

Methoxy(2-pyridyl)ketene[†]

Heidi Gade Andersen, Pawel Bednarek and Curt Wentrup*

Department of Chemistry, School of Molecular and Microbial Sciences, University of Queensland, Brisbane, Queensland 4072, Australia

Received 1 October 2002; revised 15 October 2002; accepted 15 January 2003

epoc ABSTRACT: Matrix photolysis of 3-methoxycarbonyl-1,2,3-triazolo[1,5-*a*]pyridine (**12**) affords *s-E*-2-pyridylketene (**4**), but flash vacuum thermolysis of **12** gives methoxy(2-pyridyl)ketene (**15**), predominantly in the *s-Z* conformation. Matrix photolysis of **15** affords 2-acetylpyridine. Copyright © 2003 John Wiley & Sons, Ltd. Additional material for this paper is available from the epoc website at <http://www.wiley.com/epoc>

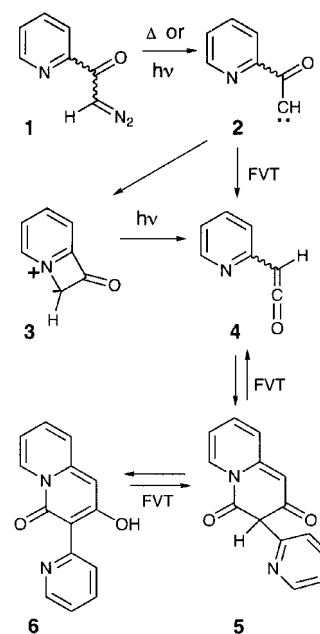
KEYWORDS: ketenes; carbenes; matrix isolation; photolysis; flash vacuum thermolysis

INTRODUCTION

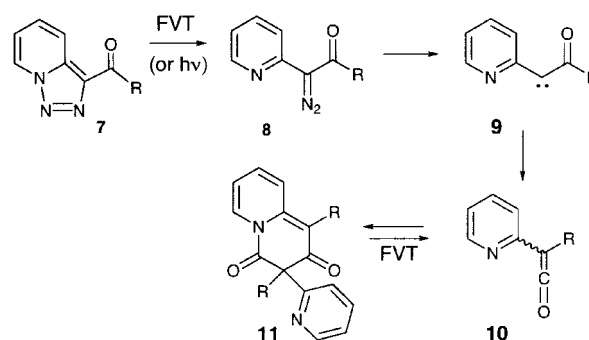
We have demonstrated recently that the photolysis of matrix isolated 2-diazoacetylpyridine (**1**) leads to the formation of the ylide **3** resulting from an interaction between the putative carbene **2** and the pyridine lone pair (Scheme 1).¹ The ylide is photochemically converted into the ketene **4**, predominantly in the *s-E* form. Flash vacuum thermolysis (FVT) of **1** gives only the ketene, this time predominantly in the *s-Z* form. The *s-E* and *s-Z* ketenes can be interconverted photochemically. Under preparative reaction conditions, ketene **4** dimerizes to 2-hydroxyquinolizin-4-one (**6**), and this reaction is reversible on FVT, regenerating the *s-Z* ketene. The dimerization and dedimerization reactions presumably take place via an unobserved quinolizinedione **5** in which the quinolizine moiety is non-aromatic. We have also reported the isolation of 3,3-disubstituted quinolizinediones of type **11**, formed by reversible dimerization of 2-pyridylketenes **10**.² The latter compounds were obtained by FVT of 3-acyl-1,2,3-triazolo[1,5-*a*]pyridines **7**, presumably via diazo compound **8** and carbene **9** (Scheme 2). The (2-pyridyl)ketenes **10** (R = CH₃ or Ph) are directly observable by infrared spectroscopy in low-temperature matrices. FVT of **11** regenerates the ketenes **10**. This dedimerization reaction has also been utilized in the synthesis of cyano(2-pyridyl)ketene.³

Photolysis of the triazolopyridines was found to be a much less efficient method of producing the 2-pyridylketenes, and substantial amounts of byproducts were

formed.² However, the matrix photolysis of 3-methoxycarbonyl-1,2,3-triazolopyridine (**12**) has been reported to yield methoxy(2-pyridyl)ketene.⁴ Our investigations



Scheme 1



Scheme 2

*Correspondence to: C. Wentrup, Department of Chemistry, School of Molecular and Microbial Sciences, University of Queensland, Brisbane, Queensland 4072, Australia.
E-mail: wentrup@uq.edu.au

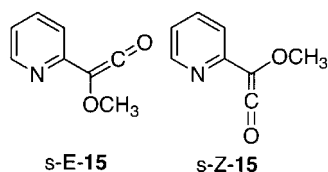
[†]Dedicated to Professor Shinjiro Kobayashi, IFOC, Kyushu University, Long-time Organizer of KISPOC Conferences.
Contract/grant sponsor: Australian Research Council.

reveal that a different ketene is in fact formed on photolysis, but FVT affords the desired methoxy(2-pyridyl)ketene.

RESULTS AND DISCUSSION

Matrix photolysis of triazole **12**. Formation of 2-pyridylketene

3-Methoxycarbonyl-1,2,3-triazolopyridine (**12**) was matrix isolated in Ar at 7 K and irradiated at 254 or 313 nm, or by using the unfiltered light of a high-pressure Hg–Xe lamp. In each case the following new bands appeared in the IR spectrum: 2283 w, 2124 s, 1737 w, 1662 m, 1592 m, 1567 w, 1484 m, 1472 m, 1439 m, 1410 w, 1384 w, 1368 w, 1286 w, 1214 m, 1198 w, 1150 w, 1055 w and 775 w cm^{-1} . Analogy with the photolyses of **1** and **7** would predict the *s-E* ketene **15** as the major product (we define *s-E* and *s-Z* to conform with the other substituted ketenes in this series as shown in the formulae).



Form A

However, the IR spectrum of the observed photoproduct matched very poorly with the calculated IR spectra of both the *s-E* and *s-Z* ketenes (see Tables 1 and 2). Moreover, calculations at the B3LYP/6–31G* level predict that the ketene vibration will be at lower wavenumber in the *s-E* (2096 cm^{-1}) than in the *s-Z* isomer (2106 cm^{-1}). As shown below, we are able to generate the *s-Z* isomer by FVT, and it absorbs at 2114 cm^{-1} in the experimental Ar matrix spectrum (Fig. 1 and Table 2). Therefore, the observed species at 2124 cm^{-1} cannot be the *s-E* isomer of the expected ketene **15**. There was also very poor agreement with the calculated IR spectrum of the methoxy-substituted ylide analogous to **3**, which is predicted to have major absorptions at 1781 and 1535 cm^{-1} .

The presence of a strong band at 2124 cm^{-1} clearly shows that the photoproduct is a ketene. But which ketene? In fact, comparison with the spectra previously obtained in our laboratory¹ unambiguously identified the photoproduct as very largely *s-E*-2-pyridylketene (**4**). As in the previous study,¹ further photolysis caused *E-Z* isomerization, so that after 2 h of broadband irradiation equal intensities of the absorption bands of *s-E-4* (2124 cm^{-1}) and *s-Z-4* (2132 cm^{-1}) were obtained. Our experimental spectrum of *s-E-4* agrees well with that reported by Tomioka *et al.*,⁴ and we conclude that the same species, *s-E-4*, and not **15**, was obtained.

Table 1. IR spectroscopic data (wavenumbers ν , cm^{-1}) for the product of matrix photolysis of **12** compared with the data for *s-E-4*

Argon 10 K	
Experimental data	<i>s-E</i> -2-pyridylketene, <i>s-E-4</i>
2124 (s)	2123 (vs)
1592 (m)	1590 (s)
1567 (w)	1567 (s)
1484 (m)	1484 (s)
1439 (m)	1433 (s)
1384 (w)	1387 (w)
1286 (w)	1292 (w)
1214 (m)	1209 (m)
1150 (w)	1156 (m)
1055 (w)	1057 (w)
775 (w)	773 (m)

It is likely that **4** is formed from **12** via the diazo compound **13** and carbene **14** (Scheme 3). The carbene formally fragments to *s-E-4* and formaldehyde **16**. Indeed, formaldehyde was identified in the matrix spectrum by bands at 2870 w, 2805 w, 1737 m, and 1164 w cm^{-1} .

The mechanism of this fragmentation has been

Table 2. Experimental and calculated IR data for *s-Z-15* and *s-E-15*

Ar, 7 K ν^a	Calc <i>s-Z-15</i>		Calc <i>s-E-15</i>	
	$\nu^{a,b}$	I^c	$\nu^{a,b}$	I^c
3087 w	3093	3	3094	3
2941 w	2981	4	2938	7
2909 w	2918	5	2889	8
2114 vs	2114	100		
2097 w			2091	100
1588 s	1583	18	1585	16
1572 w	1562	2	1557	5
1477 w	1470	1	1473	3
1468 w	1460	9	1462	12
1452 w	1456	2	1457	1
1445 w	1438	1	1447	1
1439 w	1426	6	1417	8
1386 w	1336	1	1338	6
1311 w	1295	4	1291	12
1272 w	1265	1	1271	4
1258 w	1236	6	1261	6
1147 w	1135	1	1145	2
1103 w	1081	1	1114	19
1077 w	1061	7		
1072 w			1079	1
1039 w	1027	1	1034	2
992 w	969	1	968	2
972 w	962	1	961	1
774 w	762	4	755	6

^a Wavenumbers in cm^{-1} .

^b Calculated frequencies by B3LYP/6–31G*, scaled by a factor of 0.9613.

^c Intensities relative to the most intense peak as 100%; absolute intensity of the 2114 cm^{-1} band 878 km mol^{-1} ; absolute intensity of the 2091 cm^{-1} band 692 km mol^{-1} .

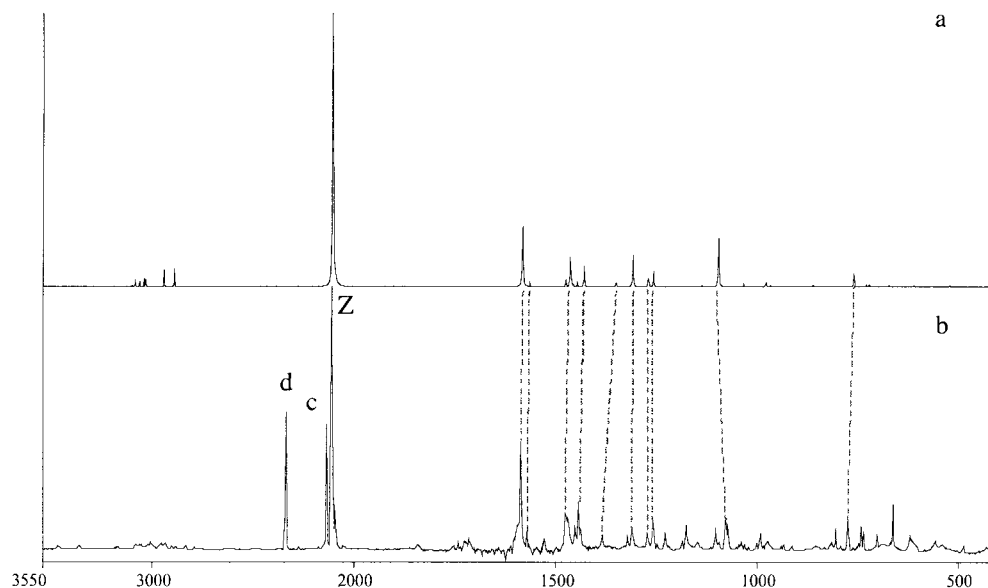
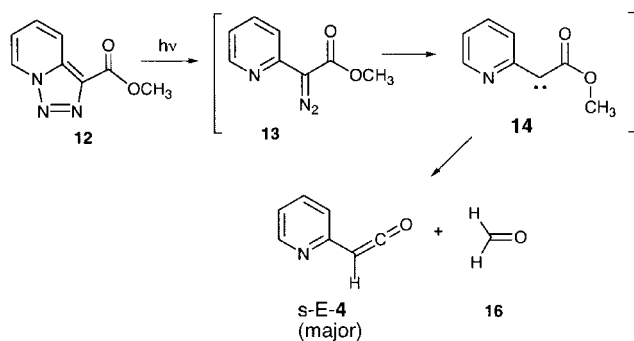
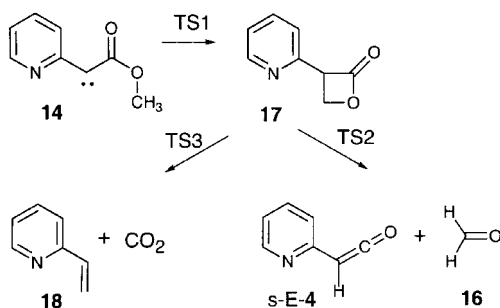


Figure 1. (a) Calculated IR spectrum of *s*-*Z*-**15** (B3LYP/6–31G*, scaled by 0.9613); (b) experimental IR spectrum (Ar, 7 K) from the FVT of **12** at 500°C. Z = *s*-*Z*-**15** (2114 cm⁻¹); c = carbon monoxide (2139 cm⁻¹); d = carbon dioxide (2345 cm⁻¹). Ordinate: absorbance (arbitrary units)

investigated theoretically at the B3LYP/6–31G* level. The closed-shell singlet carbene **14** inserts into a C–H bond of the methyl group via transition state TS1 to give a β -lactone **17** (Scheme 4). This can in principle fragment in two different ways, to the observed *s*-*E*-**4** and formaldehyde **16**, or to 2-vinylpyridine and CO₂. However, only traces of CO₂ were formed in this reaction, and it cannot be excluded that they are due to



Scheme 3



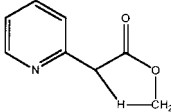
Scheme 4

traces of atmospheric CO₂. Moreover, no prominent bands in the IR spectrum can be assigned to 2-vinylpyridine, so if this compound is formed, it can only be in trace amounts. It must be kept in mind that the reaction is photochemical, whereas the calculations refer to the ground-state energy surface. The same products are not formed thermally (see the next section). There can be different preferences for fragmentation of **17** in the ground and excited states. A transition state for a hydrogen shift in **14** concerted with the breaking of the CO–O bond was not located, but it cannot be excluded that such a process could take place. The relative calculated energies of the compounds and transition states are listed in Table 3.

FVT of triazole **12**. Formation of methoxy(2-pyridyl)ketene

FVT of **12** produced a new ketene. At an FVT temperature of 400°C the starting material was recovered largely unchanged, together with a small amount of a ketene absorbing at 2114 cm⁻¹ in the Ar matrix IR spectrum. At 500°C the formation of the ketene was essentially complete. Bands due to CO (2139 cm⁻¹) and CO₂ (2345 cm⁻¹) were also present. At 600°C the ketene had disappeared, and the spectrum was dominated by CO and CO₂. The ketene is identified as largely the *s*-*Z* isomer, *s*-*Z*-**15**, by the very good agreement with the spectrum calculated at the B3LYP/6–31G* level (Fig. 1 and Table 2). A small amount of the *s*-*E* isomer, *s*-*E*-**15**, is probably also present. The calculations indicate that *s*-*Z*-**15** is 29 kJ mol⁻¹ lower in energy than *s*-*E*-**15**. In the studies of **4**, **7** and **11** it was found that FVT gave the *s*-*Z*-

Table 3. Relative energies (kcal mol⁻¹)^a at the B3LYP/6-31G* level

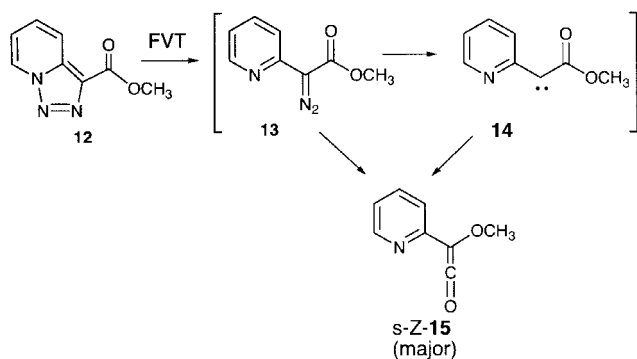
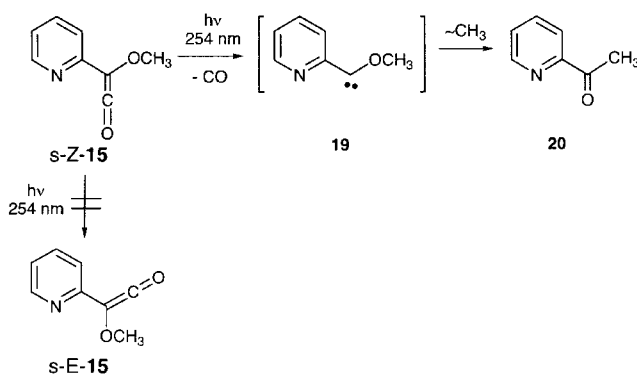
	Relative energy	Energy + ZPE	Free energy (298 K)
14 (conformation shown)	70.1	67.6	66.6
TS1 (14 → 17)			
	74.9	71.5	71.3
17	0	0	0
TS2 (17 → <i>s-E</i> - 4 + CH ₂ O)	51.1	47.8	47.8
<i>s-E</i> - 4 + CH ₂ O	31.1	25.5	14.0
TS3 (17 → 18 + CO ₂)	42.1	39.2	38.6
18 + CO ₂	-14.6	-17.7	-28.0

^a Absolute energy of **17** is -514.2454975 hartree; energy + ZPE is -514.106871 hartree; free energy (298 K) is -514.141917 hartree.

ketene isomers predominantly, and these were calculated to be of lower energy than the *s-E*-isomers.¹⁻³

The formation of **15** is readily explained as a thermal Wolff rearrangement,⁵ which may proceed either as a concerted rearrangement of the diazo compound **13** or via the carbene **14** (Scheme 5). That different products are formed under thermal and photochemical conditions may be due to (i) the involvement of different electronic states; (ii) the thermal reaction is a concerted reaction of the diazo compound **13**, but the photochemical reaction is

a reaction of the carbene **14**; or (iii) in the matrix photolysis the carbene is born in a conformation that cannot undergo the Wolff rearrangement, but under FVT conditions barriers to conformational change would be easily overcome. It is possible that minor amounts of 2-vinylpyridine are formed, and thus that the C—H insertion of carbene **14** resulting in fragmentation to CO₂ and 2-vinylpyridine is a minor process under thermal conditions.

**Scheme 5****Scheme 6**

Photolysis of ketene **15**. Rearrangement of a methoxycarbene to a methyl ketone

Having made **15**, it was possible to examine its photochemical behaviour in an Ar matrix. In the case of **4**, reversible but wavelength-dependent *Z-E* isomerization was observed.¹ In the case of *s-Z*-**15**, no *Z-E* interconversion was observed, but instead fragmentation–rearrangement to 2-acetylpyridine **20** and CO, both identified by comparison of the Ar matrix IR spectra with authentic materials. This reaction most likely proceeds via methoxy(2-pyridyl)carbene **19** (Scheme 6). There is precedence for the rearrangement of hydroxy- and alkoxy-carbenes to carbonyl compounds in other systems.⁶ For example, hydroxycarbene rearranges to formaldehyde;⁷ di(methoxycarbonyl)carbene undergoes thermal Wolff rearrangement to methoxy(methoxycarbonyl)ketene, which under FVT conditions eliminates CO to give methyl 2-oxopropanoate;⁸ dimethoxycarbene rearranges to methyl acetate;^{8,9} and phenoxy-carbene, generated by FVT of 5-phenoxytetrazole, rearranges to benzaldehyde.¹⁰

CONCLUSIONS

FVT of **12** results in a Wolff rearrangement to methoxy(2-pyridyl)ketene, largely in the *s-Z* form, *s-Z*-

15. Photolysis of **12** does not generate **15**, but instead formaldehyde and 2-pyridylketene (**4**), largely in the *s-E*-form, *s-E-4*, presumably by fragmentation of methoxy-carbonyl(2-pyridyl)carbene (**14**). Photolysis of *s-Z-15* results in extrusion of CO and formation of 2-acetylpyridine, presumably by rearrangement of methoxy(2-pyridyl)carbene (**19**).

EXPERIMENTAL

3-(Methoxycarbonyl)-1,2,3-triazolo[1,5-a]pyridine (**12**)

This compound was prepared according to the literature;^{4,11} m.p. 136 °C (lit.⁴ 138–141 °C); GC–MS, *m/z* 177; ¹H NMR (400.1 MHz, CDCl₃), δ 8.80 (ddd, ³*J*_{7,6} 7.0 Hz, ⁴*J*_{7,5} 1.0 Hz, ⁵*J*_{7,4} 1.0 Hz 1H, H-7), 8.24 (ddd, ³*J*_{4,5} 8.9 Hz, ⁴*J*_{4,6} 1.1 Hz, ⁵*J*_{4,7} 1.1 Hz 1H, H-4), 7.52 (ddd, ³*J*_{5,4} 8.9 Hz, ³*J*_{5,6} 6.8 Hz, ⁴*J*_{5,7} 0.9 Hz 1H, H-5), 7.52 (ddd, ³*J*_{6,7} 6.9 Hz, ³*J*_{6,5} 6.9 Hz, ⁴*J*_{6,4} 1.2 Hz 1H, H-6), 4.00 (s, 3H, OCH₃); ¹³C NMR (100.6 MHz, CDCl₃), δ 161.7 (CO), 135.1 (C-3a), 129.2 (C-3, C-7), 125.9 (C-4), 119.2 (C-5), 116.4 (C-6), 52.0 (OCH₃); IR (Ar, 28 K), ν 2962 (w), 1758 (w), 1719 (s), 1645 (w), 1550 (w), 1533 (s), 1528 (s), 1454 (m), 1442 (w), 1417 (w), 1376 (w), 1329 (m), 1271 (s), 1256 (m), 1229 (vs), 1163 (w), 1138 (w), 1074 (vs), 1004 (w), 814 (w), 792 (w), 775 (w), 749 (w), 682 (w) cm⁻¹. Anal. Calcd for C₈H₇N₃O₂: C 54.2, H 3.9, N 23.72%. Found: C 54.42, H 4.08, N 23.16%.

Matrix isolation experiments

Flash vacuum thermolysis. Triazolopyridine **12** (ca 10 mg portions) was subjected to FVT over the temperature range 400–600 °C. The sublimation temperature was 60–75 °C. The product was isolated in an Ar matrix at ca 23 K, and spectra were recorded at 7 K. At 400 °C, mainly starting material **12** (1719, 1229, 1074 cm⁻¹) and a small amount of *Z*-methoxy-(2-pyridyl)ketene (*s-Z-15*) (2114 cm⁻¹) were observed. A mixture of **12** and *Z-15* was obtained at 450 °C. The formation of *s-Z-15* was essentially complete at 500 °C. The intensity of bands belonging to carbon dioxide (2345 cm⁻¹) and carbon monoxide (2139 cm⁻¹) increased with the temperature. At 600 °C, carbon dioxide and carbon monoxide dominated the spectrum. Methoxy-(2-pyridyl)ketene **15**: IR (Ar, 7 K), see Table 2.

Matrix photolysis of 12. Compound **12** was deposited with Ar on the spectroscopic window at 23 K and the window was cooled to 7–10 K before commencing irradiation. The photolysis was carried out with the light of a 1000 W high-pressure Hg–Xe lamp, either unfiltered or at 313 nm selected with a monochromator (bandwidth 15 nm), or at 254 nm using a low-pressure Hg lamp (350

W). In all cases, irradiation afforded the following bands: 2283 (w), 2124 (s), 1737 (w), 1662 (m), 1592 (m), 1567 (w), 1484 (m), 1472 (m), 1439 (m), 1410 (w), 1384 (w), 1368 (w), 1286 (w), 1214 (m), 1198 (w), 1150 (w), 1055 (w), 775 (w) cm⁻¹.

Photolysis of methoxy-(2-pyridyl)ketene (*s-Z-15*).

Flash vacuum thermolysis of **12** at 500 °C generated ketene **15**, predominantly in the *s-Z* form, *s-Z-15*, which was co-deposited on the spectroscopic window at 7 K. Irradiation using the unfiltered light of the 1000 W Hg–Xe lamp or the low-pressure Hg lamp ($\lambda = 254$ nm) gave CO (2139 cm⁻¹) and 2-acetylpyridine; IR (Ar, 7 K), ν 1712, 1361, 1295, 1285, 1241, 950, 779, 591 cm⁻¹.

2-Acetylpyridine. A sample of 2-acetylpyridine was sublimed at 0 °C and deposited with Ar for matrix isolation at 23 K. IR (Ar, 23 K), ν 3500 (w broad), 3063 (w), 3016 (w), 1712 (vs), 1619 (v), 1590 (w), 1572 (w), 1439 (m), 1422 (w), 1413 (w), 1361 (vs), 1301 (w), 1295 (m), 1286 (s), 1241 (s), 1102 (m), 1044 (w), 996 (w), 950 (m), 779 (m), 740 (w), 622 (w), 591 (s) cm⁻¹.

Computational procedure

Density functional theory calculations were carried out using the Gaussian 98 series of programs.¹² Geometry optimizations, vibrational frequencies and thermochemistry were examined with the B3LYP method using the 6–31G* basis set. All wavenumbers were scaled by a factor of 0.9613.¹³ Cartesian coordinates, absolute energies and imaginary frequencies of transition states are presented in the Supplementary Information, available at the epoc website at <http://www.wiley.com/epoc>.

Acknowledgements

This research was supported by the Australian Research Council. We are indebted to the University of Queensland for a scholarship for H.G.A.

REFERENCES

1. Kuhn A, Plüg C, Wentrup C. *J. Am. Chem. Soc.* 2000; **122**: 1945–1948.
2. Plüg C, Ye X, Kuhn A, Wentrup C. *J. Chem. Soc., Perkin Trans. 1* 2002; 1366–1368.
3. Plüg C, Kuhn A, Wentrup C. *Eur. J. Org. Chem.* 2002; 2683–2685.
4. Tomioka H, Ichikawa N, Komatsu K. *J. Am. Chem. Soc.* 1993; **115**: 8621–8626.
5. Maas G. In *Methoden der Organischen Chemie (Houben-Weyl)*, Vol. E19b: *Carbene (Carbenoide)*, Regitz M (ed). Georg Thieme: Stuttgart, 1989; 1055–1409; Meier H, Zeller K-P. *Angew. Chem., Int. Ed. Engl.* 1975; **14**: 32–53.
6. Heydt H, Regitz M. In *Methoden der Organischen Chemie (Houben-Weyl)*, Vol. E19b: *Carbene (Carbenoide)*, Regitz M (ed). Georg Thieme: Stuttgart, 1989; 1628–1682.

7. Ahmed SN, McKee ML, Shevlin PB. *J. Am. Chem. Soc.* 1983; **105**: 3942–3947; Ahmed SN, McKee ML, Shevlin PB. *J. Am. Chem. Soc.* 1985; **107**: 1320.
8. Richardson DC, Hendrick ME, Jones M Jr. *J. Am. Chem. Soc.* 1971; **93**: 3790–3796.
9. Hoffmann RW, Schneider J. *Tetrahedron Lett.* 1967; **44**: 4347–4350.
10. Wentrup C. *Adv. Heterocycl. Chem.* 1981; **28**: 274 (231–361).
11. Regitz M. *Chem. Ber.* 1966; **99**: 2918–2930.
12. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98*. Gaussian: Pittsburgh, PA, 1998.
13. Wong MW. *Chem. Phys. Lett.* 1996; **256**: 391–399.