OCH_2, $^3J \approx 8$ Hz), 3.78 (t, 4H, OCH_2, $^3J = 7$ Hz), 2.02 (m, 4H, OCH_2CH_2), 1.94 (m, 4H, OCH_2CH_2), 1.11 (t, CH_3, $^3J = 7.5$ Hz), 0.91 (t, CH_3, $^3J = 9$ Hz); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 25 °C): $\delta = 158.48$ and 157.75 (2s, arom.C_q–O), 135.02–123.95 (arom. C atoms), 78.47 and 76.79 (2s, OCH_2), 31.09 (s, ArCH_2), 23.95 and 23.51 (2s, CH_2CH_3), 11.05 and 10.01 (2s, CH_2CH_3), C≡O not detected; $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 °C): $\delta = 12.9$ (s, PPh_2); MS (FAB): *m/z* calcd for $C_{65}H_{66}ClO_5P_2Ru$ [M – Cl – (CO)]: 1125; found: 1125.5 (expected isotopic profile); elemental analyses calcd for $C_{66}H_{66}Cl_2O_6P_2Ru$ (1189.18): C 66.66, H 5.59; found: C 66.54, H 5.63.

8: Yield: 95%; IR (KBr): $\tilde{\nu}$(C≡O) = 1924(s) cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): $\delta = 7.91-7.89$ and 7.37–7.35 (20H, PPh_2), 6.86 and 6.67 (B_2A spin system, 6H, *m*- and *p*-H of OAr, $^3J(A,B) = 7.5$ Hz), 6.75 (virtual t ABXX′A′B′ spin system, 4H, *m*-H of OArP, $^3J(A,X) \approx {}^3J(B,X) \approx 5$ Hz), 4.51 and 3.22 (AB spin sytem, 8H, ArCH_2Ar, $^2J(A,B) = 13$ Hz), 4.14 (pseudo t, 4H, OCH_2, $^3J \approx 8$ Hz), 3.79 (t, 4H, OCH_2, $^3J = 7$ Hz), 2.01 (m, 4H, OCH_2CH_2), 1.95 (m, 4H, OCH_2CH_2), 1.13 (t, CH_3, $^3J = 7.5$ Hz), 0.90 (t, CH_3, $^3J = 9$ Hz); $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 25 °C): $\delta = 42.4$ (s, PPh_2). Crystal data for $\mathbf{8} \cdot C_2H_4Cl_2$: $M_r = 1288.14$, orthorombic, space group *Pbcm*, $a = 19.4779(6)$, $b = 17.7412(3)$, $c = 17.2124(5)$ Å, $V = 5947.5(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.44$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu = 0.544$ mm^{-1}. Data were collected on a Kappa CCD Enraf Nonius system at 173 K. The structure was solved by direct methods and refined on F_o^2 by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. $R1 = 0.089$ and $wR2 = 0.117$ for 3296 data with $I > 3\sigma(I)$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101566. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A New Radical Allylation Reaction of Dithiocarbonates**

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In contrast to radical cyclizations, which have practically revolutionized the construction of polycyclic systems, intermolecular radical additions to olefins have had a comparatively limited impact on organic synthesis.[1] This is chiefly because of the difficulty in avoiding competing bimolecular side reactions which, in the case of intramolecular processes, can usually be controlled by the use of high dilution techniques (e.g. slow, syringe pump addition of one of the reagents). With stannane-based reactions, for example, the difficulty lies in preventing premature hydrogen atom transfer to the radical before it adds to the olefin. One special exception is the allylation reaction with allyltriorganotin.[2] In this case, the allyl transfer step is the one that regenerates the stannyl radical to propagate the chain and, even if this step is not very fast by radical reaction standards,[3] there are no other major competing pathways. This fairly general and quite useful intermolecular C–C bond forming procedure unfortunately uses tin and therefore suffers from the same drawbacks as other tin-based systems: high cost and difficulty in removing toxic organotin contaminants.[4] These are serious

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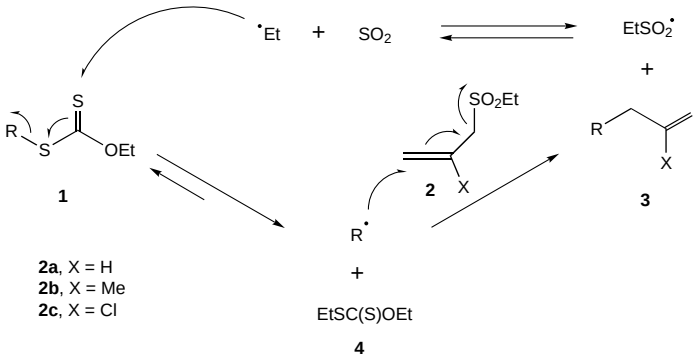
limiting factors for the large-scale application of stannane chemistry in the pharmaceutical industry. The corresponding organosilane or organogermane analogues[5] are not only more expensive, but are also less reactive. The β cleavage of the C–Si and C–Ge bond in the radical adduct is considerably slower than that of a C–Sn linkage. More recently, allyl aryl sulfones or sulfides have been examined as allylating agents, but the process still requires stoichiometric amounts of an organostannane or a distannane to generate the radical from the substrate.[6]

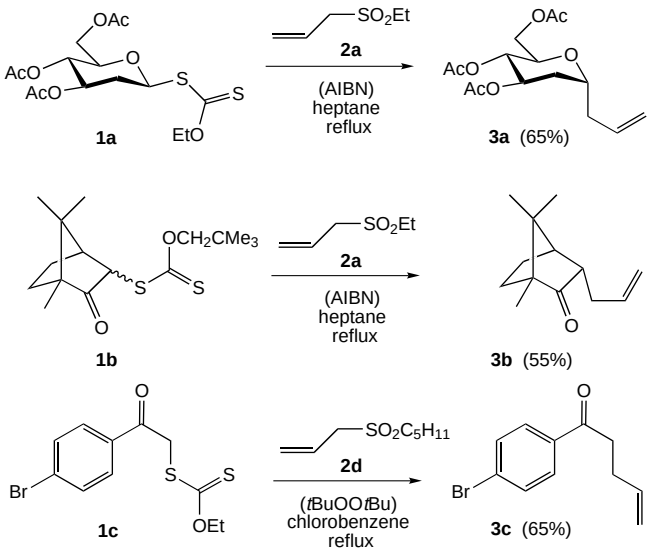
We have recently shown that it is possible to accomplish a radical allylation starting from aliphatic iodides by using allyl ethyl sulfone, without the intervention of tin or any other heavy metal.[7] Aliphatic iodides, however, are in many cases fragile and sensitive substances (e.g. anomeric iodides in sugars) that are readily degraded by a variety of ionic substitution and elimination reactions.[8] Bromides or chlorides are more robust, but react too sluggishly with ethyl radicals to propagate the chain cleanly. It seemed to us that this difficulty could perhaps be circumvented by replacing the iodide by a dithiocarbonate group (xanthate), which exhibits sufficient affinity to radicals but is less subject to ionic degradation.[9] The projected allylation sequence is summarized in Scheme 1.



Scheme 1. Radical allylation of an aliphatic xanthate with allyl ethyl sulfone.

The ethanesulfonyl radical generated in the allyl transfer step can extrude sulfur dioxide to give an ethyl radical, which is reactive enough to abstract the xanthate group from the starting material **1**. The problem of producing a carbon-centered radical is thus solved in a simple manner without using any tin-containing additives. Allyl aryl sulfones, which have previously been used as radical allylating agents,[6] produce arenesulfonyl radicals, $ArSO_2^{\bullet}$; these do not fragment to give aryl radicals and therefore cannot propagate the chain.[10]

Xanthate **1a** was easily prepared by treating the corresponding bromide with commercially available potassium *O*-ethyl xanthate. In contrast to its iodo analogue, this nicely crystalline compound can be handled and stored without any difficulty. We were pleased to find that, upon heating with a threefold excess of allyl ethyl sulfone in refluxing heptane using azoisobutyronitrile (AIBN) as initiator, the expected, and previously known,[11] 1α-allyl 2-deoxyglucose derivative **3a** was smoothly produced in 65% yield. The stereochemistry is in line with earlier observations on the addition of radicals at the anomeric position.[12] In the same way, neopentyl xanthate **1b** derived from camphor afforded the corresponding allylated product (Scheme 2).

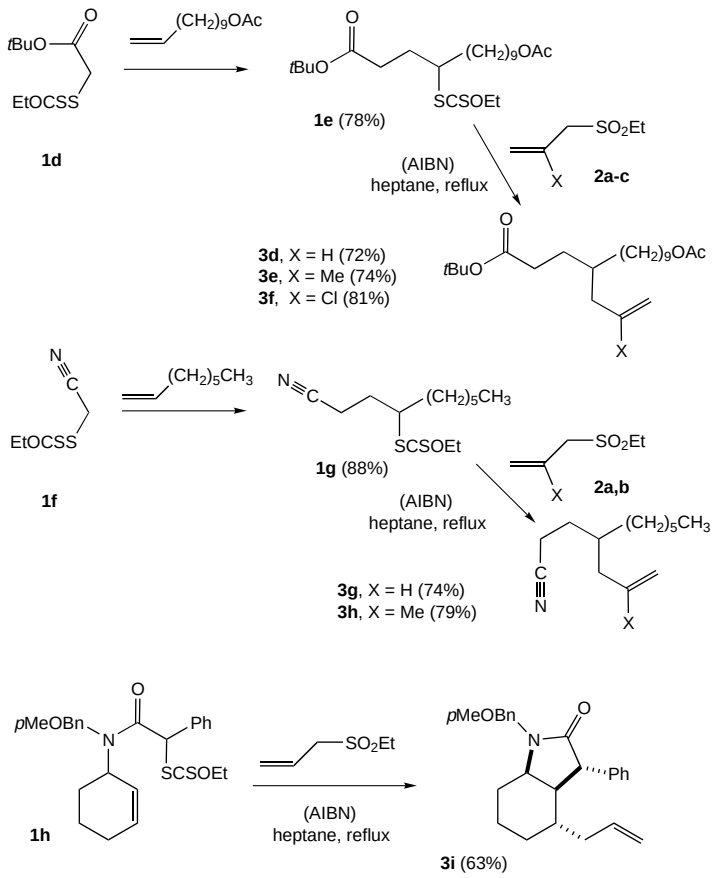


Scheme 2. Examples of radical allylation of xanthates with allyl ethyl and allyl pentyl sulfone.

If needed, a few drops of chlorobenzene may be added to the heptane to improve solubility; alternatively, chlorobenzene alone may be used in conjunction with di-*tert*-butyl peroxide as the initiator because of its longer lifetime at the higher reflux temperature. The latter conditions are illustrated by the conversion of *p*-bromophenacyl xanthate **1c** into the allylated product **3c** with use of allyl *n*-pentyl sulfone (**2d**). Even though this allylating reagent proved equally efficient in terms of yield (a pentyl radical now replaces the ethyl radical in Scheme 1), it is less volatile than **2a** and therefore less easily removed from the reaction mixture.

Another important advantage of using a xanthate precursor is that it is possible to combine the radical allylation with a xanthate transfer to introduce two new C–C bonds across an unactivated olefinic bond.[9] For example, radical addition of xanthate **1d** to 10-undecylenyl acetate gave **1e** (78%), which was readily converted into **3d** in 72% yield with allyl ethyl sulfone. It is worth stressing that such a transformation would be difficult to accomplish through the corresponding iodides. Kharasch-type additions of iodoacetates are capricious and often require the presence of hexabutyldistannane to ensure reproducibility.[1c, 13c] Moreover, the reaction frequently leads to γ-lactones by ionic ring closure through substitution of the iodine in the adduct by the carbonyl oxygen atom of the ester.[13] The conversion of octene into **1g** by addition of xanthate **1f** (derived from chloroacetonitrile) followed by allylation is another example.

The reactions in Scheme 3 show that this new allylation procedure can be extended to include allyl groups substituted in the 2-position by chlorine or a methyl group (**3e**, **3f**, and **3h**) and presumably a variety of other substituents. This opens



Scheme 3. Xanthate transfer followed by radical allylation with allyl ethyl sulfone.

up many opportunities for further modifications. The 2-chloroallyl group (in **3f**) is especially interesting in this respect since it can be converted into an acetylene by simple treatment with base.[14] Finally, the allylation may be preceded by a cyclization step as shown by the direct transformation of xanthate **1h** into **3i** (63%). Only one diasteriomer is obtained for which the stereochemistry shown is tentatively assigned on the basis of its NMR spectrum. Unlike the intermolecular examples discussed above, there is no need in this case to isolate the intermediate xanthate.

We have described here a new, flexible radical process for grafting various allyl appendages without recourse to toxic or expensive reagents. The starting xanthates are readily available either by traditional nucleophilic substitutions with xanthate salts or by a radical xanthate transfer reaction. The latter approach is especially appealing because it allows the expedient construction of complex frameworks from simple unactivated olefins.

Experimental Section

Typical experimental procedure: Under an inert atmosphere AIBN is added portionwise over several hours to a refluxing solution of the xanthate (1 mmol) and the appropriate allyl sulfone (3 mmol) in degassed heptane (4 mL; a few drops of chlorobenzene may be added to aid solubility if necessary). The reaction mixture is concentrated under vacuum, and excess allyl ethyl sulfone removed by passing a stream of dry air over the warmed (50–60 °C) residue. This treatment also eliminates the relatively volatile diethyl xanthate coproduct **4**. Finally, chromatography on silica furnishes the desired product. If chlorobenzene alone is used as the solvent, then di-*tert*-butyl peroxide is the preferred initiator.

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