rhenium alkylidene complexes;[10] and Harold H. Fox for the synthesis of $Mo(CHCMe_2Ph)(NAr)[OC(CF_3)_2CF_2CF_2CF_3]_2$.

Supplementary Material Available: NMR data, details of the kinetic studies (25 experiments), individual rate constants, and values for $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ for various interconversions (4 pages). Ordering information is given on any current masthead page.

Intramolecular Hydrogen Abstraction by Functionalized Arylcarbenes

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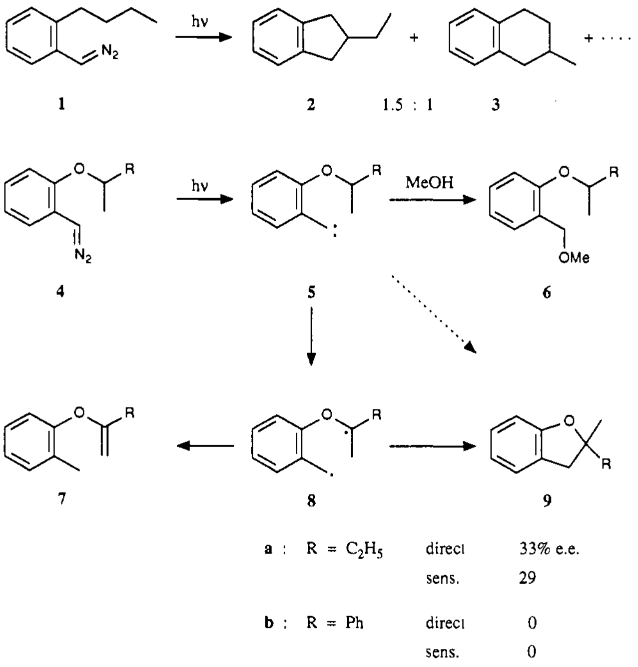
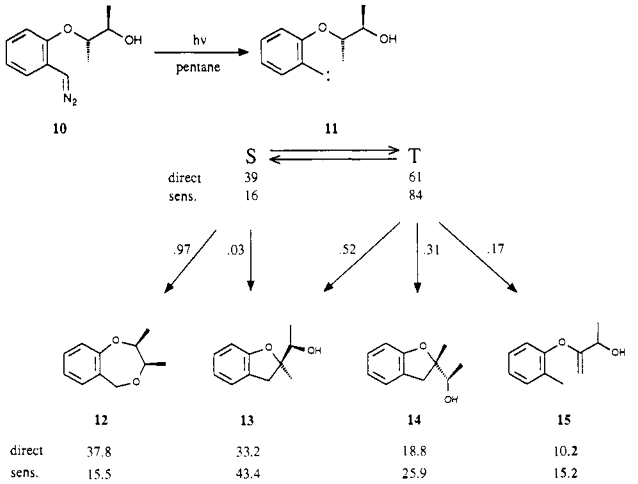
Many reactions of phenylcarbene proceed from the singlet state, although the ground state is the triplet.[1] These results have been interpreted in terms of rapid singlet-triplet equilibration, with the singlet being much more reactive than the triplet state. The concerted singlet mechanism for *intermolecular* C-H insertion reactions of phenylcarbene is supported by the lack of crossover products,[2] small deuterium isotope effects,[2] and stereoselective insertion into the tertiary C-H bonds of *rac*- and *meso*-2,3-dimethoxybutane.[3] We now report contrasting evidence for *intramolecular* C-H insertion reactions. We have found that (2-alkoxyphenyl)carbenes produce five-membered rings by way of a triplet abstraction-recombination mechanism.[4]

The intramolecular insertion of arylcarbenes into C-H bonds of an ortho side chain was pioneered by Gutsche in a study of (2-butylphenyl)carbene.[5] Photolysis of the diazo compound **1** afforded five- and six-membered rings as the major products (**2**:**3** = 1.5), both of which were thought to originate from the singlet carbene (Scheme I). The oxygen of (2-alkoxyphenyl)carbenes (**5**) exerts a strong directive effect, leading to almost exclusive formation of 2,3-dihydrobenzofurans (**9**).[6] The chirality of **9** (R $\neq$ CH_3) prompted us to examine the stereochemistry of the insertion reactions, **5** → **9**. Direct photolysis of optically active [2-[(1-methylpropyl)oxy]phenyl]diazomethane (**4a**) in pentane afforded **9a** with 33% ee.[7] Sensitization with benzophenone lowered the ee of **9a** slightly, to 29%. The loss of enantiomeric purity points to hydrogen abstraction by triplet **5a**, giving the diradical **8a**. The intervention of **8a** also accounts for the formation of **7a** (10%, relative to **9a**) by transfer of a second hydrogen atom (disproportionation).

Scheme I



Scheme II



When the *sec*-butyl group of **4a** was replaced with (*R*)-1-phenylethyl (**4b**), the racemic dihydrofuran **9b** and enhanced quantities of **7b** were formed (**9b**:**7b** = 3.5). The ethers **6a,b**, arising by intermolecular O-H insertion of singlet **5a,b**, were the major products obtained from direct photolyses of **4a,b** in methanol (**6a**:**9a** = 12.5; **6b**:**9b** = 17.5). On sensitization with 0.2 M benzophenone, the product ratios changed in favor of **9** (**6a**:**9a** = 2.2; **6b**:**9b** = 1.3). These data indicate that singlet **5** is quenched by methanol in preference to spin inversion ($k_S > k_{ST}$) while the intramolecular abstraction of hydrogen by triplet **5** is competitive with intersystem crossing ($k_T \cong k_{TS}$).

Residual optical activity, as observed in the case of **9a**, may be due to a minor contribution of singlet **5a**. On the other hand, stereoselective ring closure of the diradical **8a** can take place if the rates of rotation and spin inversion are of similar magnitude. In order to differentiate between these alternatives, we utilized hydroxyl groups as internal traps for the singlet carbene. The (R^*,S^*)-2-hydroxy-1-methylpropyl substrate **10** and the (R^*,R^*) diastereomer (not shown) were prepared from *cis*- and *trans*-2,3-dimethyloxirane, respectively, with an appropriate phenoxide.

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(1) For reviews, see: (a) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum Press: New York, 1990; Chapter 8. (b) Wentrup, C. In *Carbene(oide), Carbine, Houben-Weyl* E 19b; Regitz, M., Ed.; Thieme: Stuttgart, 1989; p 824. (c) Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311. (d) Moss, R. A., Jones, M., Jr., Eds. *Carbenes*; Wiley: New York, 1973, 1975; Vols. I and II. (e) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; Chapter 7.

(2) Savino, T. G.; Kanakarajan, K.; Platz, M. S. *J. Org. Chem.* **1986**, *51*, 1305. Analogous data have been reported for 1-naphthylcarbene: Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928.

(3) Kirmse, W.; Staubach, B. Unpublished results. The ratio of diastereomeric insertion products was 98.5:1.5 for *rac*-2,3-dimethoxybutane and 3.5:96.5 for *meso*-2,3-dimethoxybutane.

(4) A similar mechanistic dichotomy has been noted for intramolecular and intermolecular addition reactions of arylcarbenes to C=C bonds: (a) Kirmse, W.; Hömberger, G. *J. Am. Chem. Soc.* **1991**, *113*, 3925. (b) Hömberger, G.; Dorigo, A. E.; Kirmse, W.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 475.

(5) (a) Baer, T.; Gutsche, C. D. *J. Am. Chem. Soc.* **1971**, *93*, 5180. (b) Gutsche, C. D.; Bachman, G. L.; Coffey, R. S. *Tetrahedron* **1962**, *18*, 617.

(6) Crow, W. D.; Mc Nab, H. *Aust. J. Chem.* **1979**, *32*, 111. These authors generated [2-(*n*-alkoxy)phenyl]carbenes by thermolysis of tosylhydrazone sodium salts.

(7) Precursors of **4a** (72% ee) and **4b** (67% ee) were prepared from salicylaldehyde with optically active 2-butyl tosylate and 1-phenylethyl chloride, respectively. The ee of 2-[(1′-methylpropyl)oxy]benzaldehyde was determined by ^1H NMR (400 MHz) of the acetal formed with (*R*)-(+)-dimethyl tartrate. The enantiomers of 2-(1′-phenylethoxy)benzaldehyde were resolved by GC on 30-m capillary columns coated with heptakis(3-*O*-acetyl-2,6-di-*O*-methyl)-β-cyclodextrin in OV 1701. The aldehydes were converted into diazo compounds by way of the tosylhydrazones. The combined yield of 7 and 9 was 30-35%. Insertion reactions with the solvent and azine formation account for 65-70% of the substrate. The enantiomers of **9a,b** were analyzed by GC on the chiral phase indicated above. Results are corrected to 100% ee of the substrates. Experimental details are given in the doctoral thesis of I. S. Özkir, University of Bochum, 1991.

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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.

[10] Huang, X. L.; Dannenberg, J. J. *J. Org. Chem.* **1991**, *56*, 5421.

Carbotelluration of Alkynes

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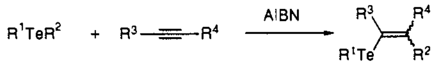
Herein we describe the carbotelluration of alkynes in which diorganyl tellurides add to carbon–carbon triple bonds regioselectively to form alkenyl tellurides, as shown in eq 1. For example,



$$\underset{\mathbf{1}}{\mathrm{R^1TeR^2}} + \underset{\mathbf{2}}{\mathrm{R^3{-}{\equiv}{-}R^4}} \xrightarrow{\text{AIBN}} \underset{\mathbf{3}}{\mathrm{(R^1Te)(R^3)C{=}C(R^4)(R^2)}} \qquad (1)$$

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$^\bullet$) to phenylacetylene (Scheme I).[1]

Scheme I

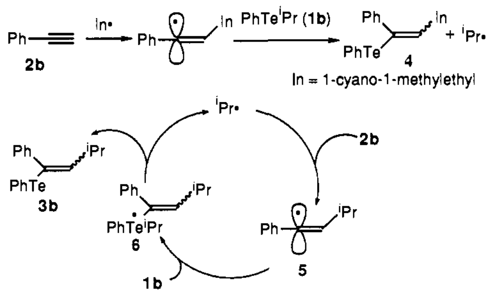
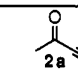
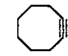


Table I. Carbotelluration of Alkynes[a]

run	telluride(**1**) ($\mathrm{R^1TeR^2}$)	alkyne(**2**) ($\mathrm{R^3C{\equiv}CR^4}$)	product **3**	% yield of **3**: ^{1}H NMR (E/Z ratio)	% yield of **3**: Isolated[b] E	% yield of **3**: 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**	$\mathrm{MeO_2C}$—≡ **2c**	**3d**	93 (29/71)	23	67
5	**1b**	$\mathrm{EtO_2C}$—≡—$\mathrm{CO_2Et}$ **2d**	**3e**	95 (37/63)	26	54
6	^{n}BuTe^{t}Bu **1c**	**2a**	**3f**	84 (88/12)	68	11
7	**1c**	$\mathrm{Me_3Si}$—≡ **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$_2$Br (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$^\bullet$ is generated by the reaction of **1b** with In$^\bullet$ 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$^\bullet$ is too stable to generate alkyl radicals from tellurides. For the generation of carbon radicals by the $\mathrm{S_H2}$ 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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