By means of the spin-state-specific products (**12** for the singlet, **14** for the triplet), the reactions of **11** can be dissected into singlet and triplet components (Scheme II).[4a] According to this analysis, O–H insertion is the predominant, if not only, reaction of singlet **11**. The contribution of the singlet to C–H insertion is close to naught. Triplet **11**, the major intermediate even in the direct photolysis of **10**, gives rise to **13** and **14** in a 1.7:1 ratio. With the (R^*,R^*) diastereomer of **10**, the ratio of **13** to **14** was 0.7:1. We conclude that retention of configuration is slightly preferred over inversion in the abstraction–recombination sequence of triplet **5a** and **11**. The analogous reaction of **5b** is unselective, owing to the enhanced stability and lifetime of the diradical **8b**.[8]

We comment briefly on the exceptional intramolecular reactivity of triplet arylcarbenes, as compared with singlets. The concerted insertion reaction of the singlet involves the p orbital as well as the σ orbital of the carbene. For the interaction of both orbitals with δ-C–H bonds, rotation must occur about the bond connecting the divalent carbon to the benzene ring, with concomitant loss of benzylic stabilization and deformation of bond angles. In contrast, the transfer of δ-hydrogen to the half-filled, in-plane σ orbital of the triplet carbene can proceed by way of a favorable six-membered transition state[9,10] in which the benzylic resonance is not disturbed. If this picture is correct, we anticipate that the concerted singlet mechanism will be restored, at least in part, for intramolecular C–H insertion reactions leading to six-membered rings. Preliminary results from our laboratory support this notion.

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[8] The benzylic resonance in **8b** will also minimize the interaction of the unpaired electron with the oxygen atom, thus lowering the rotational barrier in **8b** relative to **8a**.

[9] Dorigo, A. E.; McCarrick, M. A.; Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 7508.

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Carbotelluration of Alkynes

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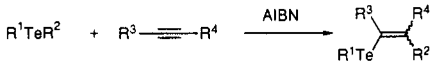
Herein we describe the carbotelluration of alkynes in which diorganyl tellurides add to carbon–carbon triple bonds regioselectively to form alkenyl tellurides, as shown in eq 1. For example,



$$R^1TeR^2 + R^3C\equiv CR^4 \xrightarrow{AIBN} (R^1Te)(R^2)C{=}C(R^3)(R^4) \quad (1)$$

1 2 3

refluxing a benzene solution of an equimolar mixture of PhTe^{i}Pr (**1b**) and phenylacetylene (**2b**) in the presence of a catalytic amount of AIBN (10 mol %) under argon for 40 min leads to the regioselective formation of **3b** in nearly quantitative yield (E/Z ratio = 56/44). The E and Z isomers were isolated in pure form in 48% and 32% yields, respectively, by column chromatography on alumina. Since **4** was obtained in ca. 2% yield as a byproduct and since carbotelluration hardly proceeds in the absence of AIBN, this carbotelluration is likely a radical chain reaction initiated by the addition of 1-cyano-1-methylethyl radical (In•) to phenylacetylene (Scheme I).[1]

Scheme I

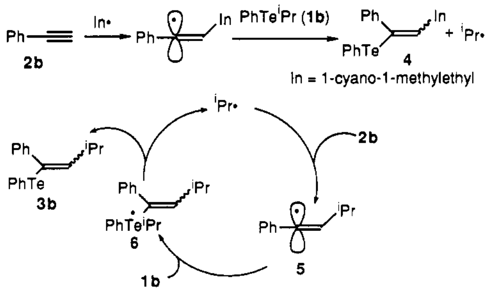
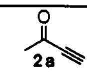
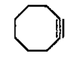


Table I. Carbotelluration of Alkynes[a]

run	telluride(**1**) (R^1TeR^2)	alkyne(**2**) ($R^3C\equiv CR^4$)	product **3**	% yield of **3**: ^{1}H NMR (*E/Z* ratio)	Isolated[b] *E*	Isolated[b] *Z*
1	PhTe^{n}Bu **1a**	 **2a**	**3a**	73 (20/80)	13	58
2	PhTe^{i}Pr **1b**	Ph—≡ **2b**	**3b**	97 (56/44)	48	32
3	**1b**	**2a**	**3c**	99 (19/81)	15	75
4	**1b**	MeO_2C—≡ **2c**	**3d**	93 (29/71)	23	67
5	**1b**	EtO_2C—≡—CO_2Et **2d**	**3e**	95 (37/63)	26	54
6	^{n}BuTe^{t}Bu **1c**	**2a**	**3f**	84 (88/12)	68	11
7	**1c**	Me_3Si—≡ **2e**	**3g**	77 (0/100)	0	63
8	**1c**	 **2f**	**3h**		52	0
9	**1c**	^{n}Hex—≡ **2g**	**3i**	42 (80/20)	40[c]	
10	^{n}BuTeCH$_2$Ph[d] **1d**	**2b**	**3j**	91 (56/44)	81[c]	

[a] Conditions: telluride (1.0 mmol), alkyne (1.0 mmol), AIBN (0.1 mmol), benzene (1.0 mL), reflux, 40 min to 4.5 h except run 10. [b] By column chromatography on silica gel except **3b** (on alumina). [c] A mixture of E and Z isomers which could not be separated by column chromatography either on silica gel or on alumina. [d] Prepared in situ and used without isolation. Conditions: n-BuLi (1.02 mmol), Te (1.0 mmol), THF (2 mL), 0 °C, 0.5 h; $PhCH_2Br$ (1.0 mmol), 0 °C, 0.5 h; phenylacetylene (1.0 mmol), AIBN (0.1 mmol), reflux, 4.5 h.

As shown in Table I, primary, secondary, and tertiary alkyl- and benzyl-substituted tellurides are all suitable substrates for this carbotelluration, and good yields of alkenyl tellurides **3** can be obtained. Alkynes having an electron-withdrawing group(s) undergo carbotelluration very efficiently, reflecting the nucleophilic nature of the attacking alkyl radicals.[2] The reaction of 1-octyne was rather slow, giving a moderate yield of the adduct (run 9) in comparison to alkynes bearing carbonyl, aryl, and silyl substituents. Cyclooctyne gives the corresponding adduct in an acceptable yield (run 8), while some internal alkynes such as 2-octyne give only poor yields of adducts under similar conditions.

The evidence that the E/Z ratio of products stays constant throughout the reaction period suggests that the stereoselectivity of the carbotelluration is kinetically controlled. Since vinyl radicals have either a π radical structure, when conjugated with an aromatic substituent, or a σ radical structure with rapid cis–trans

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[1] The alternative possibility that ^{i}Pr• is generated by the reaction of **1b** with In• in the initiation step may be ruled out since no disproportion or degradation of tellurides is observed when a 1/1 mixture of AIBN and **1b** or butyl isopropyl telluride (**1e**) is heated in refluxing benzene. This indicates that In• is too stable to generate alkyl radicals from tellurides. For the generation of carbon radicals by the S_H2 reaction on tellurium, see: (a) Barton, D. H. R.; Ozbalik, N.; Sarma, J. C. *Tetrahedron Lett.* **1988**, *29*, 6581. (b) Barton, D. H. R.; Ramesh, M. *J. Am. Chem. Soc.* **1990**, *112*, 891.

[2] (a) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (b) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. (c) Curran, D. P. *Synthesis* **1988**, 417 and 489.

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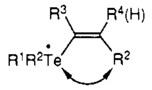
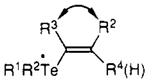
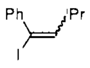
isomerization,[3] the stereoselectivity should be determined by the relative stabilities of the transition states of the S_H2 reactions on tellurium (**7a** and **7b**). These, in turn, would be affected mainly by the steric repulsion between R^2 and R^1R^2Te (**7a**) or R^3 (**7b**) in the cases of terminal alkynes (R^4 = H). Bond fission of tellurides takes place exclusively on $^{sp^3}$C–Te bonds rather than $^{sp^2}$C–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 ^{n}Bu–Te bond (run 10). This could indicate that the more stable carbon radical is liberated from tellurium via **7**.



7a



7b



8

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 PhTe^{i}Pr and ^{i}PrI with phenylacetylene afforded **3b** and **8** in 26% and 2.5% yields, respectively, indicating that the addition of PhTe^{i}Pr proceeds about *10 times faster* than that of ^{i}PrI. Actually, the intermolecular reaction of ^{i}PrI 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 carbotelluration 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 organolithiums[7] and transition metal complexes[8] and have great potential in organic synthesis. The application of this carbotelluration to a variety of unsaturated compounds and further manipulation of the products are now in progress.

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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 theoretical[2] 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 N_2 (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.

(1) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, NY, 1971. Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, NY, 1973; Vol. 1, p 1 and references therein.

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(13) By a procedure similar to that reported by Liu and Jennings: Liu, M. T. H.; Jennings, B. M. *Can. J. Chem.* **1977**, *55*, 3596. Details are given in the supplementary material.

(14) The low temperature matrix isolation apparatus and irradiation setup have been previously described in the following: Kesselmayer, M. A.; Sheridan, R. S. *J. Am. Chem. Soc.* **1986**, *108*, 99. Hayes, J. C.; Sheridan, R. S. *J. Am. Chem. Soc.* **1990**, *112*, 5879.

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