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 tetramethylpiperidinyloxyl (TEMPO, TO•) gives N-2,2,6,6-tetramethylpiperidinyl 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. 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). These effects were attributed to the high electron density at Cβ of 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, 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). This prediction was confirmed experimentally by the discovery that ketenes such as phenylketene 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. 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 this was followed by fast capture of the resulting radical by a second TEMPO.

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

\[
\begin{align*}
\text{CH} = \text{C} = \text{O} & \xrightarrow{6} \text{CH} = \text{C} = \text{C} = \text{O} \\
& \xrightarrow{\text{TO}^*} \text{TO}_2 \text{C} = \text{O}_2 \text{T} \\
\end{align*}
\]

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). However such divinylketenes have not been directly observed.

Previously 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).
Results and Discussion

These previous studies indicate that the generation, direct observation, and reaction of divinylketenes would be of great interest. We have therefore directed our efforts to the study of 14.

Birch reduction of benzoic acid provided a convenient route to cyclo-1,4-hexadiene-3-carboxylic acid (16),5a which was converted to the acid chloride 175b with SOCl₂ (eq 18). Reaction of 17 with 6 and catalytic Et₃N in toluene at –78 °C gave immediate formation of a yellow color with a precipitate, and an IR band at 2101 cm⁻¹ attributed to the ketene 14 was observed (eq 19). Addition of TEMPO led to the formation of N-2,2,6,6-tetramethylpiperidinyl benzoate (18),5c identified by its spectral properties and by comparison to an authentic sample prepared from benzoyl chloride and tetramethylpiperidinol.5d
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 $^{13}$C 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. $^1$H NMR spectra were obtained at 400 MHz (Varian Unity instrument). $^{13}$C 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 $–78 \, ^\circ\text{C}$ was added Et$_3$N (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 18c 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. EI MS m/z 261 (9, M⁺), 246. HREIMS m/z calcd for C16H23NO2 261.1735, found 261.1729.

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References and Notes


