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Toluene as a novel carrier of xanthates—preparation, use and surrogate of *S*-tri- and di-chloromethyl xanthates

Dumeunier Raphaël *, Huber Annika

Syngenta Crop Protection, Schaffhauserstrasse, CH-4332 Stein, Switzerland

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ABSTRACT

Toluene has been identified as a novel carrier of xanthates. Their corresponding fragmentative precursors proved to behave efficiently in radical group transfer reactions. As examples, unprecedented *S*-tri/di-chloromethyl xanthates could be prepared, isolated and further used in radical additions to olefins. Their precursors (de-aromatized toluene upon which is grafted, at one end, a tri/di-chloromethyl-group and, at the other end, a dithiocarbonyl group) can also be used directly in the transfer of both groups to olefins. The re-aromatizing loss of toluene by radical initiated fragmentation of the precursors brings thus new opportunities to the chemistry of xanthates, exemplified here in the intermolecular additions to olefins of new *S*-tri/di-chloromethyl xanthates.

Introduction

The transfer of alkyl residues to olefins is a very useful tool offered by radical chemistry.[1–3] In the case of trichloromethyl radical transfer, the use of trichloromethyl bromide is most certainly very efficient.[4] Other sources of trichloromethyl radical are known, such as chloroform and tetrachloromethane,[5] although more difficult to activate due to stronger C–X (X = Cl, H) bond dissociation energy. The advantageous, desulfitative use of trichloromethanesulfonyl chloride over tetrachloromethane in halogen atom-transfer radical addition, discovered in 1952,[6] has been studied and extended to other reagents recently.[7]

In general, alkyl radical transfers may advantageously be performed from the xanthate analogues of alkyl halides.[8–10] Even though they usually need to be prepared (by substitution of halide with *O*-alkyl xanthate salt), the advantages they offer as alternative reagents warrant the long standing interest they have demonstrated over the years. However, to the best of our knowledge, no *S*-tri- nor *S*-dichloroalkyl xanthate has been described so far.

As part of a synthetic route to novel fungicides, we became interested in trichloromethyl radical transfers. What is more, we planned in particular for an intermediate skeletal rearrangement before termination of our radical chain process. As can be seen from Figure 1,[8] this is one advantage that a xanthate such as **1**, (a *S*-trichloromethyl-xanthate if R- would be trichloromethyl-) would offer over the sources cited above, due to the longer lifetime of the radical **4**. Indeed, the propagation by transfer of the xanthate group to **4** via **5** may be fast, but it is reversible, radical **4** being therefore continuously regenerated from **5**, during the time of the reaction.

This obviously leaves the opportunity for the intermediate radical **4** to be diverted from its normal course. The use of xanthates offers this exact opportunity to run the radical chain under thermodynamic control, where standard reagents such as bromotrichloromethane

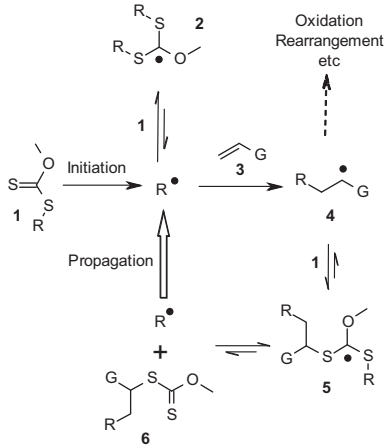

Figure 1. A typical xanthate chain reaction, with a reversible propagation step.

* Corresponding author. Tel.: +41 628660271.
E-mail address: raphael.dumeunier@syngenta.com (R. Dumeunier).

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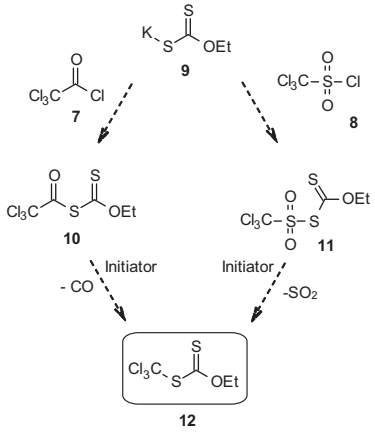

Figure 2. Approaches to **12** directly inspired from the literature.

sometimes limit the outcome of a radical transfer reaction to kinetic products.[11] Another advantage is the possible oxidation of intermediate radical **4** by the initiator peroxide when used as a stoichiometric oxidant (Radical-Polar cross-over reaction). For these two reasons, we became very interested in the synthesis and use of a *S*-trichloromethyl xanthate such as **12**.

Contrary to *S*-trichloromethyl xanthates, *S*-trifluoromethyl xanthates were prepared over a decade ago,[12–14] and we planned to follow the same steps for accessing **12**. Alongside the decarbonylative approach, the analogous desulfonylative transformation may also, *a priori*, open an access to the generation of **12** (Fig. 2).

Before reporting on the use of **12** advantageously for intermediate radical/cation rearrangements, we would like to report in this Letter the preparation of *S*-di- and *S*-tri-chloromethyl xanthates, as well as the direct use of surrogates via an aromatizing fragmentation concept hitherto unprecedented in the chemistry of xanthates.

Results and discussion

The preparation of *S*-trichloromethyl xanthate **12** as according to plans proved unsuccessful. Our efforts to approach it as depicted in Figure 2 failed in delivering any desired *S*-trichloroacetyl xanthate **10** or *S*-trichlorosulfonyl xanthate **11**. Their isolation being obviously very difficult due to high intrinsic reactivity, we attempted to decarbonylate **10** in situ, as in the precedented case of trifluoromethyl xanthate. But this one-pot approach, as well as the in situ desulfonylation of **11**, failed to deliver any desired product **12**. We then looked for less obvious accesses to **12**, ideally by using a more stable, isolable precursor than **10** or **11**.

As part of a long standing interest in little known rearomatizing chemistry,[15] we were aware of the existence of bromide **13**, described in 1997 (Fig. 3).[16] We then surmised that its substitution by potassium *O*-alkyl xanthate salts should deliver stable *S*-trichloromethyl xanthate precursors such as **15** or **16**. Similarly, the dichloromethyl analogue **14** would give an access to *S*-dichloromethyl xanthate precursor **17**. We planned to duplicate the

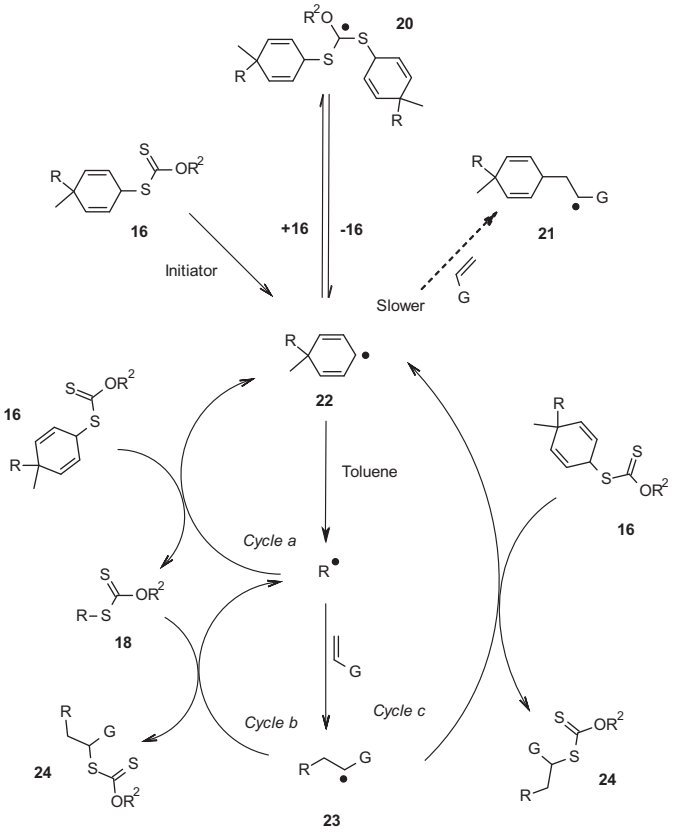

Figure 4. Design of surrogates and/or precursors of di/tri-chloromethyl xanthates.

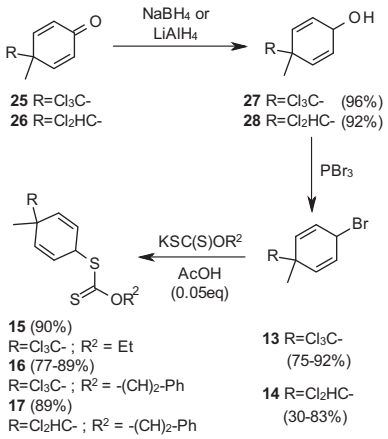

Figure 5. Synthesis of **15**, **16** and **17**.

chemistry to deliver both *S*-tri- and *S*-di-chloromethyl xanthates **18** and **19**.

As depicted in Figure 4, we indeed envisaged that after initiation, starting from example from the trichloromethyl analogue

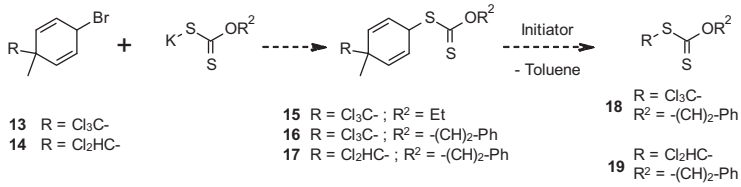

Figure 3.