potentials for addition of electrons to the heterocyclic ligand, even though the presence of a metal ion at N_5 and the sterically imposed bending of the isoalloxazine ring would be expected to increase the potential for addition of at least the first electron.

Finally, this and related work[25] now make it feasible to selectively label either the isoalloxazine or adenine rings of the FAD coenzyme by addition of Ru(II) under strictly anaerobic or redox catalytic conditions, respectively. It is hoped that coordination of Ru^{103} or Ru^{97} to FAD and related coenzymes at either of these sites will yield radiopharmaceuticals which may be of use as organ-imaging agents for diagnostic purposes.[41]

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Thermochemistry and Generation of Vinylketene

Sir:

Neutral vinylketene has so far eluded observation, although its possible formation as a red compound, stable up to −160 °C, was reported by Conia et al.[1] in some flash thermolysis studies of spiro[2.3]hexan-4-ones. Vinylketene has been postulated as an intermediate in [2 + 2] cycloaddition reactions of cyclopentadiene with the dehydrochlorination product of *trans*-2-butenoyl and 3-butenoyl chloride[2] and in other related systems.[3]

We report here that vinylketene is obtained in high yield from the gas-phase thermal decomposition of the en-yne ether[4,5] $CH_2{=}CHC{\equiv}COCH_2CH_3$ (I).

$$\mathrm{I} \rightarrow \underset{\mathrm{II}}{C_4H_4O} + C_2H_4$$

Ionized vinylketene has been proposed[6] as resulting from the electron impact induced losses of (i) H_2O from crotonic acid (and some of its isomers), (ii) CH_3OH from methyl crotonate, and (iii) C_2H_4 from cyclohexen-2-one. The latter reaction had an appearance energy (AE) which yielded a heat of formation, $\Delta H_f\,(C_4H_4O)^{+\cdot} = 194 \pm 1$ kcal mol^{-1}, a value close to but significantly lower than that of the most stable isomer[7] (furan)$^{+\cdot}$, $\Delta H_f = 197$ kcal mol^{-1}. However, the metastable peak characteristics of the reacting and nonreacting $(C_4H_4O)^{+\cdot}$ ions produced by i, ii, and iii (see Table I) show that they cannot have the structure of (furan)$^{+\cdot}$.

The ionic heat of formation of II and the metastable characteristics of ionized II are consistent with the structural assignment given to $[C_4H_4O]^{+\cdot}$ ions derived from i, ii, and iii. Ethoxyethyne readily thermally decomposes to yield ketene and C_2H_4.[11] A similar 1,5-hydrogen shift in I would produce vinylketene and C_2H_4. When I is introduced into the ion source of an AEI-GEC MS902S mass spectrometer via a heated glass inlet system ($T = 100$ °C), the highest mass in the resulting 70-eV mass spectrum has m/z 68, $[C_4H_4O]^{+\cdot}$ (67%). Prominent ions are observed at m/z 42, $[CH_2CO]^{+\cdot}$ (14%); m/z 40, $[C_3H_4]^{+\cdot}$ (37%); m/z 39, $[C_3H_3]^{+}$ (78%); m/z 38, $[C_3H_2]^{+\cdot}$ (17%); m/z 37, $[C_3H]^{+}$ (11%); m/z 28, $[C_2H_4]^{+\cdot}$ (100%); m/z

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Table I. Mass Spectral Characteristics of $[C_4H_4O]^{+\cdot}$ Ions

	metastable peaks[a]				partial 70-eV collisional activation spectra[b] (major peaks)		
	loss of CO		rel abundances				
precursor molecule	$T_{0.5}$[c]	T_{av}[c]	m/z 40	m/z 42	m/z 39	m/z 40	m/z 42
furan	17	87	100	19	100	17	12
cis/trans-crotonic acid	25	65	100	5	100	49	24
3-butenoic acid	25	65	100	5	100	53	26
cyclopropanecarboxylic acid	25	65	100	5	100	49	24
methyl crotonate	25	65	100	5	100	67	25
cyclohexen-2-one	33[d]	68	100	6.5	100	48	22
vinylketene (II)	22	60	100	5	100	45	21

[a] Measured with an AEI-GEC MS902S mass spectrometer under conditions of good energy resolution.[8] [b] Measured with a VG-Micromass ZAB 2F mass spectrometer. Acceleration voltage, 8000 V; collision gas, He. Peaks arising from unimolecular processes were separated from collision-induced processes by means of a voltage (−320 V) applied to the collision gas cell. Further experimental details are given elsewhere.[9] [c] Kinetic energy releases (millielectronvolts) evaluated from the metastable peak widths at half height ($T_{0.5}$) and T_{av} from the distribution of released energies.[10] [d] The larger energy releases observed for this compound are due to a contribution from another $[C_4H_4O]^{+\cdot}$ ion, [cyclobutenone]$^{+\cdot}$ ($T_{0.5}$ = 38 meV, T_{av} = 77 meV, which can be generated by loss of CO from 4-cyclopentene-1,3-dione).

27, $[C_2H_3]^+$ (52%); *m/z* 26, $[C_2H_2]^{+\cdot}$ (48%); *m/z* 25 $[C_2H]^+$ (9%). In marked contrast, the 70-eV mass spectrum of I, measured in an instrument wholly at room temperature,[12] showed an intense molecular ion for I, *m/z* 96, and major peaks at *m/z* 67, $[C_4H_3O]^+$, and *m/e* 29, $[C_2H_5]^+$, in addition to those at *m/z* 68, 42, 40, 39, 27, and 26.

The low energy region of the He(I) photoelectron (PE) spectrum of I, measured at room temperature, contained a diffuse peak centered at 8.67 eV. This disappeared when the sample inlet system was heated to ~100 °C, to be replaced by a sharp peak at a lower energy, 8.29 ± 0.05 eV, and another at 10.23 ± 0.05 eV. The AE of *m/e* 68, $[C_4H_4O]^{+\cdot}$, measured with energy selected electrons and now using a pyrolytic gas inlet system[12] (T range, 350-650 °C) was 8.34 ± 0.05 eV. Within experimental error, this is the same value as the ionization energy (IE) obtained from the PE spectrum; this result further supports the conclusion that a *molecular* species II, C_4H_4O, is being thermally generated from I. The magnitude of the IE for this C_4H_4O molecule is consistent with that for a conjugated ketene (cf. IE (ketene) = 9.6 eV,[7] IE (phenylketene) = 8.17 eV[13]). Furthermore, IE values for other C_4H_4O isomers are significantly higher, e.g., IE (furan) = 8.88 eV,[7] IE (methylcyclopropenone) = 9.28 eV,[6] IE (cyclobutenone) (estimated value) = 9.3 eV,[6] IE (but-2-ynal and but-3-yn-2-one) = 10.28 eV (HE(I) PE spectra, this work). These data effectively rule out C_4H_4O structures for II other than vinylketene and possibly its double-bond isomer buta-1,2-dienone. ΔH_f for vinylketene molecular ion would be 195 ± 1 kcal mol^{-1} (ΔH_f (vinylketene) = +4 kcal mol^{-1}, estimated from ΔH_f (CH_2CO) = −14.6 kcal mol^{-1},[7] ΔH_f ($CH_2{=}C{=}CH_2$) = +45.9 kcal mol^{-1},[7] ΔH_f ($CH_2{=}CHCH{=}C{=}CH_2$ = +64.9 kcal mol^{-1} [14]) in agreement with ΔH_f ($[C_4H_4O]^{+\cdot}$) from cyclohexen-2-one,[6] 194 ± 1 kcal mol^{-1}. Note the close similarity between the mass spectral characteristics for $[C_4H_4O]^{+\cdot}$ derived from I, from cyclohexen-2-one, and from other species (see Table I) whose fragmentations have been proposed to generate [vinylketene]$^{+\cdot}$. The above estimated value for ΔH_f (vinylketene) is supported by the AE for $[C_3H_4]^{+\cdot}$ derived from II, 10.36 ± 0.05 eV. This value combined with ΔH_f (CO) = −26.4 kcal mol^{-1} [7] and ΔH_f ($[CH_2{=}C{=}CH_2]^{+\cdot}$) = 269 kcal mol^{-1} [7] also gives ΔH_f (C_4H_4O) = +4 kcal mol^{-1}, in good agreement with the above estimate. Similarly, comparing ΔH_f ($CH_3CH{=}C{=}C{=}CH_2$) = +73.2 kcal mol^{-1} [14] with the ΔH_f data for ketene and allene, leads to ΔH_f (buta-1,2-dienone) = +13 kcal mol^{-1}. Such a heat of formation makes this molecular species quite incompatible with the above observations and so II can indeed confidently be identified as vinylketene. It is a relatively stable species in gas phase; for example, although samples prepared in the heated MS902 inlet system initially gave a mass spectrum characteristic of I, ions at *m/z* 96, 67, etc., quickly disappeared leaving a time-invarient mass spectrum[15] of II as reported above.

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Stereocontrolled Synthesis of the Prelog-Djerassi Lactone

Sir:

The Prelog-Djerassi lactone (**1**) is a key degradation product of the antibiotic methymycin,[1] which retains the configuration[2] of the four chiral centers present in the segment comprising

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