^{2b,c}



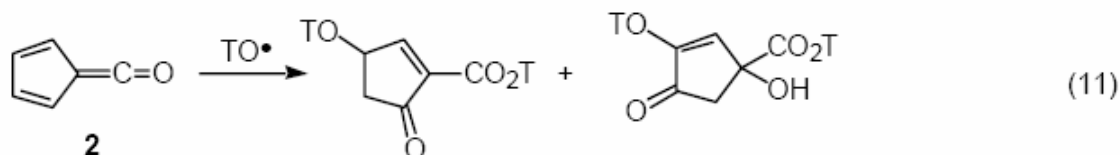
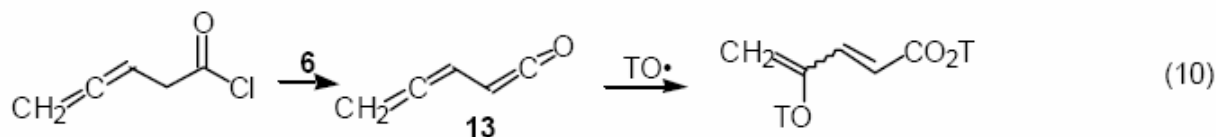
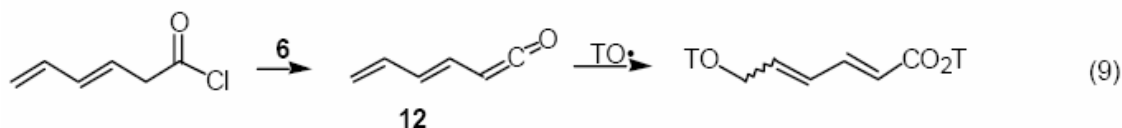
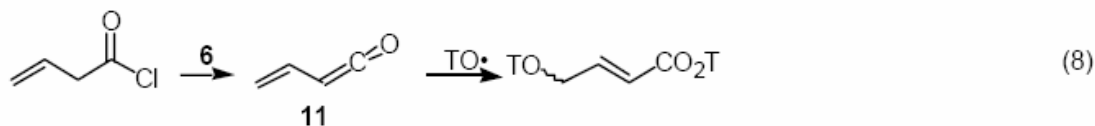
Heptafulvenone **3** had previously^{4a} been generated by the reaction of eq 5, and the structure of **3** was established by formation of characteristic trapping products. To prepare this species for direct observation we utilized new methodology developed by Lectka, et al,^{4b} using 1,8-bis(dimethylamino)naphthalene **6** as a base together with catalytic Et₃N for the dehydrohalogenation of acyl chlorides. This process worked well for the preparation of **3** (eq 6), which displayed an IR band at 2101 cm⁻¹, and reacted with TEMPO to produce the interesting group of products **7** and **8** (eq 7).^{2c} A possible mechanism for this process is shown in Scheme 1.



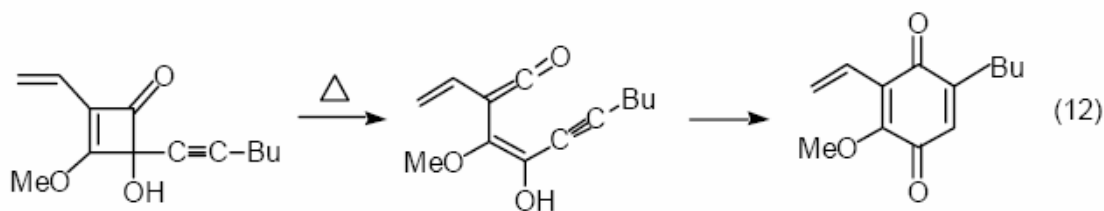
Scheme 1

This study of alkenylketenes was extended to the compounds **11-13**, all of which were identified by IR, and gave interesting reactions with TEMPO (eq 8-10).^{2e} The α -hydrogens of each of these acyl chlorides are quite acidic and the generation of these ketenes was facile. In addition pentafulvenone **2** was generated by Wolff rearrangement and directly observed by IR,

and reacted with TEMPO forming surprising products (eq 11).^{2g}



Because of the success of these studies of fulvenones and alkenylketenes it appeared desirable to extend the studies to divinylketenes. These have recently been the subject of experimental studies in which substituted divinylketenes have been generated as unobserved intermediates by the thermolysis of 2-vinylcyclobutenones (eq 12).³ However such divinylketenes have not been directly observed.



Previously^{1a} we have calculated the structures and energies of divinylketenes **14** and **15** at the HF/6-31G**/HF/6-31G* level, and these calculations permit the derivation of the isodesmic relations in eqs 13-17. These comparisons reveal that vinyl groups and alkyl groups have equivalent effects on the stability of ketenes (eq 14-16), but that ketenylidene-1,4-cyclohexadiene **14** is destabilized relative to divinylketene by 3.8 kcal/mol (eq 13), and by 7.9 kcal/mol relative to pentafulvenone **2** (eq 17).

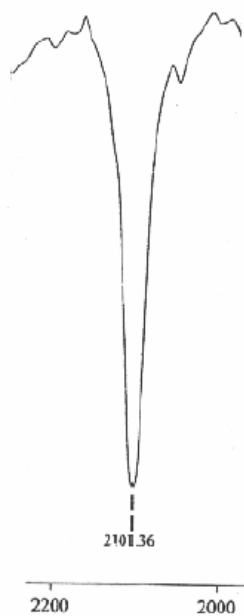
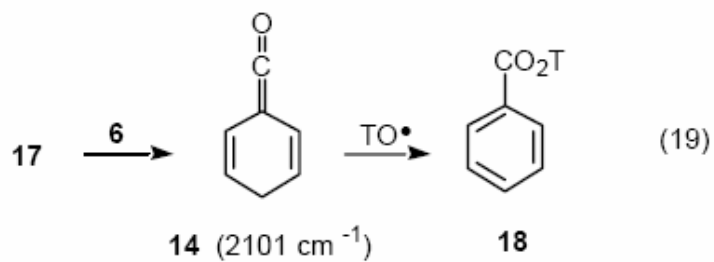
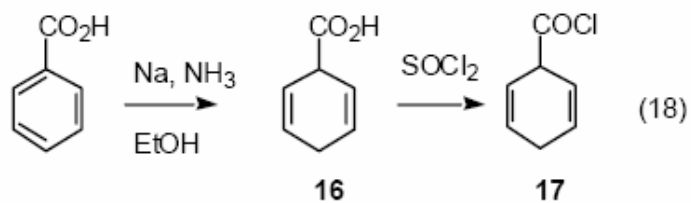
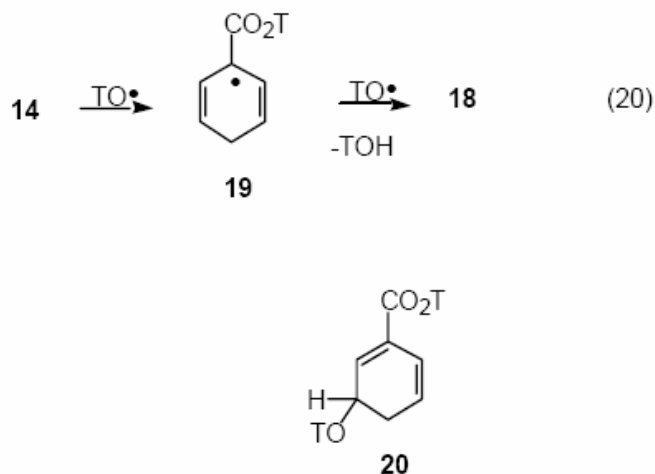


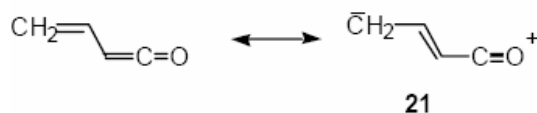
Fig 1. IR Spectrum of **14**

A possible route to **18** is shown in eq 20. Alternatively TEMPO could add to the intermediate radical **19** forming **20** which undergoes loss of TOH.



Thus the divinylketene **14** is readily available by the route of eqs 18 and 19, and reacts with TEMPO as shown in eq 20. Because of its multiple functionality **14** may also be expected to react readily with nucleophiles, electrophiles, and cycloaddition reagents, and to lead to interesting and useful products.

The destabilization of **14** relative to divinylketene **15** as indicated by eq 13 is also striking, and merits further consideration. In the absence of further information the analysis of this problem is highly speculative, but it may be noted that vinylketene has a significant conjugative interaction as depicted in **21**, as evidenced by its dipole moment^{6a} and ¹³C NMR spectrum.^{6b} The constrained divinylketene **14** is cross-conjugated, and the second vinyl group might be destabilizing in this geometry, whereas in the acyclic divinylketene **15** it might be possible to avoid this problem. However further work would be required to resolve this question.



Experimental Section

General Procedures. Reactions were carried out under an atmosphere of argon or nitrogen. ¹H NMR spectra were obtained at 400 MHz (Varian Unity instrument). ¹³C NMR spectra were obtained at 125 MHz (Varian Unity). IR spectra were obtained on a Perkin-Elmer FT-IR Spectrum 1000 spectrometer. Chromatography was carried out using silica gel.

Preparation of 3-ketenylidene-1,4-cyclohexadiene (14). To cyclohexadienyl carbonyl chloride (**15**)^{5b} (100 mg, 0.706 mmol) and **6** (151 mg, 0.706 mmol) in 6 mL toluene at $-78\text{ }^\circ\text{C}$ was added Et₃N (10 μL), with formation of precipitate and yellow color. An IR band at 2101 cm^{-1} for **14** was observed. TEMPO (220 mg, 1.41 mmol) in 1 mL toluene was added and the solution was

stirred overnight at 25 °C, filtered and concentrated. After acidification with 1N HCl the residue was extracted with ether, which was washed, dried, and concentrated. Chromatography (25% EtOAc/hexane) gave **18**^{5c} as an oil (120 mg, 46 mmol, 65%). ¹H NMR (CDCl₃) δ 1.12 (s, 6, 2CH₃), 1.27 (s, 6, 2CH₃), (1.4-1.8, m, 6, 3 CH₂), 7.46 (t, 2, *J* = 7.8 Hz), 7.6 (t, 1, *J* = 8.0 Hz), (t, 2, *J* = 8.0 Hz). ¹³C NMR (CDCl₃) δ 17.2, 21.1, 32.0, 39.2, 61.0, 128.7, 129.8, 133.1, 166.4 (one signal not resolved). IR (CDCl₃) 1744 cm⁻¹. EIMS *m/z* 261 (9, M⁺), 246. HREIMS *m/z* calcd for C₁₆H₂₃NO² 261.1735, found 261.1729.

Acknowledgements

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