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(*Z*)–(*E*) Interconversion of Olefins by the Addition–Elimination Sequence of the $(TMS)_3Si^{\bullet}$ Radical[1]

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Tris(trimethylsilyl)silyl radical is effective in isomerizing either acyclic or cyclic olefins by an addition–elimination sequence. The E/Z ratio after equilibration generally reflects the thermodynamic stability of (*Z*)- and (*E*)-alkenes. It has been shown for (*E*)- and (*Z*)-hexen-1-ol that equilibration ($Z/E = 18/82$) is reached with the $(TMS)_3Si^{\bullet}$ radical in 10 h at 80 °C, whereas with $PhS^{\bullet}$ and $Bu_3Sn^{\bullet}$ radicals the same isomeric composition is reached in 1 and 4 h, respectively. In cyclic systems like (*Z*)-cyclododecene the ratio of $Z/E = 46/54$ is reached in 8 h, while with $PhS^{\bullet}$ and $Bu_3Sn^{\bullet}$ it is much slower. An explanation of this phenomenon has been advanced. Additional information on the impact of this addition–elimination methodology in organic synthesis is given.

Introduction

Since the early work on free radical chemistry it has been known that iodine atoms[4a] and thiyl radicals[4b,4c] add reversibly to double bonds. The (*Z*)–(*E*) interconversion of olefins by the addition–elimination sequence of the $PhS^{\bullet}$ radical[5] is now an established methodology in fine chemical synthesis.[6] Furthermore, the addition–elimination concept has also been applied successfully to the synthesis of other elaborate molecules.[8]

Free radical hydrostannation of double bonds is a well established reaction for the preparation of organotin compounds.[9] Like thiyl radicals, stannyl radicals are known to add to a double bond reversibly and therefore, to isomerize alkenes.[10] However, (*Z*)–(*E*) isomerization of olefins by the addition–elimination sequence of $R_3Sn^{\bullet}$ radicals is limited to vinyltins and thus never became a general methodology,[11] the main reason probably being the competitive ionic addition of R_3SnH to olefins which occurs either with opposite stereoselectivity or with a reversed regioselectivity with respect to the free radical path.[9] Oshima and co-workers have shown that the $Ph_3Ge^{\bullet}$ radical is also effective in isomerizing some (*Z*)-alkenes into their thermodynamically more stable (*E*)-isomers.[12]

In the last few years, tris(trimethylsilyl)silane, TTMSS, has proved to be a valid alternative to tri-*n*-butyltin hydride for the majority of its radical chain reactions, although in a few cases the two reagents can complement each other.[13] Furthermore, TTMSS has been used by one of the authors as a hydrosilylating agent of alkenes.[14] These reactions proceed *via* a free-radical chain mechanism (eqs 1 and 2), and no evidence of a competitive ionic path exists. These findings, together with the facts (i) that the Si–H bond in $(TMS)_3SiH$ is ca. 5 kcal mol^{-1} stronger than the Sn–H bond, and 1 kcal mol^{-1} weaker than the Ge–H bond,[15] and (ii) that primary alkyl radicals abstract H atom from TTMSS with a rate constant of 3.8×10^5 M^{-1} s^{-1} at 25 °C[16a] which is 6 times slower and 4 times faster than the analogous reactions with Bu_3SnH[16b] and Bu_3GeH,[16c] respectively, persuaded us to investigate whether the addition of the $(TMS)_3Si^{\bullet}$ radical to olefins (eq 1) is also reversible.[17,18] We report

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(2) Consiglio Nazionale delle Ricerche.

(3) Università di Napoli.

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(6) (a) For a review, see: Sonnet, P. E. *Tetrahedron* **1980**, *36*, 557. (b) Recent examples: the facile (*Z*)–(*E*) interconversion of olefins caused by photochemically generated phenylthio radicals leading to the thermodynamic equilibrium is the key step for the syntheses of the antifungal macrocyclic lactone (−)-gloeosporone,[7a] of the antibiotic-antitumor agent (+)-hitachimycin[7b] and other naturally occuring macrolides.[7c]

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(17) The trimethylsilyl radical adds irreversibly to 1-hexene at temperatures as high as 140 °C. [Bennett, S. W.; Eaborn, C.; Jackson, R. A.; Pearch, R. *J. Organomet. Chem.* **1968**, *15*, 17.]

(18) The trichlorosilyl radical adds reversible to alkenes as evidenced by the (*Z*)–(*E*) interconversion of (*Z*)-2-butene above 150 °C. [Dohmaru, T.; Nagata, Y. *J. Phys Chem.* **1982**, *86*, 4522].

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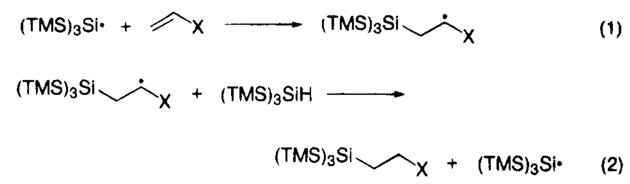
here our results concerning the (*Z*)–(*E*) isomerization of olefins and the impact of this methodology in organic synthesis.



(1)

(2)

Results and Discussion

Thermal Decomposition of Radical Initiators in the Presence of TTMSS. In the present work, the formation of the $(\mathrm{TMS})_3\mathrm{Si}^{\bullet}$ radical was obtained by thermal decomposition of an initiator (mainly AIBN was used) in the presence of TTMSS. Since it is of considerable importance to acquire information regarding the depletion of $(\mathrm{TMS})_3\mathrm{Si}^{\bullet}$ radicals, we first investigated the reaction of TTMSS with some initiators.

A degassed solution of toluene containing 0.3 M of TTMSS and 20 mol % of α,α'-azoisobutyronitrile (AIBN) was heated at ca. 82 °C for 1 h and was analyzed by GC. In agreement with the half-life-time/temperature curve of AIBN,[19] ca. 50% of the initial amount of AIBN was consumed. These results indicate that neither the $(\mathrm{TMS})_3\mathrm{Si}^{\bullet}$ radical-induced decomposition of AIBN nor the addition of TTMSS to the N=N group occur. When $\mathrm{Bu_3SnH}$ replaced TTMSS, the consumption of AIBN was ca. 70%, suggesting the coexistence of at least two different paths. These data are in complete agreement with those of Neumann et al. who have shown, under similar experimental conditions, that 30–35% of the AIBN was hydrostannated at the N=N group.[20]

Organic peroxides undergo $\mathrm{Bu_3Sn}^{\bullet}$ radical-induced decomposition.[21] These processes, which are generally in competition with the reactions of interest, degrade peroxides without adding more radicals to the system. Therefore, peroxides are not suitable initiators in radical-based reactions involving tin hydrides.[22] The decomposition of di-*tert*-butyl peroxide in the presence of TTMSS has been studied in detail.[23] The formation of polysilane in 92% yield, due to the combination of silyl radicals, indicates that the $(\mathrm{TMS})_3\mathrm{Si}^{\bullet}$ radical-induced decomposition of di-*tert*-butyl peroxide is an unfavored process. Preliminary experiments on the thermal decomposition of other organic peroxides (benzoyl peroxide and *tert*-butyl perbenzoate) in the presence of TTMSS and under the experimental conditions used in this work, suggest that the radical-induced decomposition path is also unimportant.[24]

In conclusion, α,α'-azoisobutyronitrile and organic peroxides are not susceptible to $(\mathrm{TMS})_3\mathrm{Si}^{\bullet}$ radical-induced decomposition and hence, their efficiency in radical production is unaffected when tris(trimethylsilyl)silane is used as a radical-based reducing agent.

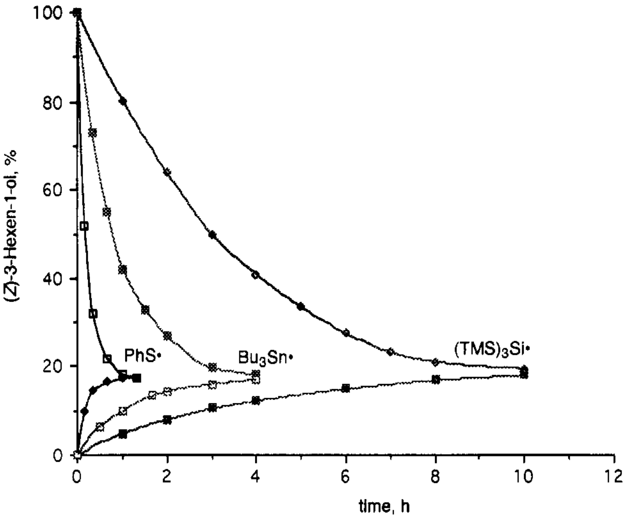


Figure 1. Reaction profile for the interconversion of (*Z*)-3-hexen-1-ol to (*E*)-3-hexen-1-ol and *vice versa* by $(\mathrm{TMS})_3\mathrm{Si}^{\bullet}$, $\mathrm{Bu_3Sn}^{\bullet}$, and $\mathrm{PhS}^{\bullet}$ radicals under identical experimental conditions (80 °C).

(*Z*)–(*E*) Interconversion of Alkenes. TTMSS adds across the double bond of a variety of monosubstituted and *gem*-disubstituted olefins with formation of anti-Markovnikov products in good yields (eqs 1 and 2).[14] On the other hand, TTMSS reacts with *vic*-disubstituted olefins to give the expected hydrosilylation product only when strong electron-withdrawing substituents are present. For example, hydrosilylation of crotononitrile and ethyl crotonate are efficient processes giving the expected product on the basis of polar effects.[14] However, no hydrosilylation product is observed with cyclohexene or similar substrates,[25] although the $(\mathrm{TMS})_3\mathrm{Si}^{\bullet}$ radical is expected to add to 1,2-dialkyl-substituted olefins with a reasonable rate constant.[26]

A solution of 0.2 M of (*Z*)-3-hexen-1-ol, 0.5 equiv of TTMSS, and AIBN (5 mol %) in benzene was refluxed for 10 h. AIBN (5%) was added at 2 h intervals in order to keep the concentration of the initiator nearly constant. The reaction was monitored by GC, and its profile is shown in Figure 1. By replacing the (*Z*)- with the (*E*)-isomer, the same *Z*/*E* ratio, i.e. 18/82, was reached in 10 h. Kuivila and Sommer have shown that (*Z*)- and (*E*)-2-butene are isomerized by $\mathrm{Bu_3Sn}^{\bullet}$ radicals which were obtained by irradiation of tributyltin hydride.[10b] By replacing $\mathrm{Bu_3Sn}^{\bullet}$ with $\mathrm{PhS}^{\bullet}$ (irradiation of PhSPh) Moussebois and Dale observed similar isomerizations.[5a] For a comparison we studied the isomerization of (*E*)- and (*Z*)-3-hexen-1-ol with $\mathrm{Bu_3Sn}^{\bullet}$ and $\mathrm{PhS}^{\bullet}$ radicals derived from $\mathrm{Bu_3SnH}$ and PhSH, respectively. Figure 1 also shows the reaction profile of these isomerizations under identical experimental conditions. The choice of radical does not influence the percentage of the isomeric composition upon equilibration, i.e. *Z*/*E* = 18/82,[27] although the equilibration of the two geometrical isomers is reached

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[19] The temperature required for half-lives of 1 h for α,α-azoisobutyronitrile is 81 °C in benzene or similar solvents (taken from Akzo Chemie catalogue).

[20] Neumann, W. P.; Sommer, R.; Lind, H. *Liebigs Ann.* **1965**, *688*, 14.

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[24] A detailed study on the thermal decomposition of some organic peroxides in the presence of organosilanes is under investigation.

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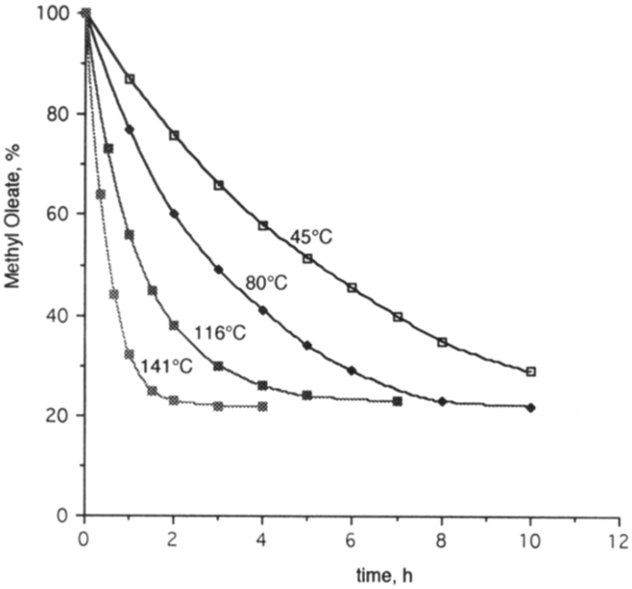
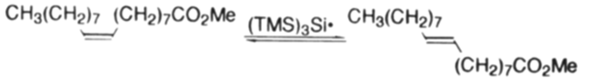


Figure 2. Reaction profile for the interconversion of methyl oleate to methyl elaidate by $(TMS)_3Si^•$ radical at different temperatures (0.5 equiv of TTMSS).

faster with the order $PhS^• > Bu_3Sn^• > (TMS)_3Si^•$. It is worth pointing out that the conversion of the starting material to the equilibrium mixture was quantitative in all three experiments. However, the observation that the $Bu_3Sn^•$ radical isomerizes alkenes much faster than the $(TMS)_3Si^•$ radical is remarkable from a synthetic point of view (*vide infra*).

The conversion of methyl oleate to methyl elaidate was carried out (eq 3).[28] Using the experimental conditions described above, i.e., 0.2 M of methyl oleate, 0.5 equiv of TTMSS and AIBN (5 mol % at 2 h intervals) in refluxed benzene, 78% of the (*E*)-isomer was formed in 10 h.



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me \underset{}{\overset{(TMS)_3Si^•}{\rightleftharpoons}} CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me \quad (3)$$

The isomerization of methyl oleate to methyl elaidate was also carried out under different experimental conditions. As depicted in Figure 2, the equilibration of the two geometrical isomers was reached faster at higher temperatures and slower at lower temperatures when the initiation step was controlled by appropriate initiator and by keeping constant the amount of TTMSS. That is, at 141 °C *t*-BuOOBu-*t* (10 mol %) was initially used, and portions of 10 mol % were added every 1 h; at 116 °C PhC(O)OOBu-*t* (15 mol %) was initially used, and portions of 5 mol % were added every 1 h; at 45 °C *t*-BuON=NOBu-*t* (10 mol %) was initially used, and portions of 5 mol % were added every 2 h. The percentage of the isomeric composition after completion was *Z*/*E* = 22/78.

The reaction profile for the conversion of methyl oleate to methyl elaidate in relation to TTMSS concentration at 80 °C is shown in Figure 3. Thus, by varying the concentration of the silyl radicals, the time to equilibration of the two geometrical isomers could be controlled. For example, when the quantity of TTMSS was decreased from 0.5 to 0.1 equiv the conversion became slower, whereas by increasing the concentration of TTMSS (1.5 equiv) the equilibration of the two isomers, i.e. *Z*/*E* = 22/78, was reached in 4 h. It is worth mentioning that when oleic acid or elaidic acid were treated with TTMSS/AIBN, followed by diazomethane esterification, the reaction mixture gave an identical *Z*/*E* ratio. These results indicate that the carboxylic acid moiety does not affect either the TTMSS or the intermediate silyl radicals.

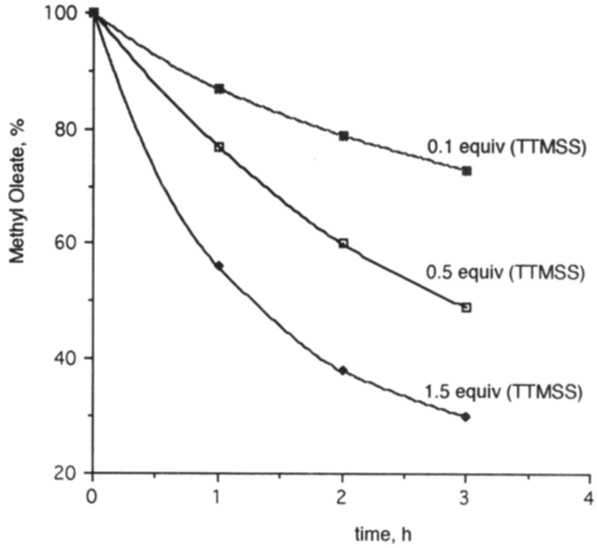
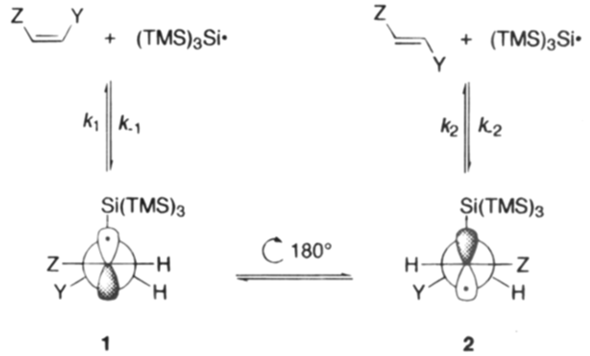


Figure 3. Reaction profile for the interconversion of methyl oleate to methyl elaidate by $(TMS)_3Si^•$ radical with different initial concentrations of TTMSS (80 °C).

Scheme 1



The mechanism that we conceived for the above isomerizations is outlined in Scheme 1. Tris(trimethylsilyl)silyl radical, initially generated by a small amount of AIBN, adds to the (*Z*)- or (*E*)-alkene to form radical **1** or **2**, respectively. Interconversion between the two radical adducts by rotation about the carbon−carbon bond, followed by β-scission then leads to the formation of either the (*Z*)- or (*E*)-alkene.

By using the Boltzmann distribution expression, in the case of 3-hexen-1-ol, we obtained a $\Delta E = 1.06$ kcal mol^{-1} at 80 °C which is equal to the difference in the stability of the two isomers, i.e. $\Delta_f H°(E) - \Delta_f H°(Z) = 1.0$ kcal mol^{-1}.[29] The fact that the *Z*/*E* ratio after equilibration reflects the thermodynamic stability of (*Z*)- and (*E*)-hexen-1-ols suggests that conformers **1** and **2** are equally

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(27) The equilibrium mixture of the recovered 2-butenes consisted of *Z*/*E* = 25/75 and 28/72 for $Bu_3Sn^{•10b}$ and $PhS^{•5a}$ radicals, respectively, at ca. 20 °C.

(28) (a) For early work, see: Markley, K. S. *Fatty Acids: Their Chemistry, Properties, Production, and Users*; Interscience Publishers: New York, 1960. (b) Reed, G. A.; Dimmel, D. R.; Malcolm, E. W. *J. Org. Chem.* **1993**, *58*, 6364 and references cited therein.

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Table 1. ***Cis-Trans*** **Isomerization of $R^1CH{=}CHR^2$ by Tris(trimethylsilyl)silyl Radicals**[a]

R^1	R^2	substrate *Z*/*E*[b]	*Z*/*E*[b] product
C_6H_5	C_6H_5	99/1	1/99
		1/99	1/99
C_6H_5	C(O)OEt	98/2	1/99
		0/100	0/100
C(O)OEt	C(O)OEt	98/2	33/67[c]
		0/100	2/98[c]

[a] In refluxed benzene for 2 h. [b] *Z*/*E* ratio determined by GC; the real values are approximated to the nearest integer. [c] ca. 10% of hydrosilylation adduct is observed.

populated. However, when steric effects are introduced by the substituents Y and Z, it is expected that the population of the two conformers **1** and **2** will differentiate. In fact, a $\Delta E = 2.49$ kcal mol^{-1} has been calculated for methyl oleate and elaidate at the same temperature.

Based on the considerations given above, we have tested the generality of the (*Z*)−(*E*) isomerization. Treatment of (*Z*)-stilbene with 0.5 equiv of TTMSS and AIBN (10 mol %) in refluxed benzene for 2 h followed by quantitative GC analysis gave a 96% yield of a 1/99 mixture of *Z*/*E* (Table 1). By replacing (*Z*)-stilbene with the (*E*)-isomer identical results were obtained. $\Delta E = 3.22$ kcal mol^{-1} has been calculated from the Boltzmann distribution expression against the $\Delta_f H°(E) - \Delta_f H°(Z) = 3.82$ kcal mol^{-1}.[29] Similar results were found for the (*Z*)−(*E*) isomerization of (Z)- and (E)-ethyl cinnamates (Table 1). The reaction of diethyl fumarate with TTMSS, under addition conditions of 1.2 equiv of TTMSS, furnished an 85% yield of the hydrosilylation product.[14] By decreasing the amount of TTMSS (0.5 equiv), after 2 h only 10% of the hydrosilylation product was obtained together with the unreacted alkene in a 2/98 mixture of *Z*/*E*. However, the reaction of diethyl maleate under the same conditions produced about the same amount of hydrosilylation product, and the remaining alkene was in a mixture of *Z*/*E* = 33/67 (Table 1).

We have also extended our study to include cyclic systems. A solution of 0.2 M (*Z*)-cyclododecene, 0.5 equiv of TTMSS, and AIBN (5 mol %) in benzene was refluxed for several hours. AIBN (5%) was added at 2 h intervals in order to keep the concentration of the initiator nearly constant. The isomeric composition during the reaction time was monitored by GC, and its profile is shown in Figure 4. A ratio of *Z*/*E* = 46/54 was obtained after 8 h. By replacing TTMSS with Bu_3SnH or PhSH, the equilibration, surprisingly, became slower. Figure 4 also shows the reaction profile for $Bu_3Sn^\bullet$- and $PhS^\bullet$-mediated isomerizations under identical experimental conditions. Thus, the equilibration of the two geometrical isomers is reached faster in the order $(TMS)_3Si^\bullet > PhS^\bullet > Bu_3Sn^\bullet$. It is worth pointing out that no consumption of starting material was observed during any of the above experiments. When a commercially available mixture of *Z*/*E* = 33/67 was used as starting material, the ratios of 33/67, 34/66, and 37/63 were obtained for Bu_3SnH, PhSH, and TTMSS, respectively, after 3 h.

Assuming that the addition rates of $(TMS)_3Si^\bullet$ or $Bu_3Sn^\bullet$ radicals are similar,[26] from the behavior of the above discussed 3-hexen-1-ol we deduced that the *β*-fragmentation of the intermediate tin-adduct alkyl radical is much faster than that of the analogous silyl-adduct. Therefore, a possible explanation for the opposite behavior of the cyclic olefin could be that the *β*-fragmentation is faster with respect to the rearrangement of the backbone in the tin cyclic adduct. Conversely, the *β*-fragmentation in the silyl cyclic adduct is slow enough to allow for a conformational change in the ring (cf. Scheme 2). The results of the $PhS^\bullet$-mediated isomerization could be similarly explaned if steric effects are taken into consideration.

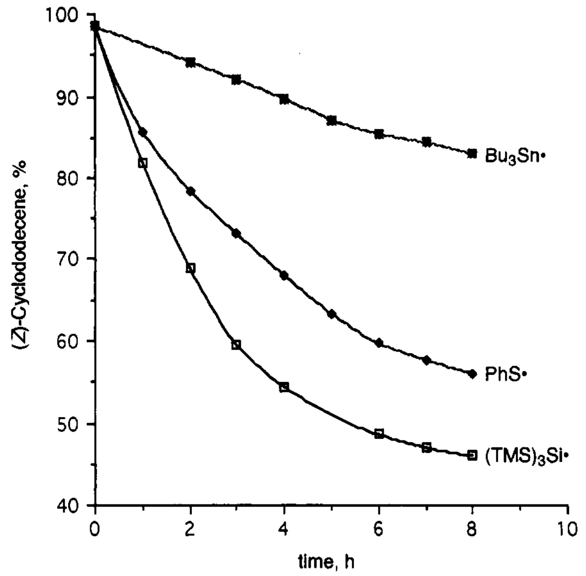
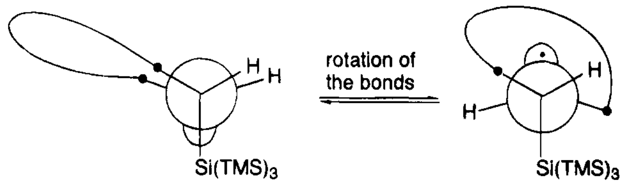


Figure 4. Reaction profile for the interconversion of (*Z*)-cyclododecene to (*E*)-cyclododecene by $(TMS)_3Si^\bullet$, $Bu_3Sn^\bullet$, and $PhS^\bullet$ radicals under identical experimental conditions (80 °C).

Scheme 2



3 **4**

1,5,9-Cyclododecatriene (1,5,9-CDT) is an important industrial product obtained by the cyclotrimerization of butadiene in the presence of an appropriate metal catalyst.[30] Three of the four possible isomers, i.e, (*E,E,E*)-1,5,9-CDT (**5**), (*Z,E,E*)-1,5,9-CDT (**6**), and (*Z,Z,E*)-1,5,9-CDT (**7**), are formed in the cyclotrimerization of butadiene[30] and are commercially available in their pure form. The fact that their (*Z*)−(*E*) isomerization has been of interest,[31] led us to look for analogous transformations using the $(TMS)_3Si^\bullet$ radical (Scheme 3).[32,33]

A solution of 0.2 M of one of the isomers of 1,5,9-CDT, 0.5 equiv of TTMSS, and *t*-BuOOBu-*t* (10 mol %) in *tert*-

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[30] For a review, see: Zakharkin, L. I.; Guseva, V. V. *Russian Chem. Rev.* **1978**, *47*, 955.

[31] The photosensitized transformations of the geometrical isomers of 1,5,9-CDT have been studied in detail. For example, see: (a) Crandall, J. K.; Mayer, C. F. *J. Am. Chem. Soc.* **1967**, *89*, 4374. (b) Nozaki, H.; Nosikawa, Y.; Kawanisi, M.; Noyori, R. *Tetrahedron* **1967**, *23*, 2179. (c) Attridge, C. J.; Maddock, S. J. *J. Chem. Soc. (C)* **1971**, 2999.

[32] Thioglycolic acid isomerizes somehow (*Z,E,E*)-1,5,9-CDT to (*Z,E,E*)-1,5,9-CDT. It has been suggested that the corresponding thiyl radical is responsable for this reaction. See: Duck, E. W.; Locke, J. M. *Chem. Ind. (London)* **1965**, 507.

[33] It is worth mentioning that Cl_3SiH under free radical conditions (benzoyl peroxide as initiator) does not cause any transformation of (*Z,E,E*)-1,5,9-CDT, whereas the hydrosilylation of one *trans* olefinic arrangement occurs in the presence of chloroplatinic acid as catalyst. See: Takahasi, H.; Okita, H.; Yamaguchi, M.; Shiihara, I. *J. Org. Chem.* **1963**, *28*, 3353.

Scheme 3

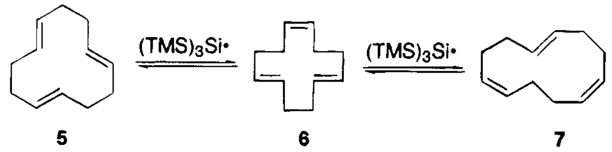


Table 2. Isomerization of 1,5,9-Cyclododecatrienes by Tris(trimethylsilyl)silyl Radicals[a]

starting material[b]	5	6	7
5	78	20	2
6	79	19	2
7	78	20	2
5 + 6 + 7 (57:36:7)	79	19	2

[a] The real values are approximated to the nearest integer. [b] For the identification of starting material see Scheme 3.

butylbenzene was heated at 143 °C for 5 h. A second portion of *t*-BuOOBu-*t* (5 mol %) was added after 2 h in order to keep a nearly constant concentration of initiator. The reaction was monitored by GC. The results are reported in Table 2. When a mixture of the three isomers was used as starting material, the equilibration of the three isomers was reached in 3 h. It is evident that the final isomeric composition is independent of the starting material and an average value of 78.6:19.6:1.8 for **5:6:7** can be calculated.[34] Based on GC analysis using tridecane as an internal standard and authentic samples as calibrants, yields are found to be between 75–80%. It is worth noting, that similar behavior was observed by acetophenone-sensitized photoisomerization of 1,5,9-CDT.[35] However, the equilibration of the three isomers was reached after 7–15 days of irradiation (200 W high Hg lamp), depending on the starting isomer, in ca. 70% yield.

The reaction profile of the (*Z,Z,E*)-1,5,9-CDT transformation to other geometrical isomers is shown in Figure 5. It is clear that the initial formation of (*Z,E,E*)-1,5,9-CDT is followed by a second isomerization to (*E,E,E*)-1,5,9-CDT as reported in Scheme 3. Examination of the Dreiding model indicates that with a small rearrangement of the backbone of the radical molecule, **3** is converted to **4** and *vice versa* (Scheme 2).

Stereoselective Formation of (*E*)- or (*Z*)-Alkenes. The factors controlling stereoselectivity in radical reactions are of current interest.[36] In free radical chemistry, the replacement of a functional group by a hydrogen atom is performed by using group 14 hydrides as reducing agents, i.e. Bu_3SnH or $(TMS)_3SiH$. The corresponding group 14-centered radicals may add reversibly to the double bonds present in the molecule and in principle could determine the outcome of the alkene stereochemistry. Furthermore, we have shown that the $(TMS)_3Si^{\bullet}$ radical isomerizes alkenes slower or faster than $Bu_3Sn^{\bullet}$ radical, depending on the nature of the substrate. It is conceivable that a judicious choice of reaction temperature, reaction time and reducing agent could insure the desired reduction or cyclization process, and, at the same time, could determine the stereochemistry of the alkene.

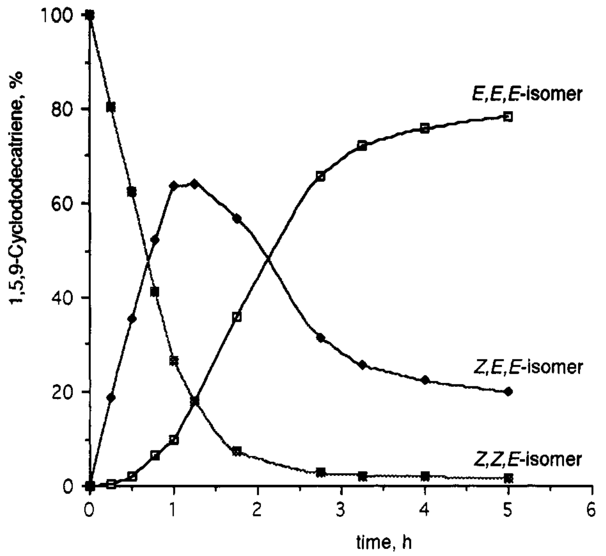
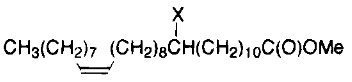
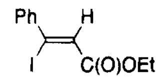


Figure 5. Reaction profile of (*Z,Z,E*)-1,5,9-CDT transformation to other geometrical isomers by $(TMS)_3Si^{\bullet}$ radical at 143 °C.

During the present studies, few papers appeared in the literature under these circumstances.[37–40] Johnson and Poulos in synthesizing (*Z*)-methyl triacont-21-enate (**8a**), *via* the reduction of thiocarbonate **8b** or iodo **8c** derivatives, with TTMSS, have obtained the (*E*)-methyl triacont-21-enate.[39] We propose that the reduction process was accompanied by a postisomerizaton of the (*Z*)-alkene which formed first.


$CH_3(CH_2)_7\;(CH_2)_8\overset{X}{C}H(CH_2)_{10}C(O)OMe$

8a X = H
8b X = OC(S)OPh
8c X = I



9

The reaction of iodide **9** with TTMSS in refluxing benzene for 2 h afforded the reduction product in good yield. However, the choice of initiator influenced the isomeric composition of the resulting alkene i.e. for $(PhCO_2)_2$, *Z*/*E* = 71/29 and for AIBN, *Z*/*E* = 17/83.[1] The α-phenyl-substituted vinyl radical, generated by iodine abstraction by $(TMS)_3Si^{\bullet}$ radical, is expected to be π-type and due to the unsymmetrical shielding of the β-substituents, the (*Z*)-isomer is expected to be the predominant product,[41] since the approach of the hydrogen donor is more hindered from the side of the ester group. An explanation for these results based on a postisomerization of the (*Z*)-alkene by the silyl radicals and the efficency of their formation was proposed in our preliminary communication.[1]

Radical deoxygenation of *vic*-diols to olefins by reaction of Bu_3SnH or $(TMS)_3SiH$ with the corresponding bis-

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[34] We cannot exclude the formation of (*Z,Z,Z*)-1,5,9-CDT in yield of <0.5%.

[35] The isomer distribution depends on the type of carbonyl compound used.[31b]

[36] (a) For a review on the stereoselectivity of intermolecular free-radical reactions, see: Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969. (b) For an Account on the stereochemistry of intramolecular free-radical cyclization reactions, see: RajanBabu, T. V. *Acc. Chem. Res.* **1991**, *24*, 139. (c) For an Account on acyclic stereochemical control in free-radical reactions, see: Porter, N. A.; Giese, B.; Curran, D. P. *Acc. Chem. Res.* **1991**, *24*, 296.

[37] Parker, K. A.; Fokas, D. *J. Org. Chem.* **1994**, *59*, 3927.

[38] Lowinger, T. B.; Weiler, L. *J. Org. Chem.* **1992**, *57*, 6099.

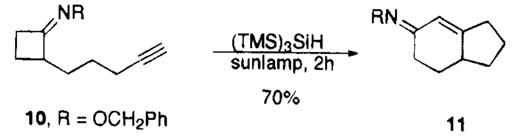
[39] Johnson, D. W.; Poulos, A. *Tetrahedron Lett.* **1992**, *33*, 2045.

[40] Emmer, G.; Weber-Roth, S. *Tetrahedron* **1992**, *48*, 5861; **1993**, *49*, 291.

[41] Chatgilialoglu, C.; Ferreri, C. In *Supplement C2: The Chemistry of triple-bonded functional groups*; Patai, S., Ed.; Wiley: Chichester, 1994; Chapter 16.

(dithiocarbonate) derivatives has been performed on complex biologically active molecules like the potent immunosuppressive agents FK 506 and FR 900520, in which the region C(9)–C(11) is known to influence protein binding.[40] The *E*/*Z* ratio strongly depends on the reagent and condition used, and with the choice of suitable reaction temperature, reaction time, and reducing agent high stereoselectivity can be obtained. Although the complexity of the substrates does not allow for any satisfactory mechanistic interpretation (two possible reaction paths were discussed), the experimental data were reported in some detail, so we can suggest that the interconversion of the two geometrical isomers may occur *via* the addition–elimination mechanism involving either (TMS)$_3$Si$^\bullet$ or Bu$_3$Sn$^\bullet$ radicals.

Finally, Pattenden and Schulz have reported that treatment of the acetylene derivative **10** with (TMS)$_3$SiH leads, in one pot, to the bicyclic compound **11**.[42] The proposed mechanism is based on the addition–elimination concept. That is, the (TMS)$_3$Si$^\bullet$ radical adds to the triple bond to form an adduct radical followed by a cascade of radical cyclization–fragmentation–transannulation–ring expansion and termination *via* ejection of the (TMS)$_3$Si$^\bullet$ radical to afford the bicyclic product. As this kind of addition–elimination methodology becomes more and more important in programming synthetic strategies,[8] it is expected that (TMS)$_3$SiH will find its place not only as an alternative to Bu$_3$SnH or PhSH but as a complementary reagent, depending on the required conditions.



(4)

Experimental Section

Materials. Di-*tert*-butyl hyponitrite,[43] (*Z*)-cyclododecene,[44] and ethyl 3-iodo-3-phenylpropionate[45] were prepared following literature procedures. All other materials were commercially available and used as received.

Thermal Decomposition of AIBN in the Presence of TTMSS or Bu$_3$SnH. A 25 mL stock solution of toluene containing a small amount of decane as an internal GC standard and 0.2618 g of AIBN was prepared. Samples containing 2 mL of stock solution and 200 μL of TTMSS or 170 μL of Bu$_3$SnH were degassed and sealed under argon in Pyrex ampules. After heating at 86 °C (internal ca. 82 °C) for 1 h, the reaction mixtures were analyzed by gas chromatography. Four independent experiments for each reducing agent gave 45, 52, 53, and 58% consumption of AIBN in the reaction with TTMSS and 65, 69, 74, and 75% consumption of AIBN in the reaction with Bu$_3$SnH.

General Procedure for Isomerization of Alkenes. A 10-mL round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, and inlet thermometer was charged with 0.5 mmol of alkene, 0.025 mmol of AIBN, and 2 mL of benzene. After careful degassing of the resulting solution, 0.25 mmol of TTMSS was added. The solution was then refluxed and treated with 0.025 mmol of AIBN at 2 h intervals in order to keep the concentration of the initiator nearly constant. The reaction mixture was analyzed by GC every hour, and the products of interest were identified by comparison of their retention times with authentic materials.

Acknowledgment. Financial support from the Progetto Stzategico del CNR "Tecnologie Chimiche Innovative" is gratefully acknowledged.

JO9501102

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[42] Pattenden, G.; Schulz, D. J. *Tetrahedron Lett.* **1993**, *34*, 6787.

[43] Mendenhall, G. D. *Tetrahedron Lett.* **1983**, *24*, 451.

[44] Ohno, M.; Okamoto, M. *Org. Synth.* **1969**, *49*, 30.

[45] Marek, I. Alexakis, A.; Normant, J.-F. *Tetrahedron Lett.* **1991**, *32*, 5329.