

Communications to the Editor

An Unusual Cleavage of an Energetic Carbene

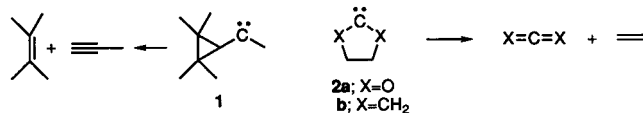
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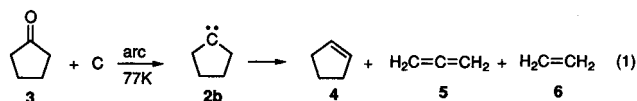
Transformation of a carbene from a divalent to a tetravalent species is generally a highly exothermic process for which numerous pathways have been observed.¹ Particularly interesting examples are two-bond β cleavages, such as that of cyclopropylmethylenes **1** to an alkene and an alkyne² and the cleavage of 2,5-dioxacyclopentylidene **2a** to CO₂ and an alkene.³ In the latter reaction, the stability of CO₂ provides a thermodynamic driving



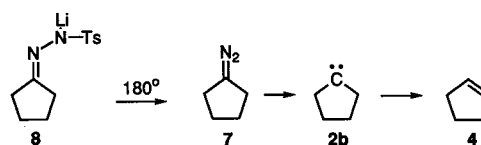
force. We now report that the parent cyclopentylidene, **2b**, will undergo an analogous cleavage when generated with sufficient excess energy.

The deoxygenation of carbonyl compounds by atomic carbon, which is generally exothermic by over 100 kcal/mol, is a convenient route to carbenes which possess excess energy,^{2c,4} and the carbon atom deoxygenation of cyclopentanone, **3**, is expected to generate highly energetic **2b**. Co-condensation of arc-generated carbon⁵ with **3** at 77 K leads to cyclopentene, **4**, allene, **5**, and ethylene, **6**, in a 4:1:1 ratio (eq 1). These results raise the possibility that the high exothermicity of the deoxygenation generates **2b** with enough energy to cleave to **5** and **6** in competition with rearrangement to **4**. While it is conceivable that the cleavage products arise from chemically activated **4**, none of the reported thermal or photochemical decompositions of **4** show this type of fragmentation.⁶

Since we observe that generation of **2b** from diazo compound **7** by pyrolysis of tosylhydrazone lithium salt **8** at 180 °C gives **4** as the only detectable carbene product, it seems likely that the

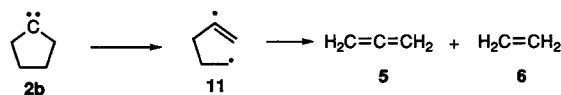


excess energy in the C-atom reaction is responsible for the observed cleavage.



To investigate the energy surfaces connecting **2b** with the observed products, we have carried out a computational study in which geometries were optimized and energies calculated at the B3LYP/6-311+G(d)+ZPC level.^{7,8} Table 1 shows energies of relevant species relative to the ground state of **2b**. Since deoxygenation of carbonyl compounds by carbon occurs along a singlet energy surface,⁹ we have focused our calculations on singlet species. Carbene **2b** was found to have a singlet ground state with an S–T splitting of 8.7 kcal/mol. Not surprisingly, the most favorable reaction of **2b** was H migration to **4** which has a barrier of only 5.7 kcal/mol and is exothermic by 63.0 kcal/mol. Several other intramolecular reactions including ring contraction to methylenecyclobutane **9** ($\Delta H^\ddagger = 51.0$ kcal/mol) and β C–H insertion to give bicyclo[2.1.0]pentane **10** ($\Delta H^\ddagger = 27.5$ kcal/mol) were calculated to have high barriers and seem unlikely to play a role in the chemistry of **2b**.

In examining the energy surface leading from **2b** to **5** and **6**, a reaction calculated to be exothermic by 23.2 kcal/mol, it is immediately obvious that a concerted cleavage preserving the C_{2v} symmetry of **2b** would lead to a planar allene and thus be a high-energy process. Indeed, such a structure can be located lying 56.1 kcal/mol in energy above **2b** with two negative eigenvectors. A similar problem does not occur in the concerted cleavage of **2a** in which a calculated barrier of 10 ± 1 kcal/mol has been reported.^{3d,10} Since a careful search of the closed-shell surface connecting **2b** with **5** and **6** fails to reveal a low-energy concerted transition state, we have considered the possibility that the reaction proceeds in a stepwise manner via biradical **11**.



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(10) We calculate a barrier of 8.1 kcal/mol at the B3LYP/6-311+G(d)+ZPC level.

Table 1. Relative Energies (kcal/mol)

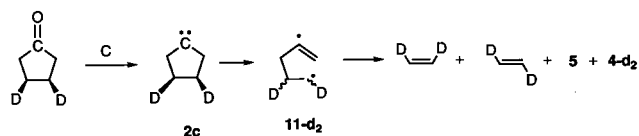
species	B3LYP/ 6-311+G(d)		CAS-PT2//B3LYP/ 6-311+G(d)	
		+ZPC		+ZPC
2b	0.0	0.0	0.0	0.0
4	-65.2	-63.0		
(5 + 6)	-18.6	-23.2		
9	-44.9	-44.0		
10	-33.9	-32.1		
concerted TS	62.5	56.1		
TS2b/4	6.8	5.7		
TS2b/9	52.0	51.0		
TS2b/10	28.2	27.5		
³ 2b	7.7	8.7		
2b*	18.5	19.4	36.6	37.5
11	22.4	18.9	23.6	20.1
TS2b/11	38.6	36.0	40.8	38.2

An estimate of the energy of **11** from 1-pentene using the vinyl and methyl BDEs places it 23 kcal/mol above **2b** in energy. Single point CAS-PT2 calculations^{11,12} using B3LYP/6-311+G(d) geometries place **11** 20.1 kcal/mol above **2b** in energy. These data indicate that when **2b** is generated by conventional methods of carbene synthesis its cleavage via biradical **11** is unfavorable by at least 20–23 kcal/mol and will not be competitive with H migration to give **4** ($\Delta H^\ddagger = 5.7$ kcal/mol).

Since we have demonstrated that excited singlet (¹B₁) methylene is generated in the C-atom deoxygenation of formaldehyde,⁹ we have investigated the possibility that the corresponding excited state of **2b** (**2b***) is involved in the present deoxygenation. A CAS-PT2 calculation^{10,11} using B3LYP/6-311+G(d) geometries gives an S₁–S₀ separation in **2b** of 37.5 kcal/mol.¹² These results indicate that the exothermicity of formation of **2b** by C-atom deoxygenation (108 kcal/mol) could be channeled into the production of **2b*** in which cleavage to **11** is thermodynamically feasible. A single point CAS-PT2 calculation places the transition state connecting **2b** and **11** 0.7 kcal/mol higher in energy than **2b***.

To test for the predicted lack of concert in the cleavage of **2b**, we have investigated the stereochemistry of the cleavage of *cis*-3,4-dideuteriocyclopentylidene, **2c**. Thus, deoxygenation of *cis*-

3,4-dideuteriocyclopentanone¹⁵ with C atoms at 77 K gives *cis* and *trans*-1,2-dideuterioethylene in a 3:1 ratio as determined by IR spectroscopy.¹⁶ When the reaction is carried out in the gas phase with C atoms generated by the 80 °C thermolysis of diazotetrazole,¹⁸ a 1:1 ratio of *cis* and *trans*-1,2-dideuterioethylene is produced. These results are consistent with the predicted two-step cleavage of **2b** in which rotation about the 3–4 bond competes with rupture of the second bond in biradical **11-d**₂. A further indication that excited species are involved in the formation of **5** and **6** is the fact that adding 200 Torr of N₂ to the gas-phase reaction reduces the yield of **5** to only a trace.¹⁹



While these experimental and computational results are consistent with the intermediacy of excited singlet **2b**, they do not require it. However, it is clear that the excess energy available to the carbene generated by the C-atom deoxygenation brings about the cleavage reaction. These data raise the interesting possibility that carbenes generated by highly exothermic pathways may undergo a set of reactions characteristic of the singlet excited state. We are continuing to explore this possibility which may open a new dimension in carbene chemistry.

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Supporting Information Available: Experimental procedures for the deoxygenation of **3**, preparation of *cis*-3,4-dideuterio-cyclopentanone, and analysis of *cis* and *trans*-1,2-dideuterioethylene. Tables of absolute energies and geometries of relevant intermediates and transition states. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) The single point CAS-PT2 calculations on CH₂ and C₅H₈ used a (8, 8) and (12, 12) complete active space, respectively. ANO basis sets of 4s3p1d and 2s1p were employed for carbon and hydrogen. Geometries and zero point corrections were obtained at the B3LYP/6-311+G(d) level.

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(16) Pure samples of *cis* and *trans*-1,2-dideuterioethylene were prepared¹⁷ and IR calibration curves constructed.

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(19) Since generation of C atoms from 5-diazotetrazole is always accompanied by ethylene formation (from C + residual THF solvent),¹⁸ only the fact that the yield of **5** is drastically reduced is relevant in this experiment.

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(12) A CAS-PT2//B3LYP/6-311+G(d) calculation of the ¹B₁–¹A₁ gap in methylene gave 23.7 kcal/mol¹³ as compared with an experimental value of 21.1 kcal/mol.¹⁴