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A direct, versatile route to functionalized trialkoxysilanes†‡

Béatrice Quiclet-Sire,* Yuuki Yanagisawa§ and Samir Z. Zard*

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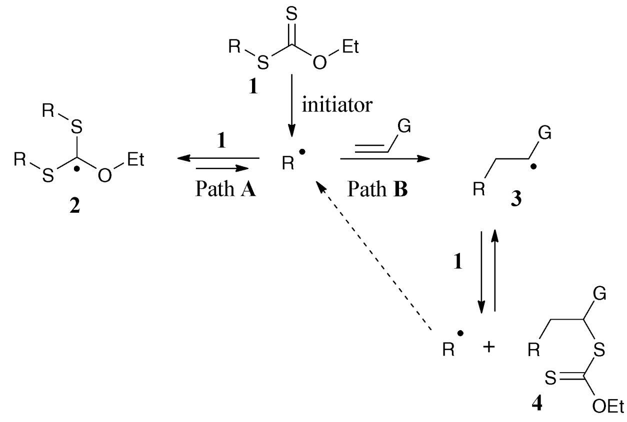
The peroxide initiated radical addition of dithiocarbonates (xanthates) to trialkoxy vinylsilanes leads to functionalized trialkoxysilanes. Prior addition of the dithiocarbonates to an alkene before reaction with the vinylsilane can be used to increase the complexity of the final product.

We describe herein a direct, convergent route to highly functionalized trialkoxysilanes. Trialkoxysilanes have played and continue to play a central role in materials science, surface science, and nanotechnology. Among numerous applications, they have been used to form sol–gel and organogelators;[1] to modify various surfaces, especially silica and metal oxide surfaces through the controlled formation of monolayers;[2] to create organic–inorganic hybrid materials and nanocomposites;[3] and to allow the assembly of hybrid and supported catalysts.[4] However, in order to further expand and optimize the utility of trialkoxysilanes, flexible, versatile and functional group tolerant methods for their concise synthesis must be developed.

The relative hydrolytic fragility of alkoxysilanes in general, and trialkoxysilanes in particular, has considerably restricted the range of acceptable reaction types and experimental conditions that may be harnessed for their preparation. Access to trialkoxysilanes therefore hinges on a relatively limited number of approaches. The most commonly employed process is the hydrosilylation of alkenes and alkynes, most often catalyzed by rhodium complexes.[5] The acylation of commercially available 3-aminopropyl- and 3-hydroxypropyltrialkoxysilane also constitutes a practical route. Both amine and alcohol, however, arise from the hydrosilylation of allylamine and allyl alcohol, respectively. The coupling of isocyanate-containing trialkoxysilanes with amines and alcohols has also been used.[6] A click dipolar cycloaddition reaction between an azide-substituted trialkoxysilane and alkynes has been used.[7] Very recently, a "radical click" procedure was reported involving the photochemically induced radical addition of 3-mercaptopropyltriethoxysilane to alkenes.[8]

We have over the past years developed the radical addition of dithiocarbonates (xanthates) to alkenes, as a method for the creation of new carbon–carbon bonds in an inter- or intra-molecular fashion.[9] A simplified mechanism is outlined in Scheme 1. One of the key elements is that the reaction of the intermediate radical R$^\bullet$ with its precursor dithiocarbonate **1** is reversible and degenerate (Path **A**) and therefore does not compete with the desired addition to the alkene. In other words, radical R$^\bullet$ is continuously regenerated from adduct **2** and thus acquires a relatively long effective lifetime, even in a concentrated medium, allowing it to participate in comparatively slow radical processes not easily accessible using other methods. In particular, intermolecular additions to ordinary, *unactivated* alkenes (Path **B**) become routinely possible.

This addition transfer of dithiocarbonates and related thiocarbonylthio derivatives is the basis of the RAFT-MADIX controlled polymerization process, which has proved to be an exceedingly powerful technology for the synthesis of block polymers and various



Scheme 1 Simplified mechanism for the radical addition of a dithiocarbonate (xanthate) to an alkene.

Laboratoire de Synthèse Organique, CNRS UMR 7652, Ecole Polytechnique, F-91128 Palaiseau, France. E-mail: zard@poly.polytechnique.fr; Fax: +33 169335972; Tel: +33 169335971

† This communication is dedicated with respect to the memory of Professor Manfred Schlosser (Ecole Polytechnique Fédérale, Lausanne, Switzerland).

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§ Present address: Graduate School of Material Sciences, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0101, Japan.

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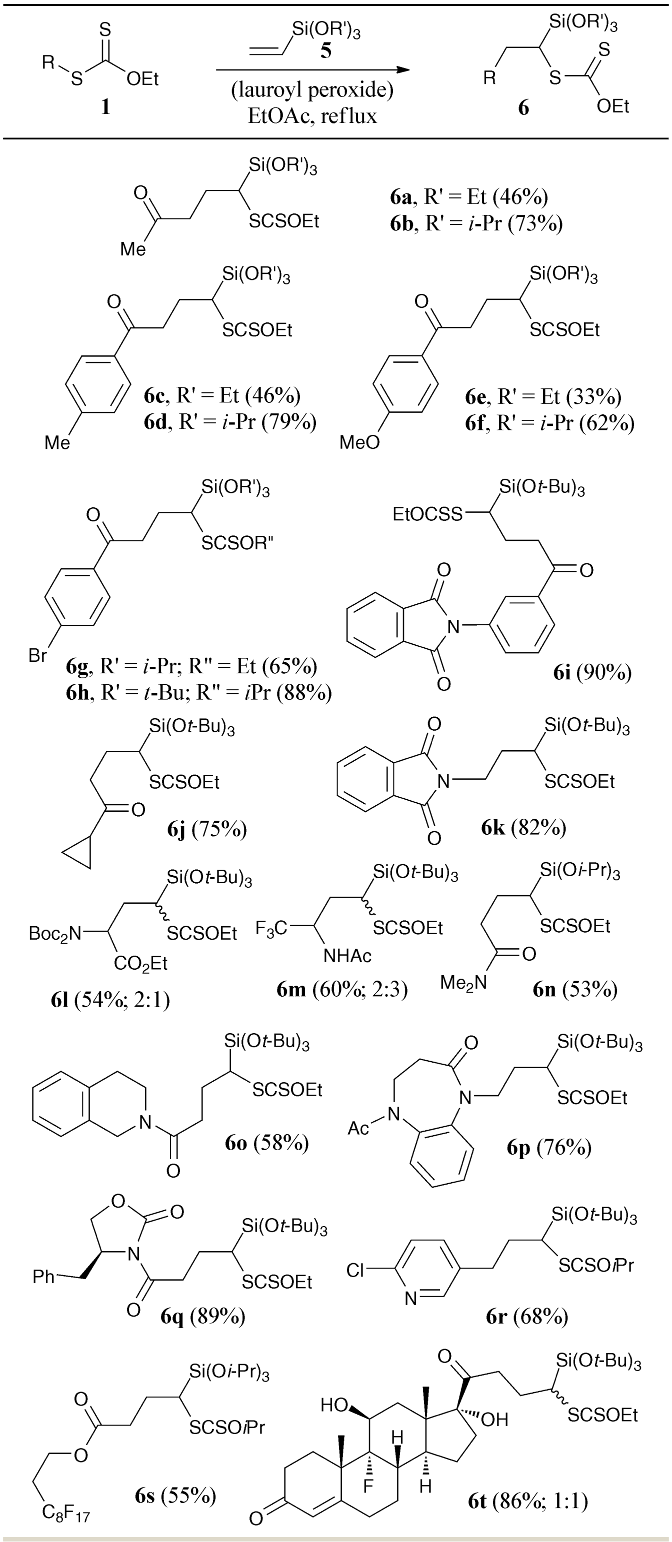
Table 1 Examples of radical additions to trialkoxy-vinylsilanes



6a, R′ = Et (46%)
6b, R′ = *i*-Pr (73%)
6c, R′ = Et (46%)
6d, R′ = *i*-Pr (79%)
6e, R′ = Et (33%)
6f, R′ = *i*-Pr (62%)
6g, R′ = *i*-Pr; R″ = Et (65%)
6h, R′ = *t*-Bu; R″ = *i*Pr (88%)
6i (90%)
6j (75%)
6k (82%)
6l (54%; 2:1)
6m (60%; 2:3)
6n (53%)
6o (58%)
6p (76%)
6q (89%)
6r (68%)
6s (55%)
6t (86%; 1:1)

other polymer architectures.[10] It has also been applied very recently in the modification of carbon nanotubes.[11] We have now examined extending this chemistry to the important case of trialkoxysilanes by using trialkoxy vinylsilanes as the alkene partners. In case of success, this would open a direct, versatile, and convergent route to highly functionalized trialkoxysilanes of potential utility in materials science.

Our initial trials involved the lauroyl peroxide initiated addition of dithiocarbonates to triethoxy vinylsilane **5a** (R′ = Et). They indeed proved to be successful with a variety of dithiocarbonates (Table 1, examples **6a**, **6c**, and **6e**), but were also somewhat frustrated by the tendency of the triethoxysilyl products to partially hydrolyze during chromatographic separation leading to fluctuations in the yield of products. This problem was remedied by the simple expedient of using the more hydrolytically robust triisopropoxy-vinylsilane **5b** (R′ = i-Pr) or, even better, tri-*t*-butoxy-vinylsilane **5c** (R′ = *t*-Bu). The process now becomes reliable and allows the introduction of a broad range of functional groups, as shown by the examples assembled in Table 1. These include aliphatic and aromatic ketones (**6a–j**), protected amines (**6k** and **6m**) and amino acid (**6l**; Boc = *t*-butoxycarbonyl), amides (**6n–p**), imide (**6q**), heteroaromatics such as pyridine (**6r**), ester (**6s**) and even a complex corticosteroid (**6t**). In the case of adducts **6h** and **6s**, the corresponding *O*-isopropyl dithiocarbonates were used to perform the addition, as these were available from another ongoing project. Imide **6q** is in fact an activated amide, which could participate in crosslinking transformations with polyamines such as α,ω-diamines, triamines, diaminobenzene, *etc.*[12] The possibility of introducing a simple trifluoromethyl group or a long perfluorinated alkyl chain is illustrated by examples **6m** and **6s**. The latter compound would be very useful for creating super hydrophobic surfaces.[13]

One implicit condition for the success of the radical additions, not obvious from the simplified mechanistic scheme (Scheme 1), is that the initial radical $R^\bullet$ has to be more stable than the adduct radical **3** (neglecting polar effects, in a first approximation). This condition has been respected in all the above examples.[14] While keeping in mind this constraint, it is possible in many instances to take advantage of the presence of the dithiocarbonate group in the adducts to accomplish a second intermolecular radical addition and thus obtain even more richly functionalized products. This modular approach is exemplified by the addition of dithiocarbonate **7** first to vinylidene carbonate to furnish intermediate **8**,[15] followed by a second addition to vinylsilane **5c** to give finally compound **6u** containing a protected amine and a masked diol (Scheme 2). Incidentally, dithiocarbonate **7** was used to prepare compound **6k** (Table 1).

The presence of the dithiocarbonate group in the products provides a convenient entry into the vast chemistry of organosulfur compounds. Thus, the dithiocarbonate moiety is readily cleaved by amines to give the corresponding thiol (1,2-diaminoethane is especially effective in this respect);[16] it may also be directly oxidized with performic acid to a sulfonic acid;[17] or simply reductively removed and replaced by a hydrogen atom using a number of reducing agents.[18] The last transformation is illustrated by the two examples shown in Scheme 3. First, a bis-dithiocarbonate **9** is used to perform a double addition leading to compound **6v** in high yield as a 1 : 1 mixture of diastereoisomers. Reduction with tris-trimethylsilylsilane[19] gives sulfur-free bis-trialkoxysilane **10**, a compound that could prove to be useful as a crosslinking agent. The second transformation involves addition of beta-lactam dithiocarbonate **11** and reduction of

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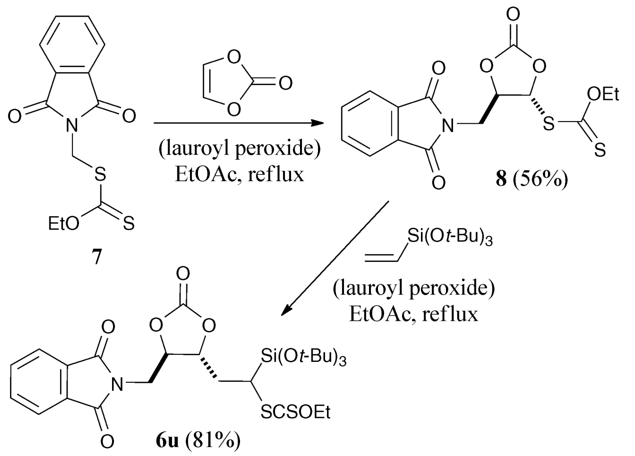
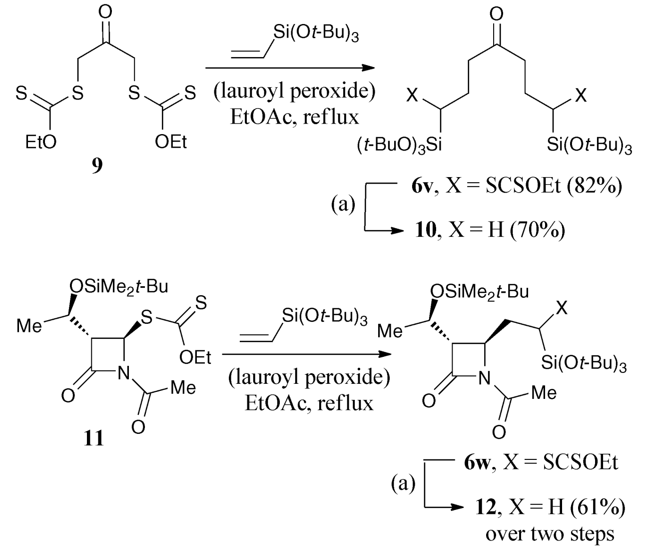


Scheme 2 An example of two consecutive intermolecular radical additions to form a highly functionalized trialkoxysilane.



(a) $(Me_3Si)_3SiH$, AIBN, PhMe-cyclohexane (1:1) reflux.

Scheme 3 Complex examples of dithiocarbonate radical additions to tri-*t*-butoxy-vinylsilane and reduction.

the corresponding adduct **6w** without prior purification to afford compound **12** in 61% overall yield.

In summary, we have described a flexible, convergent, atom-economical, and easily scalable approach for the synthesis of highly functionalized trialkoxysilanes. Indeed, many of the compounds obtained in the present study would be very difficult, if not impossible, to prepare by existing routes. Hitherto inaccessible trialkoxysilanes and alkoxysilanes in general can now be readily tailor-made. Even complex and sensitive corticosteroids and betalactams can be incorporated into the products. The ability to introduce numerous different functional groups should open new possibilities for surface modification, for supported catalysts, and for sol–gel formation. It could also simplify the spectroscopic identification of the modified surfaces through the inclusion, for example, of easily ''visible'' aromatic ketones or fluorinated groups. The presence of the dithiocarbonate could be exploited not only for further chemical elaboration, but also as an infrared marker (typical bands at 1220–1240 cm^{-1} and 1030–1040 cm^{-1}). Elemental analysis for sulfur would further allow quantitative characterization of the modified structures. Finally, the possible introduction of a thiol by cleavage of the thiocarbonate group could be used to construct novel organic–inorganic hybrid materials, in view of the strong affinity of thiols for metallic surfaces.[20]

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