of **2** from **3** is assumed to proceed with retention of configuration in the allenyl unit.[10]

Also here other conversion modes of **1a** into **2b** and **2c** than the one outlined in eq 2 must be important in view of the low ee values, especially for X = Cl. Such competing processes could be, for instance, the occurrence of syn 1,3-substitution (vide supra) and/or the initial formation of the cation $\mathrm{Ph^{+}CHC{\equiv}CH}$. A rapid racemization of **1a** by $\mathrm{HCuX_2}$ prior to its conversion into **2** is not likely as we found that, after treatment of **1a** with less than 1.0 equiv of $\mathrm{HCuX_2}$ (studied for X = Cl, Br) followed by recovering and analysis of unconverted **1a**, no detectable racemization of **1a** had taken place. In some separate experiments the methyl ether of **1a**, (*R*)-$\mathrm{PhCH(OMe)C{\equiv}CH}$ (**1b**),[11] and the sulfinate ester of **1a** ($R_c$)-$\mathrm{PhCH(OS(O)Me)C{\equiv}CH}$ (**1c**)[11] were reacted with $\mathrm{HCuX_2}$. Ether **1b** reacted much slower with $\mathrm{HCuX_2}$ than alcohol **1a**. When X in the cuprate was I, no satisfactory conversion could be realized. When X was Cl or Br, the allenes **2b** and **2c** were obtained in excellent yield (≥95%) by reaction of **1b** with 2.0 equiv of $\mathrm{HCuX_2}$ during 30 min at 25 °C. Within experimental error the enantiomeric purities of the formed levorotatory allenes **2b** and **2c** were identical with those found starting from **1a**. However, the reaction of optically pure sulfinate ($R_c$)-**1c** with $\mathrm{HCuCl_2}$ and $\mathrm{HCuBr_2}$ proceeded with better anti stereoselectivity. Thus, treatment of **1c** at 25 °C with 1.0 equiv of $\mathrm{HCuCl_2}$ during 2 min or with 1.0 equiv of $\mathrm{HCuBr_2}$ during 0.5 min, quantitatively produced levorotatory **2b** and **2c** showing $[\alpha]^{20}_{\mathrm{D}}$ values (in EtOH) of −150° and −630°, respectively. These specific rotations correspond to ee values of 24% for (*R*)-**2b** and 52% for (*R*)-**2c**.[6] From other work it is known that the sulfinate group is an excellent leaving group in organocopper(I) reactions.[10b,c] The increased stereoselectivity obtained by using this group is undoubtedly due to an increased contribution of the reaction mode of eq 2 to the substitution process (replace the OH function in eq 2 by OS(O)Me). Interestingly, also the reaction of ($R_c$)-**1c** with $\mathrm{HCuI_2}$ showed anti stereoselectivity, albeit to a small extent (ee ≃ 6%).[6]

To summarize, the presented study shows that syn stereoselectivity is not a general feature for the 1-haloallene formation from propargylic alcohols by using the Landor reagent. Comparison of Landor's data with those presented here indicates that the nature of the substituents at the propargylic center of the starting alcohol may importantly influence the stereochemical course of the allene formation. The study further shows that the Landor reagent can also be used to substitute groups other than hydroxyl, in the case of the sulfinate group even with a better stereochemical result.

## Experimental Section

**General Procedures.** All reactions were carried out in an inert atmosphere of dry nitrogen. Optical rotations were measured in a Perkin-Elmer Model 241 polarimeter by using standard cuvettes (*l* = 10 cm) at 20 °C.

**Materials.** Aqueous solutions of hydrochloric acid (37%, w/w), hydrobromic acid (47% w/w), and hydroiodic acid (57%, w/w) were purchased from Merck-Darmstadt. Hydroiodic acid was distilled prior to use. The copper(I) halides were obtained according to the method of Keller and Wycoff.[12] Optically pure (*R*)-(−)-$\mathrm{PhCH(OH)C{\equiv}CH}$ (**1a**; $[\alpha]^{25}_{\mathrm{D}}$ 20.8°, in dioxane) was prepared according to our procedure.[5] Optically enriched (*R*)-(−)-$\mathrm{PhCH(OMe)C{\equiv}CH}$ (**1b**; $[\alpha]^{20}_{\mathrm{D}}$ −29.0°, in EtOH; ee 50%) was obtained by adding, at −60 to −50 °C, 13.5 mL of *n*-butyllithium (1.50 M) in hexane to a stirred solution of 2.64 g of **1a** (20.0 mmol, ee 50%) in 60 mL of dry THF. After 5 min, 10 mL of dimethyl sulfoxide and 5.8 g of methyl iodide (58.0 mmol) were successively added. The mixture was stirred during 1.0 h at 25 °C and then poured into 200 mL of an aqueous $\mathrm{NH_4Cl}$ solution. The product was extracted with pentane/ether (80/20 v/v, 2 × 100 mL). The combined extracts were washed with a dilute $\mathrm{NH_4Cl}$ solution (5 × 300 mL), dried with $\mathrm{K_2CO_3}$, and concentrated in vacuo, yielding colorless **1b** in 94% yield and in high purity (>98% by GLC). The methanesulfinate ($R_c$)-(−)-$\mathrm{PhCH(OS(O)Me)C{\equiv}CH}$ (**1c**; $[\alpha]^{20}_{\mathrm{D}}$ −15.8°, in EtOH, ee 25%)[13] was prepared from (*R*)-**1a** (ee 25%) and methanesulfinyl chloride by using triethylamine as a base.[10b]

**General Procedure for the Conversion of 1a–c into Allenic Halides 2a–c.** Compounds **1a–c** (3.0 mmol) were added, at 25 °C, to a solution of $\mathrm{HCuX_2}$ (3.0 or 6.0 mmol, see text) in water. After shaking the resulting mixture during 0.5–30 min (see text), the products were isolated by extraction with pentane (4 × 10 mL). The combined extracts were washed once with 10 mL of concentrated HX (see under Materials paragraph) in order to remove CuX and then with a dilute aqueous $\mathrm{K_2CO_3}$ solution in order to remove all acid. The extracts were dried with $\mathrm{K_2CO_3}$; and the solvent was evaporated in vacuo. The obtained allenes proved to be identical with those already described in ref. 1. The $[\alpha]_{\mathrm{D}}$ values were determined immediately (X = I; column chromatography caused some racemization) or after column chromatography (X = Cl or Br; $\mathrm{Al_2O_3}$ + 5% $\mathrm{H_2O}$, elution with pentane). In the latter cases only a slight increase of the rotations was observed by the chromatographic purification. The required cuprates $\mathrm{HCuX_2}$ were obtained by shaking, at 25 °C, CuX (3.0 or 6.0 mmol) during 2 min with an equimolar amount of HX in water (for concentrations of HX, see under Materials paragraph).

**Acknowledgment.** This investigation was supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for the Advancement of Pure Research (ZWO).

**Registry No.** (*R*)-(−)-**1a**, 61317-73-5; (*R*)-(−)-**1b**, 89178-57-4; (*R*)-(−)-**1c**, 70000-50-9; (*S*)-(+)-**2a**, 81158-19-2; (*R*)-(−)-**2b**, 68276-38-0; (*R*)-(−)-**2c**, 89178-58-5; $\mathrm{HCuCl_2}$, 18460-62-3; $\mathrm{HCuBr_2}$, 43403-59-4; $\mathrm{HCuI_2}$, 87890-94-6; CuI, 7681-65-4; HI, 10034-85-2; HCl, 7647-01-0; HBr, 10035-10-6; CuCl, 7758-89-6; CuBr, 7787-70-4.

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(9) The copper(III) concept is frequently used to explain organocopper(I)-induced cross-coupling reactions, but its validity is still a matter of discussion. It has been critized, for instance, by: Pearson, R. G.; Gregory, C. D. *J. Am. Chem. Soc.* **1976**, *98*, 4098. These authors believe that Cu(II) rather than Cu(III) species are involved.

(10) See, for related mechanistic proposals, for instance: (a) Luche, J. L.; Barreiro, E.; Dollat, J. M.; Crabbé, P. *Tetrahedron Lett.* **1975**, 4615. (b) Vermeer, P.; Westmijze, H.; Kleijn, H.; Van Dijck, L. A. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 56. (c) Oostveen, E. A.; Elsevier, C. J.; Meijer, J.; Vermeer, P. *Ibid.* **1982**, *101*, 382.

(11) In practice no optical pure **1b** and **1c** were used. Compound **1b** mainly consisted of the *R* enantiomer (ee 50%); for compound **1c** the ee value for the $R_c$ compound amounted to 25%. The indicated $[\alpha]_{\mathrm{D}}$ values for **2b** and **2c** obtained from these substrates are extrapolated values and refer to optically pure substrates.

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(13) Hydrolysis of the ester showed that no loss of enantiomeric purity had occurred during its preparation.

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# Hydrogen Abstraction Selectivities for Ground-State, $S_\pi$, and Excited-State, $S_\sigma$, Succinimidyl Radicals: Cyclopentane/Cyclohexane. Origins and Resolution of Disputed Data[1]

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Three distinctive hydrogen abstractors have been recognized[2-10] in systems containing $\mathrm{Br_2}$ and NBS: Br, $S_\pi$, and $S_\sigma$. The search for limiting conditions in which these radicals exhibit their properties singularly has been the challenge in this field. Confusion has in all instances been traced to reaction conditions that allow two or even all three hydrogen abstractors to operate simultaneously.

Tanner and co-workers[1] have reported data which is claimed to refute the $S_\pi$–$S_\sigma$ rationalization of succinimidyl radical behavior. Their reaction conditions have been shown to be those for simultaneous involvement of three hydrogen-abstracting chain carriers, Br·, $S_\pi$, and $S_\sigma$ in varying proportions. In our hands this same competitive system, cyclopentane/cyclohexane, showed the following relative rates under limiting conditions which elicit separately the singular behavior of the hydrogen abstractors: Br 8.9, $S_\pi$ 1.25, and $S_\sigma$ 0.88. This is a substantial contradiction of their claims.

A hydrogen abstractor less selective than Br· was first recognized in NBS systems by Traynham and co-workers in 1972;[11] they presented additional evidence[12] in 1974 and identified this new radical as succinimidyl. Their review of the literature pointed to earlier isolated observations which they could interpret as consistent with their succinimidyl assignment. In 1974 we recognized the reason why NBS reagent can operate with Br· carrier in Ziegler allylic brominations employing $CCl_4$ solvent and with succinimidyl behavior in $CH_2Cl_2$, $CHCl_3$, or $CH_3CN$ solvents: The solubility of NBS in $CCl_4$ is insufficient for the rate of R· + NBS → RBr + S to contribute noticeably under Ziegler conditions.[13]

In 1978 we initiated publication of our work demonstrating that under conditions which exclude a Br· carrier, two clearly distinguishable, more reactive hydrogen abstractors operate;[2,3] these were assigned $S_\pi$ and $S_\sigma$ structures. Since then our focus has been the definition of reaction conditions suitable for characterization of each of these hydrogen abstractors.

## Limiting Conditions

**Bromine Atom.** With many substrates $Br_2$ in nonpolar solvents often provides clean Br· hydrogen abstractions. The presence of hydrogen bromide may distort the selectivities by reversal of the hydrogen abstraction step, an effect that becomes apparent with massive accumulation of this reaction product. Hydrogen bromide has been removed with a variety of scavengers to preclude this effect (NBS,[14] anhydrous $K_2CO_3$, ethylene oxide, etc.). Although on occasion there are some minor complications in the use of these scavengers,[15] the selectivities of the bromine atom are uniformly identical.

**$S_\sigma$.**[2,4] *N*-bromo- or *N*-chlorosuccinimides are good sources if halogen scavengers are present, such as ethylene, *tert*-butylethylene, vinylidene chloride, etc., to avoid competing halogen atom hydrogen abstractions. A fast competitive reaction of $S_\sigma$ is the *reversible* ring opening to $\cdot CH_2CH_2CONCO$, which is substantially converted to β-bromopropionyl isocyanate (BPI) in the presence of NBS but not in the presence of NCS (the latter traps alkyl radicals $10^2\times$ slower).[10]

$S_\sigma$ radicals show a remarkable similarity to Cl· in hydrogen abstractions and additions to alkenes or arenes.[2–4,8,10]

Theoretical treatments have shown that ring opening is symmetry allowed for $S_\sigma$ but not for $S_\pi$.[16]

**$S_\pi$.**[2–10] Three useful methods are available at present for generating this variety of succinimidyl, for which a recent ESR spectrum[17] has confirmed the $S_\pi$ structure for the ground state. *The three methods generate hydrogen abstractors from NBS that exhibit identical selectivities*[9,10] *and are free of the ring-opening reactions.*[2–10]

**Method A**[5,9] employs NBS in $CH_2Cl_2$ or $CHCl_3$ solvent with vinylidene chloride scavenger (for $Br_2$ and Br·), with approximately 0.3 mole fraction $BrCCl_3$.

This method involves trapping of alkyl radicals by $BrCCl_3$. The $CCl_3$ radicals react with NBS to make $S_\pi$. Under these conditions it was demonstrated that $CCl_3$ does not participate in H abstractions: no $HCCl_3$ is produced, and when $DCCl_3$ is added to the reaction mixture it is recovered quantitatively, undiluted by $HCCl_3$.[9] With 21% conversion of NBS under these conditions no BPI was detected.[9]

**Method B**[5,9,10] employs the same system as A, except that *tert*-butylethylene is also equally effective, and approximately 2.5 M benzene is used in place of the $BrCCl_3$.

This method depends on rapid trapping of $S_\sigma$ by benzene to make a cyclohexadienyl radical, which in turn reacts with NBS to make $S_\pi$.[5,10] With a variety of substrates and with NBS conversions of 50–60%, we have not detected BPI as a product.[10] In exactly analogous work with the 2,2-dimethylglutarimidyl[10] radical and larger conversions of the NBG, the $S_\sigma$ conditions give 95% ring opening, and with these same benzene-$S_\pi$ conditions there is no detectable ring opening of this glutarimidyl radical.

**Method C**[2–10] employs $Br_2$ and NBS in $CH_2Cl_2$ or $CHCl_3$ solvents, with $[Br_2] > 10^{-2}$ M and [NBS] at its saturation concentrations (0.1–0.2 M).

This method depends on S· generation in the thermoneutral reaction of Br· with NBS. With the substrates $CH_2Cl_2$, *tert*-butyl chloride, 2,2-dichloropropane, and neopentane, the selectivities are distinctly different from Br· selectivity, and independent of considerable variation in $[Br_2]$. With extensive conversion of NBS, no BPI is detected under these conditions, and it has been demonstrated that BPI introduced into the system survives unchanged.[4,5,9]

These compositions were developed to ensure that $S_\pi$ was the major chain carrier. The rationales for these "recipes" have been delineated elsewhere.[2–5,9] Method C is the most limited of the three methods since it is applicable without ambiguity only if the substrate is relatively unreactive to Br· attack.[2] We have been able to use method C for $S_\pi$ studies with neopentane, methylene chloride,

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*tert*-butyl chloride, and 2,2-dichloropropane. For these substrates methods A–C show identical selectivities and no ring opening to BPI.[9,10] With more reactive substrates (for example secondary C–H) method C operates with Br· only.[2] The advantage of methods A and B result from the presence of alkenes that serve as scavengers for Br· and $Br_2$, so that these methods can operate with $S_\pi$ as the major hydrogen abstractor over a wide range of substrate reactivities.

### Cyclopentane/Cyclohexane Brominations with Br•, $S_\sigma$, and $S_\pi$

With this background we address *the recent report*[1] *that BPI is formed in the presence of* $Br_2$ and the accompanying conclusion[1] that *if two states of succinimidyl exist, they are chemically indistinguishable.*

It is noteworthy that this report (a) presents again an alternative explanation based on a mix of chain carriers, Br· and S·, which has been substantially addressed,[9] for these NBS systems, and (b) *the authors make no attempt to integrate into their mechanism the extensive assortment of published observations which are consistent with the* $S_\pi$–$S_\sigma$ *hypothesis.* In their narrowly based set of cyclopentane–cyclohexane competition studies they did not find the limiting conditions for $S_\pi$ behavior. In fact, the "$S_\pi$ behavior" they employed (essentially method C) for this cycloalkane competition could not be used for this purpose because with these substrates Br· is the sole carrier (vide infra). We address here the narrow challenge they have raised by reexamining the same cycloalkane competitions in the presence of alkenes, to avoid the Br· chain (methods A and B).

To avoid clouding of the issue, we have done single experiments employing our standard procedures for $S_\sigma$, $S_\pi$, and Br. These experiments show the singular behavior of these carriers, exactly as is reported elsewhere for a broad range of substrates.

We present below competitive brominations of cyclopentane/cyclohexane mixtures under the limiting conditions to elicit the distinctive behavior of the three potential chain carriers.

$S_\sigma$[4]

$[c\text{-}C_5H_{10}] = 1.00$ mL (1.77 M)
$[c\text{-}C_6H_{12}] = 0.90$ mL (1.54 M)
NBS = 0.30 g (1.7 mmol)
$[CH_2{=}CCl_2] = 0.080$ mL (0.15 M)
4.0 mL $CH_2Cl_2$

$c\text{-}C_5H_9Br$ 0.298 mmol
$c\text{-}C_6H_{11}Br$ 0.289 mmol
BPI 0.48 mmol

$$\frac{k_{c\text{-}C_5H_{10}}}{k_{c\text{-}C_6H_{12}}} = 0.88$$

irradiated 2.5 h through Pyrex, heterogeneous initially, homogeneous after 2.5 h

This relative rate is essentially the same as reported by Tanner et. al.[1] in the presence of $C_2H_4$ and for the chlorination with $Cl_2$.[18]

$S_\pi$: Method A[5]

$[c\text{-}C_5H_{10}] = 1.00$ mL (1.77 M)
$[c\text{-}C_6H_{12}] = 0.90$ mL (1.54 M)
NBS = 0.30 g (1.7 mmol)
$[CH_2CCl_2] = 0.080$ mL (0.16 M)
2.0 mL $BrCCl_3$
2.0 mL $CH_2Cl_2$

$c\text{-}C_5H_9Br$ 0.0235 mmol
$c\text{-}C_6H_{11}Br$ 0.016 mmol
BPI 0[19]
$CHCl_3$ 0[19]

$$\frac{k_{c\text{-}C_5H_{10}}}{k_{c\text{-}C_6H_{12}}} = 1.2$$

irradiated 4.5 h through Pyrex; heterogeneous throughout

$S_\pi$: Method B[5,9,10]

$[c\text{-}C_5H_{10}] = 1.00$ mL (1.77 M)
$[c\text{-}C_6H_{12}] = 0.90$ mL (1.54 M)
NBS = 0.30 g (1.7 mmol)
$[CH_2{=}CCl_2] = 0.080$ mL (0.14 M)
2.0 mL $C_6H_6$
2.0 mL $CH_2Cl_2$
0.08 mmol di-*tert*-butyl peroxyoxalate

$c\text{-}C_5H_9Br$ 0.0381 mmol
$c\text{-}C_6H_{11}Br$ 0.0220 mmol
BPI 0[19]

$$\frac{k_{c\text{-}C_5H_{10}}}{k_{c\text{-}C_6H_{12}}} = 1.3$$

maintained at 30 °C, 4.5 h, heterogeneous throughout

Br·: Method C[2,5,9,14]

$[c\text{-}C_5H_{10}] = 1.00$ mL (1.52 M)
$[c\text{-}C_6H_{12}] = 1.00$ mL (1.32 M)
NBS = 0.30 g (1.7 mmol)
$[Br_2] = 0.028$ M
5.0 mL $CH_2Cl_2$

$c\text{-}C_5H_9Br$ 0.973 mmol
$c\text{-}C_6H_{11}Br$ 0.095 mmol
BPI 0[19]
SH 1.7 mmol

$$\frac{k_{c\text{-}C_5H_{10}}}{k_{c\text{-}C_6H_{12}}} = 9.0$$

irradiated 1.5 h through Pyrex to the discharge of color

Br·: Method D[9,15]

$[c\text{-}C_5H_{10}] = 1.00$ mL (1.52 M)
$[c\text{-}C_6H_{12}] = 1.00$ mL (1.32 M)
$[Br_2] = 0.10$ mL (0.28 M)
1.53 g $K_2CO_3$ (anhydrous)
4.0 mL $CH_2Cl_2$

$$\frac{k_{c\text{-}C_5H_{10}}}{k_{c\text{-}C_6H_{12}}} = 8.8$$

irradiated 0.5 h through Pyrex for complete decolorization

These values are essentially the same as those reported by Tanner et. al.,[1] and earlier by Traynham and Lee,[12] employing $Br_2$ only.

### Conclusions

1. Three distinctive selectivities are exhibited by Br·, $S_\sigma$, and $S_\pi$ radicals.
2. There is no ring opening under the $S_\pi$ conditions of methods A, B, or C.
3. These results are in complete accord with all of our earlier reports.
4. At present there is no indication for alteration of the $S_\pi$–$S_\sigma$ rationalizations.

### Origins and Resolution of the Disputed Data

There is agreement between all authors on the selectivity of Br· in this system.

There is also agreement on $S_\sigma$ selectivity. Tanner and co-workers, using our NBS–alkene method obtained selectivity values of 0.8–0.9, in excellent agreement with our value of 0.88.

The 1974 Traynham and Lee's selectivity of 1.65 was obtained by using NBS alone, since the beneficial effect of an olefin scavenger had not yet been recognized. This value is attributable now to early involvement of $S_\sigma$ and later in the reaction to involvement of $S_\pi$ or Br or both.

Traynham and Lee did not use reaction conditions that might have generated singularly an $S_\pi$ carrier.

Tanner and co-workers used only a variation on method C to probe $S_\sigma$ behavior, and that with initial concentrations of 0.03–0.04 M NBS and 0.002–0.01 M $Br_2$; also these

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[18] Srinivasan, R.; Sontagg, F. I. *Can. J. Chem.* **1969**, *47*, 1627.
[19] See Experimental Section.

values diminish during the course of the reaction. These concentrations are too low for limiting conditions and thus the variation of selectivities from 1.8 to 8.5 with increasing bromine concentration which they report can be understood. They are the result of hydrogen abstractions with variable mixtures of $S_\sigma$, $S_\pi$, and Br chain carriers. It is noteworthy that even with the low concentrations of bromine they employed, with increasing bromine concentration, the BPI yields they report approach the value of zero we report at $[Br_2] > 10^{-2}$ M. There would have been agreement if their studies had been used to explore the trend of their data.

The choice of only method C, by Tanner and co-workers, for cyclopentane/cyclohexane in probing the properties of $S_\pi$ was unfortunate since these secondary C–H systems operate efficiently with the Br· mediated chains. However, methods A and B can be used unambiguously on these systems for determining the selectivity with $S_\pi$ since these "recipes" eliminate both Br· and $S_\sigma$ as competitive hydrogen abstractors.

## Experimental Section

All experiments are carried out as described earlier,[2–5,9] with repeated high vacuum degassing to eliminate oxygen. Photoinitiations were carried out with a medium-pressure mercury arc filtered through several layers of Pyrex. The volatile fraction, $C_6H_{11}Br$, $C_5H_9Br$, and $CHCl_3$ (detection limit 0.004 mmol) were analyzed by gas chromatography using an internal standard. BPI was recognized in the crude reaction mixture by its strong IR absorption at 2245 cm$^{-1}$ and separated when present from the nonvolatiles by vacuum trap to trap distillation into a −10 °C trap, followed by $^1$H NMR analysis with an internal standard.

**Analysis of BPI.** $^1$H NMR ($CDCl_3$): $\delta$ 3.05 (t, 2 H, $J$ = 3 Hz), 3.55 (t, 2 H, $J$ = 3 Hz), detection limit (0.02 mmol). IR ($CH_2Cl_2$, cm$^{-1}$): most prominent band at 2245 (SNCO), 1735 (m), 1400 (m), 1070 (m), detection limit (0.006 mmol).

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**Registry No.** Cyclopentane, 287-92-3; cyclohexane, 110-82-7; succinimidyl, 24344-83-0.

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# Reactions of Unsaturated Carbenes with Metal–Metal Bonds. Insertion Reactions with Se–Se and Te–Te Bonds

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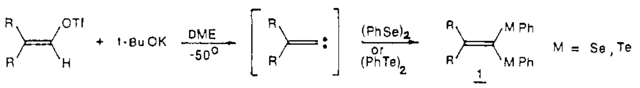
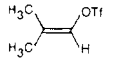
In recent years, the organic compounds of selenium and tellurium have proved to have an extremely rich chemistry. Their properties have aroused interest in many areas from synthesis[1] to use as electrical conductors.[2] Of particular interest are the compounds containing two heteroatoms bonded to the same carbon center, in which the substituent effects can greatly influence the reactivity of that site and may provide for a series of unique transformations about the carbon skeleton.[3]

However, little information is available in the case where two chalcogen groups are bound to an sp$^2$ hybridized carbon. Jensen and Henriksen reported the synthesis of such compounds in 1970 by the reaction of carbon diselenide with active methylene compounds.[4] Similar diselenides were prepared by Gröbel and Seebach via the Peterson olefination reaction.[5] No studies of possible synthetic utility of these compounds have been published to our knowledge, perhaps due to the lack of an easy high-yield preparation of these systems.

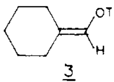
Scheme I



It occurred to us that our previous work with unsaturated carbenes[6] might provide a simple pathway to compounds of this type via the insertion reaction shown in Scheme I. Literature data showed that these metal–metal bonds were indeed reactive to insertion by saturated carbenes,[7] and while not truly analagous the sulfur–sulfur bond of disulfides had been reacted with both saturated[8] and unsaturated carbenes.[9] We therefore began a study of diphenyl diselenide and diphenyl ditelluride with triflates **2** and **3**.



2



3

In practice, the reactions proved to be easily performed and isolation and purification are quite straightforward. Reaction temperatures of −50 to −55 °C were maintained with a cold bath of bis(2-ethoxyethyl) ether and dry ice. Higher temperatures gave lower yields of product while lower temperatures led to solubility problems, especially with diphenyl ditelluride. No noticeable color change occurs during addition of *tert*-butoxide, and after changing solvent to hexane and filtering the precipitated salts, TLC shows only two major components present. These are easily isolated in pure form by column chromatography. The organic byproducts of the reaction come off the column well ahead of the highly colored band of excess trap. Since diphenyl diselenide and diphenyl ditelluride are fairly expensive, the recovery of highly pure unreacted starting material is an additional advantage in this method. The almost colorless carbene adduct follows soon after the last of the excess starting material, and this band is best monitored by TLC. Removal of the solvent at reduced pressure gives the products as viscous oils. Yields and spectral data are listed in Table I.

Spectra data matches well with expectations. The IR spectrum shows the monosubstituted phenyls, aliphatic C–H bands, and a weak carbon–carbon double bond in the area of 1730 cm$^{-1}$, which agrees well with the literature.[4] The mass spectra is very diagnostic due to the large number of isotopes of selenium and tellurium. In all cases, the calculated molecular ion isotope pattern matches extremely well with the experimental isotope pattern. The most abundant isotope of the pattern has been listed for each compound in Table I.

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