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[5] The reaction of poly(**2a**) with ethyl vinyl ether (twofold excess with respect to the hydroxy moieties) was carried out in the presence of *p*-toluenesulfonic acid (1.0 mol%) in DMSO at 50°C for 10 min. Addition to water precipitated a polymer in 98% yield whose acetal content was confirmed to be quantitative by ^{1}H NMR spectroscopy. The polymer thus obtained is soluble in various organic solvents including MeOH, THF, benzene, hexane, and CH_2Cl_2.

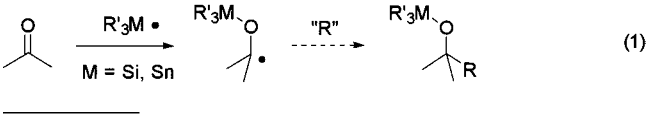
[6] Both poly(**2b**) and poly(**2c**) have high solubility in THF, a poor solvent for poly(**2a**). Thus, the GPC measurements were performed without treatment with ethyl vinyl ether.

[7] Since the block copolymer is soluble in THF, benzene, and CH_2Cl_2 which reflects the solubility of poly(**3**) segment, the GPC measurement was also performed directly without treatment with ethyl vinyl ether, and gave a unimodal elution peak ($M_n = 8.3 \times 10^3$, $M_w/M_n = 1.12$).

Novel Group-Transfer Three-Component Coupling of Silyltellurides, Carbonyl Compounds, and Isocyanides[**]

Hiroshi Miyazoe, Shigeru Yamago,[*] and
Jun-ichi Yoshida[*]

Silyl and stannyl radicals add to the carbonyl oxygen atom to generate α-alkoxy radicals, and this is an elemental step in the radical-mediated reduction of carbonyl compounds with silyl and stannyl hydride reagents.[1, 2] Addition of the α-alkoxy radicals to radical acceptors would form a new C–C bond [Eq. (1)].[3] Indeed, α-stannyloxy radicals thus formed have been utilized for intramolecular C–C bond formation,[4] but there is no report on the intermolecular version, probably because reduction of the α-alkoxy radical by the metal hydride competes with C–C bond formation. Since organotellurium compounds are excellent precursors for carbon-centered radicals,[5, 6] we envisaged that silyl tellurides would act as silyl radical precursors which do not contain reducing hydrido groups.[7] We examined reactions of silyl tellurides in the presence of several radical acceptors and found a new coupling reaction of phenyl trimethylsilyl telluride (**1**), carbonyl compounds, and phenyl isocyanide [Eq. (2)]. Here we report on this new three-component coupling reaction, which is of both mechanistic and synthetic interest.



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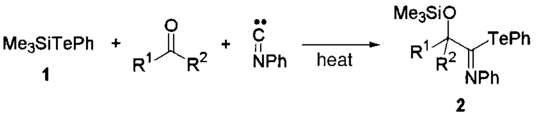
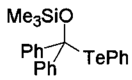


(2)

The coupling reaction of **1**,[8] benzophenone, and phenyl isocyanide proceeded under mild thermal conditions, and the group-transfer product **2a** ($R^1 = R^2 = Ph$) was formed in 82% yield after heating at 100°C for 12 h in propionitrile. The tellurium atom plays a crucial role in this reaction, and the use of the corresponding silyl selenide or sulfide led to complete recovery of the starting materials. In addition, various silyl and stannyl hydrides did not promote C–C bond formation, and either the recovery of the starting materials or the reduction of the carbonyl group was observed. Monitoring the reaction in CD_3CN by ^{1}H NMR spectroscopy indicated that the formation of the α-silyloxytelluride **3** competed with that of **2a** and that the amount of **3** gradually decreased with the progress of the reaction. Indeed, isolated **3** reacted with phenyl isocyanide at 100°C to give **2a** in 92% yield. The coupling reaction was inhibited by the addition of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) radical (1.0 equiv) and mainly afforded silylated TEMPO **4** (63%); this suggests the intermediacy of trimethylsilyl radicals. The reaction proceeded faster in polar solvents such as propionitrile, DMF, and pyridine than in nonpolar solvents such as toluene, and the smooth reaction in basic media also ruled out the involvement of carbocation intermediates.[9]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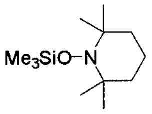
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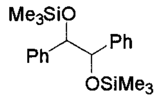
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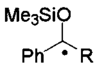
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The present reaction is generally applicable to a variety of ketones and aldehydes, and its scope and efficiency are summarized in Table 1. Aromatic ketones reacted smoothly and gave the desired adducts in high yields when almost equimolar quantities of each reagent were used (entries 1–6). Aliphatic ketones and aldehydes also gave the desired adducts in good yields (entries 7 and 8), but they were slightly less reactive than aromatic ketones. The reaction of benzaldehyde

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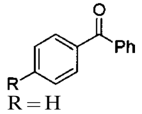
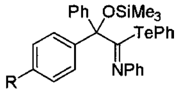
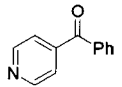
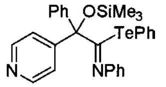
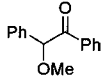
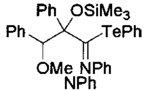
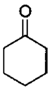
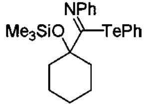
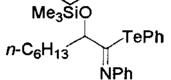
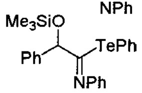
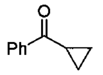
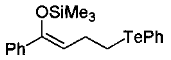
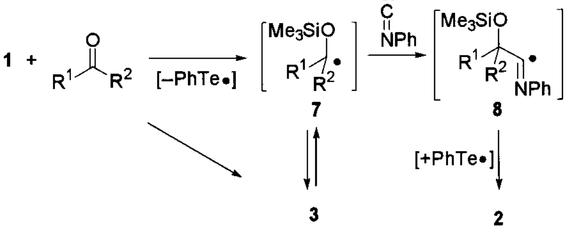
Table 1. Three-component coupling reactions.[a]

Entry	Carbonyl compound	t [h]	Product	Yield [%]
1	 R = H	12		82
2	R = OMe	24		73
3	R = NMe$_2$	12		84
4	R = Cl	12		39 (63)[b]
5		24		48[c] (81)[b]
6		24		56[d] (73)[b]
7		12		61[e]
8	n-C$_6$H$_{13}$CHO	12		55[e]
9	PhCHO	12		46[f, g]
10		12		93

[a] The reaction was carried out by heating a solution of **1** (1.1 equiv), carbonyl compound (1.0 equiv), and phenyl isocyanide (1.1 equiv) at 100 °C in propionitrile. [b] Yield based on converted carbonyl compound. [c] Two equivalents of phenyl isocyanide were used. [d] A 55:45 mixture of diastereomers was obtained. [e] Reaction was carried out at 120 °C with two equivalents of phenyl isocyanide. [f] Reaction was carried out in toluene. [g] The dimer **5** was formed in 54% yield.

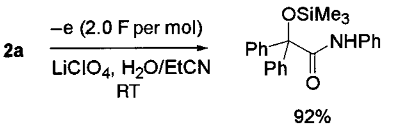
gave the desired coupling product in moderate yield together with the dimer **5** (entry 9), which was probably formed by homocoupling of the α-siloxy radical **6a** (R = H). The generation of the α-siloxy radical species was further confirmed by the reaction of cyclopropyl phenyl ketone, and the ring-opened alkyl telluride, formed by the cyclopropylmethyl radical rearrangement of **6b** (R = cyclopropyl),[10] was obtained as the sole product (entry 10).

The formation of **3** and **5** suggests the most probable reaction pathway involves the generation of the silyl radical from **1** and its addition to the carbonyl compound (Scheme 1).[11] Subsequent reaction of the resulting radical **7** with isocyanide gives the imidoyl radical **8**, which undergoes a group-transfer reaction, presumably with **1**, to form **2**. The radical **7** also undergoes a group-transfer reaction to give **3**. However, **3** acts as a dormant species that regenerates **7** under the reaction conditions. At present, however, other possibilities, including the ionic reaction of **1** and carbonyl compounds to generate **3**, cannot be rigorously ruled out.



Scheme 1. Probable reaction pathway for the formation of **2**.

Besides the novelty of the reaction type, the synthetic utility of the present reaction is noteworthy. The product **2** could be transformed into a variety of α-hydroxy carbonyl compounds by exploiting the reactive C–Te bond.[12] For example, oxidative hydrolysis of **2a** afforded the corresponding α-silyloxy amides [Eq. (3)].[6c] Experiments to ascertain the precise mechanism as well as the further synthetic explorations are currently under investigation.[13]



(3)

Experimental Section

2a: A mixture of **1** (151.2 mg, 0.55 mmol), benzophenone (91.1 mg, 0.50 mmol), and phenyl isocyanide (56.2 mg, 0.55 mmol) in propionitrile (0.5 mL) in a sealed tube was heated at 100 °C for 12 h. Removal of the solvent followed by purification on silica gel afforded **2a** as light orange oil (232.5 mg, 0.41 mmol, 82%). IR (neat): $\tilde{\nu} = 1660$, 1595, 1485, 1445, 1250, 1210, 1170, 1100, 1070, 925, 885, 840, 800, 760, 730, 690, 640 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = -0.01$ (s, 9H), 6.47–6.50 (m, 2H), 6.69–6.74 (m, 3H), 6.80–6.86 (m, 2H), 6.90–6.96 (m, 1H), 7.01–7.04 (m, 2H), 7.36–7.44 (m, 6H), 7.61–7.65 (m, 4H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 1.6$, 88.3, 114.7, 118.0, 123.4, 126.8, 127.7, 127.8, 128.1, 128.2, 130.0, 140.4, 142.9, 149.0, 169.5; FAB-MS (3-nitrobenzyl alcohol): m/z: 566 [M+H]$^+$; elemental analysis calcd for C$_{29}$H$_{29}$NOSiTe (%): C 61.84, H 5.19, N 2.49; found: C 61.81, H 5.28, N 2.47.

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[11] While the direct observation of silyl radicals by ESR spectroscopy failed, a spin-trapping experiment with **1** and *N-tert*-butyl-*α*-phenylnitrone (1 equiv) in benzene at 50 °C resulted in detection of the corresponding nitroxyl radical at $g = 2.0059$ with $a_N = 1.41$ mT and $a_H = 0.21$ mT. For spin trapping of trimethylsilyl radicals, see: a) B. B. Adeleke, S.-K. Wong, J. K. S. Wan, *Can. J. Chem.* **1974**, *52*, 2901; b) H. Chandra, I. M. T. Davidson, M. C. R. Symons, *J. Chem. Soc. Perkin Trans. 2* **1982**, 1353.

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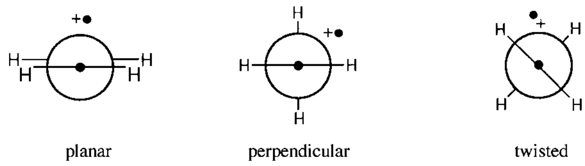
Structural Characterization of Novel Olefinic Cation Radicals: X-ray Crystallographic Evidence of σ–π Hyperconjugation[**]

Jay K. Kochi[*], Rajendra Rathore, Chengjian Zhu, and Sergey V. Lindeman

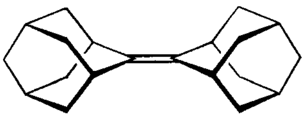
Alkyl-substituted ethylene cation radicals are highly reactive intermediates that occur when a variety of electrophilic addition reactions such as epoxidation, hydroxylation, ozonation, oxidative cleavage, dimerization, and cationic polymerization[1–3] proceed by prior electron transfer. As early as 1947, Mulliken and Roothaane[4] predicted the structure of the parent ethylene cation radical to be twisted by 30° due to the contributions from both the planar structure (normal π bonding) and the perpendicular structure (hyperconjugative bonding) (Scheme 1).



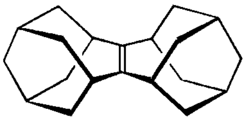
Scheme 1. Predicted structures of the parent ethylene cation radical.

Owing to the importance of ethylene as a precursor in polyethylene production, its cation radical has been subject to scrutiny in great detail using highly sophisticated theoretical methods including extended basis sets.[5] Experimentally, vacuum ultraviolet studies[6] and photoelectron spectroscopy[7] in the gas phase support a nonplanar structure of ethylene cation radical with a twist of 25°. On the other hand, more recent EPR studies[8] in frozen matrices at 4 K conclude that it can be almost planar (8°). In the last two decades, a number of sterically rigid olefinic cation radicals such as those from adamantylideneadamantane, and pagodadiene have been characterized in solution by using a variety of spectroscopic techniques.[9–11] However, despite enormous theoretical and experimental effort,[12] there is a singular lack of definitive X-ray crystallographic information on the structure of any alkyl-substituted olefinic cation radical.[13]

Herein, we report the successful isolation of the novel cation radical derived from the olefinic donor sesquihomoadamantene (SH), an isomer of the well-known adamantylideneadamantane (AA). Sesquihomoadamantene was originally prepared by Wynberg et al.[14] and it contains a tetrasubstituted double bond with rigid cyclic (cage) substituents.[15] Most importantly, sesquihomoadamantene is planar and singularly nonstrained. Therefore its conversion to the cation radical could reveal the typical structural changes that can be expected upon the oxidative conversion of an olefinic donor.



AA



SH

The one-electron oxidation of sesquihomoadamantene (SH) in dichloromethane at −78 °C either electrochemically[16] or chemically (using the well-known one-electron oxidant nitrosonium hexachloroantimonate)[17] yielded a dark purple solution of the corresponding cation radical, the quantitative formation of which was established spectrophotometrically [Eq. (1)].[18]

$$SH + NO^{+}SbCl_6^{-} \rightarrow SH^{+\bullet}SbCl_6^{-} + NO \qquad (1)$$

The purple salt was isolated as a microcrystalline powder by slow diffusion of toluene into the solution of $SH^{+\bullet}SbCl_6^{-}$ in dichloromethane at −78 °C; and the purity of the highly colored precipitate was determined to be greater than 98 % by iodometric titration.[17] The identity of the isolated cation

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