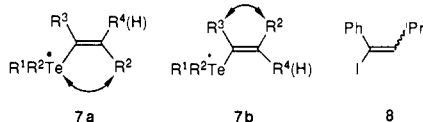


isomerization,³ the stereoselectivity should be determined by the relative stabilities of the transition states of the S_H2 reactions on tellurium (7a and 7b). These, in turn, would be affected mainly by the steric repulsion between R² and R¹R²Te (7a) or R³ (7b) in the cases of terminal alkynes (R⁴ = H). Bond fission of tellurides takes place exclusively on sp²C-Te bonds rather than sp³C-Te bonds (runs 1-5), on tertiary C-Te bonds rather than primary C-Te bonds (runs 6-9), and on the Bn-Te bond rather than the nBu-Te bond (run 10). This could indicate that the more stable carbon radical is liberated from tellurium via 7.



Recently, Curran and co-workers established a very useful synthetic method for the preparation of iodomethylene-substituted cycloalkanes by the photoinitiated radical cyclization of iodoalkylacetylenes.^{2c,4} This also involves a similar S_H2 process on iodine. A competitive reaction of PhTeⁱPr and ⁱPrI with phenylacetylene afforded 3b and 8 in 26% and 2.5% yields, respectively, indicating that the addition of PhTeⁱPr proceeds about 10 times faster than that of ⁱPrI. Actually, the intermolecular reaction of ⁱPrI with a stoichiometric amount of phenylacetylene affords only a 13% (E/Z = 53/47) yield of 8 under conditions identical to run 2.

A variety of heteroatom-containing compounds having an H-Z bond (where Z = heteroatom (group)) easily add to carbon-carbon unsaturated bonds. Although this transformation has been widely used in organic synthesis, as exemplified by hydrosilation and hydrostannation, the similar addition of C-Z compounds hardly proceeds and often affords unsatisfactory results, except the reactions of some alkyl halides.^{2,4} The carbottelluration described herein appears to be the first example of this type of reaction that is quite efficient and very general.^{5,6}

Alkenyl tellurides as well as other diorganyl tellurides undergo facile transmetalation with organolithiums⁷ and transition metal complexes⁸ and have great potential in organic synthesis. The application of this carbottelluration to a variety of unsaturated

compounds and further manipulation of the products are now in progress.

Acknowledgment. This work was supported by a Grant in Aid for Scientific Research on Priority Areas (No. 04217101) from the Ministry of Education, Science, and Culture, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining MS, NMR, and elemental analyses.

Dicyclopropylcarbene: Direct Characterization of a Singlet Dialkylcarbene[†]

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Analogy to methylene might suggest that unconstrained dialkylcarbenes have triplet ground states.¹ Supporting experimental or theoretical² evidence is scarce, however. Rapid intramolecular reactions in the singlet states usually preclude intermolecular trapping or direct spectroscopic characterization.³⁻⁶ The only dialkylcarbenes previously instrumentally observed were triplets by EPR.⁷ As in carbocations, a cyclopropyl group can significantly stabilize a singlet carbene via homoconjugative interactions.⁸⁻¹¹ In this vein, we now report the first spectroscopic characterization of a singlet dialkylcarbene, dicyclopropylcarbene (1).

In contrast to earlier reports,¹² we have found that dicyclopropyldiazirine (2) can be synthesized from the cyclohexylimine of the corresponding ketone.¹³ Irradiation of 2, matrix isolated in N₂ (1:700, 6 K, 334 nm, 28 h), produced two major products whose IR spectra exhibited differential photochemical behavior.¹⁴

[†] Dedicated to Professor Orville L. Chapman, on the occasion of his 60th birthday.

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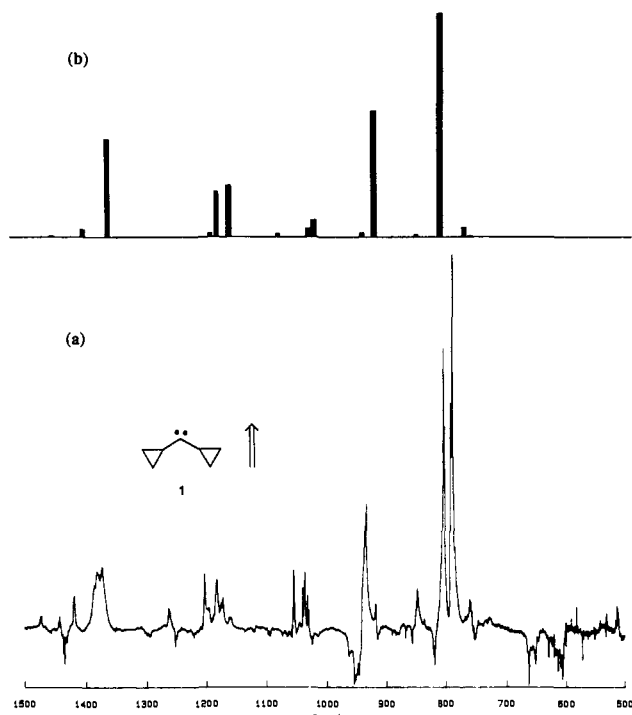
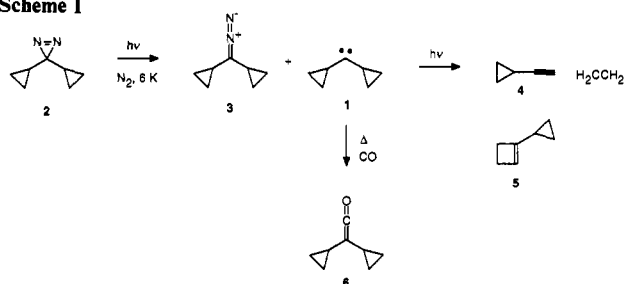


Figure 1. (a) Difference IR spectrum of carbene **1** (positive peaks, in absorbance). Spectrum generated by subtracting IR of N_2 matrix containing **1** (from 28-h 334-nm irradiation of **2**) before and after 1-h irradiation at 475 nm. Negative peaks are due to photoproducts of **1**. (b) Calculated (MP2/6-31G*) IR spectrum of carbene **1a** on same wavelength scale. Frequencies have been multiplied by a factor of 0.93.

Scheme I



One set of bands included a strong absorption at 2053 cm^{-1} , consistent with dicyclopropyldiazomethane (**3**). The other set of bands, with strongest absorption at 802 cm^{-1} , we assign to carbene **1** (Figure 1). Subsequent irradiation of the matrix at 475 nm for 1 h destroyed the IR peaks of **1** and increased those of ethylene, cyclopropylacetylene (**4**),¹⁵ and 1-cyclopropylcyclobutene (**5**),¹⁶ which were initially present in minor amounts. The diazo compound **3** was stable at these wavelengths and only slowly produced the same photoproducts with broad-band irradiation $>340\text{ nm}$. These results are summarized in Scheme I.

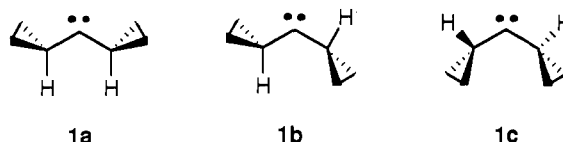
Confirmation of the assignment of the IR spectrum of **1** came from trapping experiments. Irradiation of diazirine **2** in an Ar matrix doped with CO (50:1 Ar:CO, 20 K) produced carbene **1** in the IR. Warming the matrix to 38 K resulted in a decrease of the IR bands of **1** with concurrent growth of a strong absorbance at 2112 cm^{-1} , along with other new bands. This frequency matches that recently reported¹⁷ for dicyclopropylketene (**6**).

The UV/vis spectrum of the irradiated matrix of **2** showed a broad band at 400–600 nm ($\lambda_{\text{max}} 490\text{ nm}$), along with a stronger

absorbance at $\lambda_{\text{max}} 230\text{ nm}$; both bands grew and disappeared simultaneously with the IR of **1**. The “action spectrum” of photodestruction of the IR peaks assigned to **1** roughly matched the UV/vis spectrum, substantiating that the same species was observed by both methods. Irradiation of matrices containing **1** at either end of the long- or short-wavelength UV/vis absorbances caused all of the IR bands of the carbene to disappear simultaneously (as well as the UV/vis spectra). This implies the presence of only one conformer of **1**.¹⁸

The above spectroscopic results suggest that **1** is a ground-state singlet. Triplet methylene absorbs well only below 200 nm in wavelength, whereas the singlet shows broad absorption from 550 to 950 nm.¹⁹ Shevlin and McKee^{8c} have estimated, on the basis of ab initio calculations, that triplet cyclopropylmethylene is ca. 1 kcal/mol lower than the singlet.²⁰ It is thus not unreasonable that two cyclopropylcarbinyl interactions as in **1** would favor a singlet ground state.

Three conformations of **1** (**1a**, **1b**, and **1c**) can maximally benefit from interaction between the empty carbenic p orbital and the Walsh orbitals of both cyclopropanes. Only **1a** and **1b**,^{8c,d} however, would be expected to exhibit low barriers for ring expansion. We thus carried out ab initio calculations to address these conformational issues in more detail.²¹ The geometries of **1a**, **1b**, and **1c** were optimized at the MP2/6-31G* level (relative energies: 0, 4.0, and 12.8 kcal/mol for **1a**, **1b**, and **1c**, respectively, uncorrected for zero point energy). Vibrational calculations indicated that a C_{2v} structure for **1c** was not an energy minimum (in contrast to **1a** and **1b**). Relaxation to a skewed C_2 geometry, however, produced a local minimum. The vibrational spectrum calculated for **1a**, scaled by a factor of 0.93,²² is in excellent agreement with the observed IR (Figure 1b).²³ In contrast, calculated vibrations for **1b** or **1c** do not fit the experimental spectra. The calculated wavelengths for the lowest energy electronic transition from the CIS method²¹ (configuration interaction with single excitations, 6-31G*) for **1a**, **1b**, and **1c**, respectively, are 475, 538, and 629 nm. The ab initio calculations thus support the contention that **1** is a ground-state singlet, and that only conformation **1a** is observed.^{24,25}



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Supplementary Material Available: Synthetic details for **2**, experimental IR data for **1**, and ab initio calculated geometries and vibrational frequencies for **1a**, **1b**, and **1c** (14 pages). Ordering information is given on any current masthead page.

Intramolecular Carbon-Carbon Bond Formation by the Anodic Oxidation of Unsaturated α -Stannyl Heteroatom Compounds. Synthesis of Fluorine-Containing Heterocyclic Compounds

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Although group 14 organometallic compounds are normally utilized as carbanion equivalents,^{1,2} recent investigations reveal that they also serve as carbocation equivalents if one employs electrochemical oxidation.³ For example, anodic oxidation of α -silyl ethers results in facile cleavage of the carbon-silicon bond and introduction of a nucleophile such as an alcohol onto the carbon (Scheme I). However, the introduction of carbon nucleophiles to form a new carbon-carbon bond by anodic oxidation of such compounds has remained an unexplored area of research.^{4,5}

In this paper we wish to report that the anodic oxidation of α -stannyl ethers and carbamates containing carbon-carbon double bonds can lead to effective intramolecular carbon-carbon bond formation (Scheme II). A fluorine atom is introduced onto one of the original olefinic carbons in the cyclized product. The method outlined here is a new approach to both electrochemical carbon-carbon bond formation⁶ and the synthesis of fluorine-containing compounds.^{7,8}

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(2) Organostannanes are also used as carbon radical equivalents. For example: Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.

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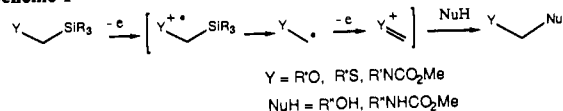
(5) Carbon-carbon bond formation has been achieved by photoelectron-transfer reactions of organometallic compounds. See, for example: (a) Cho, I.-S.; Tu, C.-L.; Mariano, P. S. *J. Am. Chem. Soc.* 1990, 112, 3594-3607. (b) Mizuno, K.; Nakanishi, K.; Otsuji, Y. *Chem. Lett.* 1988, 1833-1836 and references cited therein. Oxidative carbon-carbon bond formation using thallium(III) trifluoroacetate has been reported: (c) Ochiai, M.; Arimoto, M.; Fujita, E. *Tetrahedron Lett.* 1981, 22, 4491-4494.

(6) Anodic oxidation: (a) Moeller, K. D.; Tino, L. V. *J. Am. Chem. Soc.* 1992, 114, 1033-1041. (b) Hudson, C. M.; Marzabadi, M. R.; Moeller, K. D.; New, D. G. *J. Am. Chem. Soc.* 1991, 113, 7372-7385 and references cited therein. Cathodic reduction: (c) Amputch, M. A.; Little, R. D. *Tetrahedron* 1991, 47, 383-402. Lombardo, F.; Newmark, R. A.; Kariv-Miller, E. *J. Org. Chem.* 1991, 56, 2422-2427. Shono, T.; Kise, N.; Uematsu, N.; Morimoto, S.; Okazaki, E. *J. Org. Chem.* 1990, 55, 5037-5041 and references cited therein.

(7) Reviews, for example: (a) Welch, J. T. *Tetrahedron* 1987, 43, 3123-3197. (b) Gerstenberger, M. R. C.; Haas, A. *Angew. Chem., Int. Ed. Engl.* 1981, 20, 647-667. (c) Schlosser, M. *Tetrahedron* 1978, 34, 3-17.

(8) Electrochemical fluorination, for example: (a) Fuchigami, T.; Shimojo, M.; Konno, A.; Nakagawa, K. *J. Org. Chem.* 1990, 55, 6074-6075. (b) Brigaud, T.; Laurent, E. *Tetrahedron Lett.* 1990, 31, 2287-2290 and references cited therein.

Scheme I



Scheme II

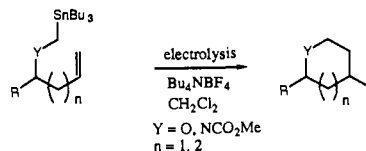


Table I. Intramolecular Carbon-Carbon Bond Formation by the Anodic Oxidation of Unsaturated α -Stannyl Ethers and Carbamates^a

substrate	electrolyte	electricity (F/mol)	product	yield, %
	Bu ₄ NBF ₄ ^b	2.3		93
	Bu ₄ NBF ₄	3.1		83
	Bu ₄ NPF ₆	2.5		98
			(cis / trans = 2.8 : 1)	
			(cis / trans = 1.2 : 1)	
	Bu ₄ NBF ₄	4.6		68
			(cis / trans = 1.2 : 1)	
	Bu ₄ NBF ₄	3.2		95
			(cis / trans = 3 : 1)	
	Bu ₄ NBF ₄	3.2	complex mixture	
	Bu ₄ NBF ₄	3.1		61 ^c
				28
	Bu ₄ NBF ₄	2.3		70
			(cis / trans = 1.5 : 1)	
	Bu ₄ NBF ₄	2.0		50
			(cis / trans = 3.1 : 1)	

^aThe reactions were normally carried out with 0.25 mmol of the substrate. ^bMethanol was used as solvent. ^cA mixture of two stereoisomers (1.8:1).

We initially examined the anodic oxidation of α -stannyl ether **1** (Scheme III) because in the case of α -silyl ethers the radical intermediate generated by the first one-electron oxidation would be oxidized spontaneously on the surface of the anode (Scheme I). The oxidation potentials of carbon radicals are generally much