2-Cyano(2-pyridyl)ketene

Carsten Plüg,[a] Xuan Ye,[a] Arvid Kuhn,[a] and Curt Wentrup*[a]

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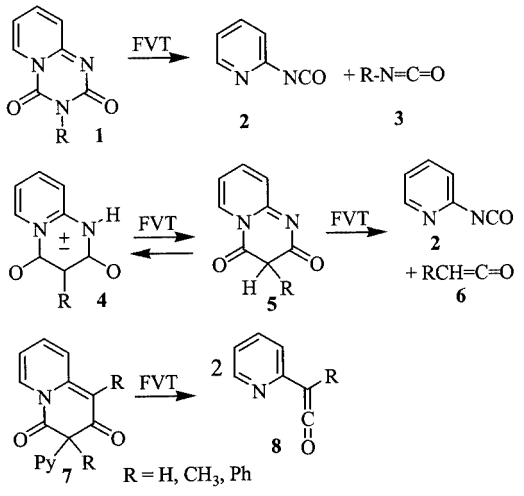
Flash vacuum thermolysis of quinolizinones is a new way of generating ketenes. The title ketene is obtained from 1-cyano-2-hydroxyquinolizine-4-one and characterized by its Ar matrix infrared spectrum.

Introduction

In recent papers we have described the cycloreversion of pyrido[1,2-*a*][1,3,5]triazinediones **1** to two isocyanates, **2** and **3**,[1,2] the cycloreversion of mesoionic pyridopyrimidinylium olates **4** to 2-pyridyl isocyanate **2** and ketenes **6**, taking place via the higher energy tautomeric pyridopyrimidinediones **5**,[1] and the cleavage of quinolizine-2,4-diones **7** to two molecules of 2-pyridylketenes **8**.[3] All these reactions take place under the conditions of flash vacuum thermolysis (FVT), and the products, being unstable, were characterised by matrix isolation IR spectroscopy in conjunction with theoretical calculations of the spectra.



It was therefore logical to try to apply the latter reaction to the preparation of novel ketenes, and we now report the successful generation of 2-cyano(2-pyridyl)ketene (**11**) by FVT of the quinolizine-4-one **9**.

Results and Discussion

1-Cyano-2-hydroxyquinolizine-4-one (**9**) was prepared according to the procedure of Kappe.[4] It exists in the enol form in the solid state and in DMSO solution. There is only one set of signals in the ^{1}H and ^{13}C NMR spectra, the OH proton appears at δ = 12.15 ppm in [D$_6$]DMSO solution, and there is no signal corresponding to the methylene group in the dione tautomer **10**. However, the emergence of a strong C=O stretching band at 1717 cm^{-1} (compare compounds **7**[3b]) in the Ar matrix-isolated material indicates that the compound exists (partially) in the dione form **10** in the gas phase, and this tautomer is therefore expected to be populated on FVT.[1,3a] FVT of **9** at 770 °C with co-condensation of the thermolysis product with Ar to form a matrix at 7 K resulted in the IR spectrum shown in Figure 1. Unsubstituted ketene **12** is clearly produced, and all the bands due to this compound, marked with a 'k' in the figure, match the literature values[5] within 1−3 cm^{-1}.

The IR spectra of the *s*-*Z* and *s*-*E* forms of 2-cyano(2-pyridyl)ketene (**11**) were calculated using the density functional method at the B3LYP/6-31G* level.[6] As we have found in other cases,[3] there is excellent agreement between the experimental spectrum and the calculation for the *s*-*Z* isomer. The latter (*s*-*Z*-**11**; structure shown) is predicted at the same level of theory to be 4.3 kcal/mol more stable than *s*-*E*-**11**, and the *s*-*Z* forms of 2-pyridylketenes are also predicted to be of lower energy for other substituents (H, Me, MeO, Ph in place of CN).[3,7] These calculations also predict that the main ketene bands of the *s*-*Z* isomers appear at higher wavenumbers (by 10−12 cm^{-1}) than for the *s*-*E* isomers. In the case of **11**, the values are 2149 cm^{-1} (*s*-*Z*-**11**) and 2135 cm^{-1} (*s*-*E*-**11**). Inspection of Figure 1 reveals that all the calculated bands for *s*-*Z*-**11** are matched in the experimental spectrum, whereas the agreement is poorer for the *s*-*E* form. It cannot be excluded, however, that a minor amount of the *s*-*E* form is present.

Because ketenes are of substantial current interest in synthetic and mechanistic chemistry,[8] new methods for their

[a] Chemistry Department, The University of Queensland, Brisbane, Qld 4072, Australia
E-mail: wentrup@mailbox.uq.edu.au

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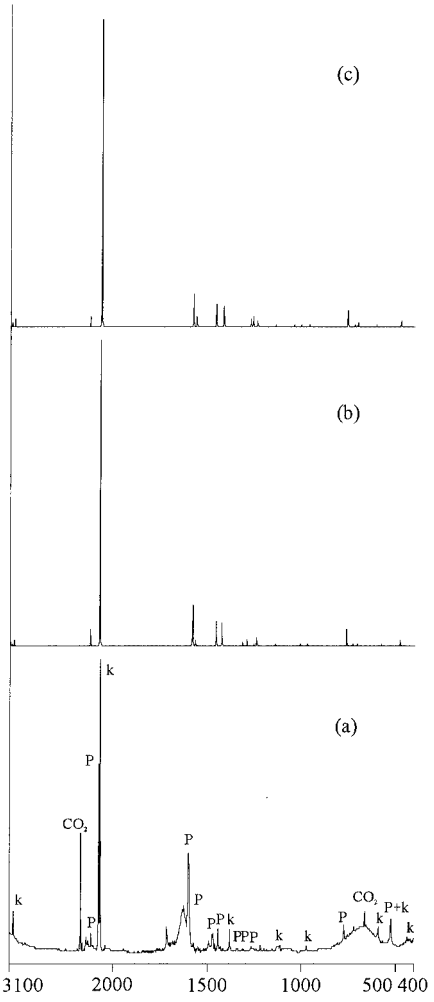
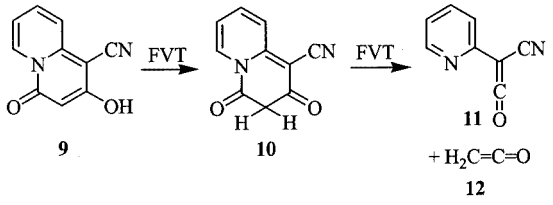


Figure 1. IR spectra of **11**: (a) experimental spectrum [FVT of **10** at 770 °C/10^{-5} mbar; spectrum recorded in Ar matrix at 7 K; P = pyridyl(cyano)ketene **11**, k = ketene **12**]; (b) calculated spectrum of *s*-*Z*-**11**; (c) calculated spectrum of *s*-*E*-**11** (B3LYP/6-31G*; scaling factor 0.9613)



preparation are important. Cyanoketenes[9] and alkoxycarbonylketenes[10] are highly reactive species that cannot be isolated under conventional reaction conditions. Alkyl(cyano)ketenes are more stable; in particular, *tert*-alkyl substituents provide steric protection and allow the spectroscopic observation of these ketenes in solution,[11] but neat cyano(methyl)ketene is only stable until ca. 120 K in the presence of 3,5-dimethylpyrazole.[12] The present work presents a new way of generating reactive ketenes and offers the possibility of producing a variety of 2-pyridylketenes by FVT of appropriately substituted quinolizinones.

Experimental Section

The apparatus used for FVT and matrix isolation has been described previously.[3a,13] Compound **9**[4] has the following properties: ^{1}H NMR ([D$_6$]DMSO): δ = 5.81 (s, 1 H), 7.23 (t, 1 H), 7.73 (d, 1 H), 7.82 (t, 1 H), 8.95 (d, 1 H), 12.15 (br. s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 76.4 (Cq), 90.7 (CH), 115.3 (Cq), 115.5 (CH), 121.5 (CH), 128.7 (CH), 136.6 (CH), 146.2 (Cq), 157.4 (Cq), 166.5 (Cq) ppm (the multiplicities are based on a DEPT experiment). MS: *m*/*z* (%) = 186 (100). IR (KBr): $\tilde{\nu}$ = 3500−2300 (m, br), 2219 (s), 1692 (s), 1637 (s), 1595 (vs) cm^{-1}. IR (Ar, 7 K): $\tilde{\nu}$ = 3572 (m), 2212 (m), 1717 (vs), 1624 (s), 1594 (s), 1493 (s), 1461(m), 1217 (m) cm^{-1}.

Compound **9** was sublimed into the FVT apparatus at 170 °C. Thermolysis to ketenes **11** and **12** commenced at ca. 600 °C, and the optimal conditions were 770 °C at 10^{-5} mbar. The FVT product was condensed at 20 K together with Ar at a rate of 5 mbar/minute in the course of 20 minutes, and IR spectra were recorded at 7 K. Data for ketene: found 3063, 2141, 2085, 1945, 1380, 1123, 1113, 973, 613, 590, 524, 436 cm^{-1} {ref.:[5] 3062, 2142, 2085, 1947, 1381, 1126, 1115, 974, 612, 591, 525, 438 cm^{-1}}. For direct comparison, a sample of ketene was also produced by FVT of ethoxyacetylene.[14] Data for ketene **11**: 2232, 2155, 1600, 1595, 1469, 1442, 1339, 1306, 1266, 771, 524 cm^{-1}.

Supporting information for this article is available (see footnote on the first page of this article): B3LYP/6-31G* calculations of Cartesian coordinates, absolute energies and IR spectra of ketenes *s*-*Z*-**11** and *s*-*E*-**11**.

Acknowledgments

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