

An Unexpected Stereochemical Control of Alkene Formation by the Choice of Radical Initiator. The Reversible Addition of $(\text{Me}_3\text{Si})_3\text{Si}\cdot$ Radicals to Alkenes.

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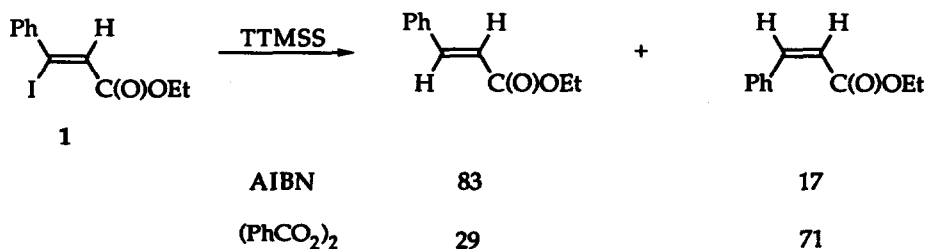
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Summary: Tris(trimethylsilyl)silyl radical is effective in isomerizing some (*Z*)-olefins into their thermodynamically more stable (*E*)-isomers by an addition-elimination path.

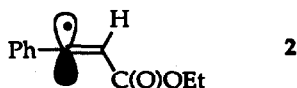
The factors controlling stereoselectivity in radical reactions are of current interest.¹⁻³ The stereoselectivities of vinyl radical reactions in the past have been steered by varying α - and β -substituents as well as reaction temperatures.¹ Recently Giese et al. have shown that the stereochemistry of vinyl radical reactions can also be guided in a particular direction by changing the abilities of hydrogen donation in the reducing agents.⁴ In this communication, we report that even the choice of radical initiator, in some cases, can influence the stereochemical outcome of these reactions.

During our work on $(\text{Me}_3\text{Si})_3\text{SiH}$ (TTMSS) as a radical-based reducing agent⁵ we noticed that this silane reacts with iodide **1** to give the dehalogenated product. That is, a mixture of iodide **1**, TTMSS (1.5 equiv), and 10% of an initiator (AIBN or benzoyl peroxide) in refluxing benzene for 2 h afford the desired product in ca 90% yield. However, the choice of initiator influenced the isomeric composition of the resulting alkene (Scheme 1).⁶

Scheme 1

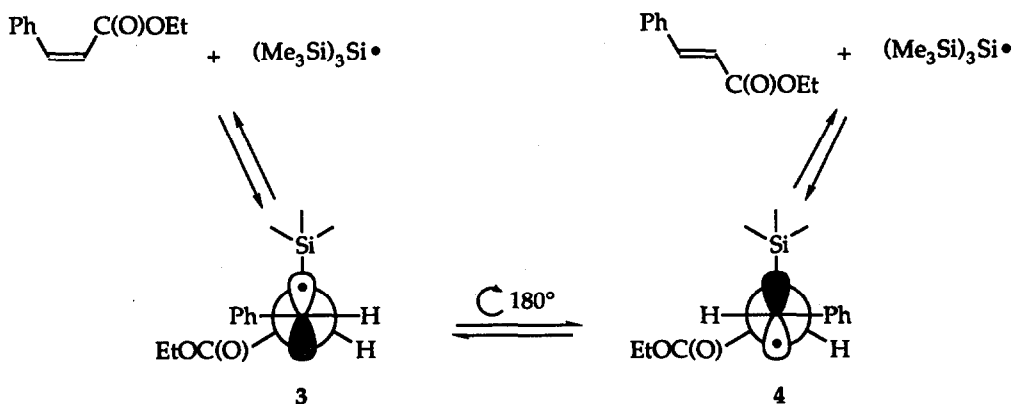


The α -phenyl-substituted vinyl radical **2**, generated by iodine abstraction by tris(trimethylsilyl)silyl radicals, is expected to be π -type. That is, strong spectroscopic⁷ and chemical⁸ evidence indicates that the α -phenyl-substituted vinyl radicals are linear, π -radicals rather than bent, σ -radicals. Furthermore, due to the unsymmetrical shielding of the β -substituents in radical **2**, the (*Z*)-isomer is expected to be the predominant product.^{1,4} That is, the approach of the hydrogen donor will be more hindered from the side of the ester group. Therefore, a plausible explanation for the results in scheme 1 is that an isomerization is involved when AIBN has been used as initiator.

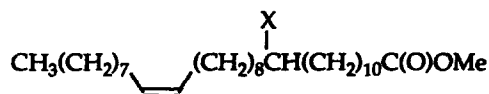


The following observations: (i) the radicals generated from the decomposition of AIBN or $(\text{PhCO}_2)_2$ are unable to isomerise either (*Z*)- or (*E*)-ethyl cinnamate,⁹ (ii) no evidence for *cis-trans* isomerization of the ethyl cinnamates in the presence of TTMSS, and (iii) $(\text{Me}_3\text{Si})_3\text{Si}\cdot$ radical-induced decomposition of AIBN or $(\text{PhCO}_2)_2$ is an unimportant path under our reaction conditions,¹⁰ persuaded us to study the isomerization of (*Z*)-ethyl cinnamate with the $(\text{Me}_3\text{Si})_3\text{Si}\cdot$ radical. To a solution of 0.048 g (0.27 mmol) of (*Z*)-ethyl cinnamate and TTMSS (0.5 equiv) in 1.26 mL of benzene was added 10% of AIBN or $(\text{PhCO}_2)_2$. The solution was stirred at 80°C for 2 h and the reaction mixture was analysed by GC. The measured *Z/E* ratio of 14/86 and 75/25 for AIBN or $(\text{PhCO}_2)_2$, respectively, indicating that $(\text{Me}_3\text{Si})_3\text{Si}\cdot$ radicals are responsible for the isomerization and that their formation, under our experimental conditions, are more efficient using AIBN as initiator rather than $(\text{PhCO}_2)_2$. Thus, the addition of $(\text{Me}_3\text{Si})_3\text{Si}\cdot$ radical to (*Z*)-isomer produces the adduct radical **3** which can undergo half rotation about the carbon-carbon bond (scheme 2). Decomposition of the adduct radical **4** can lead to formation of (*E*)-isomer. To our knowledge this is the first example of reversible addition of silyl radicals under normal conditions in solution.^{11,12}

Scheme 2

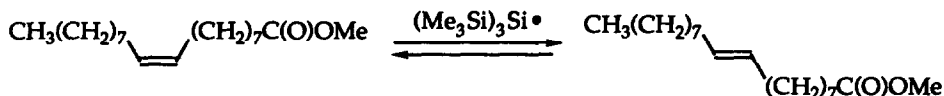


Recently, Johnson and Poulos in synthesising (*Z*)-methyl triacont-21-enate (**5a**), via the reduction of thiocarbonate **5b** or iodo **5c** derivatives with TTMSS, have obtained the (*E*)-methyl triacont-21-enate.¹³ That is, during the reduction process a *cis* to *trans* isomerization occurred.



- 5a** X = H
5b X = OC(S)OPh
5c X = I

They suggested that this isomerization could be due to the addition of TTMSS across the double bond followed by thermal elimination of TTMSS to generate the thermodynamically more stable (*E*)-isomer during the reduction processes. Curiously, they also report that methyl oleate does not rearrange to methyl elaidate, under identical experimental conditions, and therefore, the observed isomerization is intricately involved with the radical reduction. In order to throw some light in this peculiarity, we reinvestigated the isomerization of methyl oleate to methyl elaidate and vice versa by tris(trimethylsilyl)silyl radicals:



Using the same experimental conditions of Johnson and Poulos,¹³ i.e., 0.2 M of methyl oleate, 1.5 equiv of TTMSS and AIBN (25%) in refluxed benzene a *E/Z* ratio of 80/20 is formed after 2 h. By replacing methyl oleate with methyl elaidate, the equilibration, *E/Z*=80/20, is reached in 2h.¹⁴ When oleic acid or elaidic acid was treated with TTMSS/AIBN, followed by methyl esterification, the reaction mixture gave the same *E/Z* ratio.¹⁵ Therefore, it is conceivable that the isomerization of (*Z*)-methyl triacont-21-enate is not intricately involved with the radical reduction, and that the addition-elimination of $(\text{Me}_3\text{Si})_3\text{Si}\cdot$ radical is responsible for the isomerization.

In conclusion, tris(trimethylsilyl)silyl radical adds to carbon-carbon double bonds reversibly, resulting in the isomerization of alkenes. Further work on these reactions is in progress.

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References and Notes

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3. 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.
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15. These results indicate that carboxylic acid moiety do not affect either the TTMSS or the intermediate silyl radicals.

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