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β-Nitro Xanthates as Olefin Precursors

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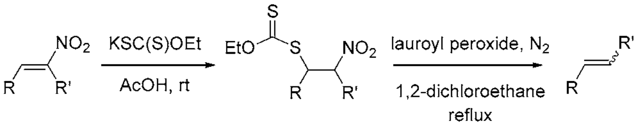
ABSTRACT



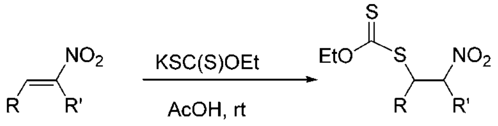
Potassium *O*-ethyl xanthate readily adds to α,*β*-unsaturated nitro compounds to give stable *β*-nitro xanthates, which undergo tin-free elimination to form olefins in good yield and good *E* selectivity upon simple heating with lauroyl peroxide in refluxing 1,2-dichloroethane.

Radical elimination of nitrogen dioxide to form olefins was developed by Kornblum et al.[1] and by Ono et al.[2] in early investigations on the radical reactivity of nitro groups and *gem*-dinitro compounds. This concept was used later by Barton et al. in their tin-free olefin synthesis.[3] The process relies on the reaction of methyl radicals, generated from stoichiometric amounts of *N*-acetoxy-2-thiopyridone (Barton ester), with the relatively unstable β-nitro trithiocarbonates. Recently, Yao has uncovered an efficient styrene synthesis starting with β-nitrostyrenes and exploiting once again the β-elimination of nitrogen dioxide.[4]

As part of our program aimed at developing useful tin-free radical procedures, we explored the reactivity of β-nitro xanthates.[5] Indeed, these compounds should also undergo elimination in the presence of a source of reactive radicals to give the corresponding olefins.

To ascertain the feasibility of this approach to olefins, we needed a simple way to access such β-nitro xanthates. The Michael addition of nucleophiles to vinylic nitro compounds is usually an efficient reaction and has already been applied to the synthesis of β-nitro dithiocarbamates.[6] We were pleased to see that the addition of 4 equiv of potassium *O*-ethyl xanthate to a solution of a vinylic nitro compound in acetic acid readily furnished the desired compound (Scheme 1).

Scheme 1. Synthesis of β-Nitro Xanthate **2**



1 **2**

We applied this reaction to various nitro-olefins.[7] The reaction is compatible with mono- or disubstituted vinylic nitro compounds. The yield is generally good and the substitution pattern can be varied substantially (Table 1). The β-nitro xanthates were always isolated as a mixture of diastereoisomers and were easily handled and stored, in contrast to the analogous trithiocarbonates.[3]

We have also found that these compounds could be readily obtained directly from the acetylated Henry adducts.

We anticipated that the xanthate salt, even in the presence of acetic acid, would be sufficiently basic to deprotonate α

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[1] Kornblum, N.; Boyd, S. D.; Pinnick, H. W.; Smith, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4316.

[2] Ono, N.; Miyake, H.; Tamura, R.; Kaji, A. *Tetrahedron Lett.* **1981**, *18*, 1705. Ono, N.; Miyake, H.; Kamimura, A. *Tetrahedron* **1985**, *41*, 4013.

[3] Barton, D. H. R.; Jaszberenyi, J. Cs.; Tachdjian, C. *Tetrahedron Lett.* **1991**, *32*, 2703. For a similar application see: Kobertz, W. R.; Bertozzi, C. R.; Bednarski, N. D. *J. Org. Chem.* **1996**, *61*, 1894.

[4] Yao, C.-H.; Chu, C.-M.; Liu, J.-T. *J. Org. Chem.* **1998**, *63*, 719. Liu, J.-T.; Yao, C.-F. *Tetrahedron Lett.* **2001**, *42*, 6147. Liu, J.-T.; Jang, Y.-J.; Shih, Y.-K.; Hu, S.-R.; Chu, C.-M.; Yao, C.-F. *J. Org. Chem.* **2001**, *66*, 6021.

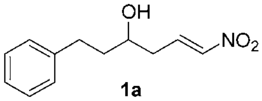
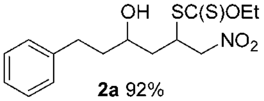
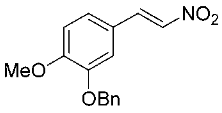
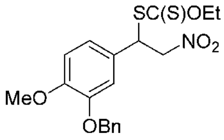
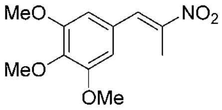
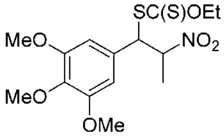
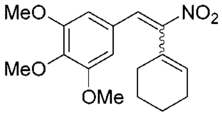
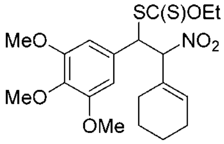
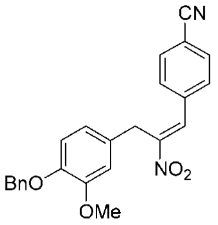
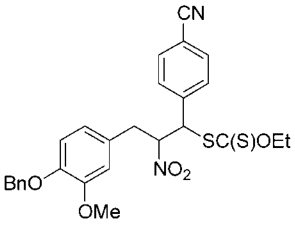
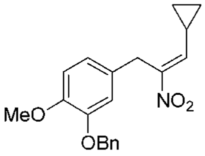
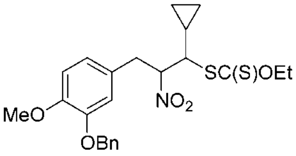
[5] For reviews see: Zard, S. Z. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 672. Zard, S. Z. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 1, pp 90−108.

[6] Guo, B.; Ge, Z.; Cheng, T.; Li, R. *Synth. Commun.* **2001**, *31*, 3021.

[7] Nitro olefins **1** were either commercillay available or synthesized according to the classical Knœvenagel reaction: Jones, G. *Org. React.* **1967**, *15*, 204−599.

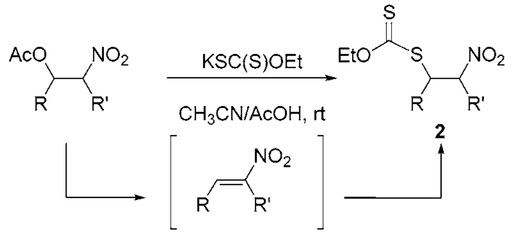
10.1021/ol035027c CCC: $25.00

Table 1. Synthesis β-Nitro Xanthate **2**

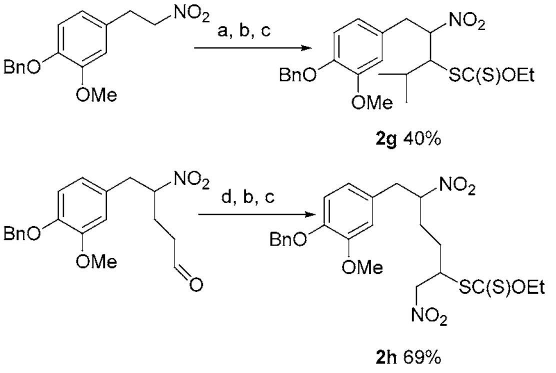
vinyl nitro compound **1**	β–nitro xanthate **2** (yield)
 **1a**	 **2a** 92%
 **1b**	 **2b** 87%
 **1c**	 **2c** 84%
 **1d**	 **2d** 54%
 **1e**	 **2e** 80%
 **1f**	 **2f** 85%

to the nitro group, and thus generate the vinylic nitro compound as an intermediate (Scheme 2). The xanthate salt would then add to the olefin and form the expected compound. We successfully applied this variation to two examples (Scheme 3). In both cases, the acetylated Henry adducts were not purified but were directly treated with potassium *O*-ethyl xanthate in acetonitrile and acetic acid. In the case of compound **2g**, we used the modified Henry conditions described by Gómez-Sánchez.[8]

Scheme 2. Synthesis of β-Nitro Xanthate **2** from Acetylated Henry Adducts



Scheme 3. Synthesis β-Nitro Xanthate **2**[a]

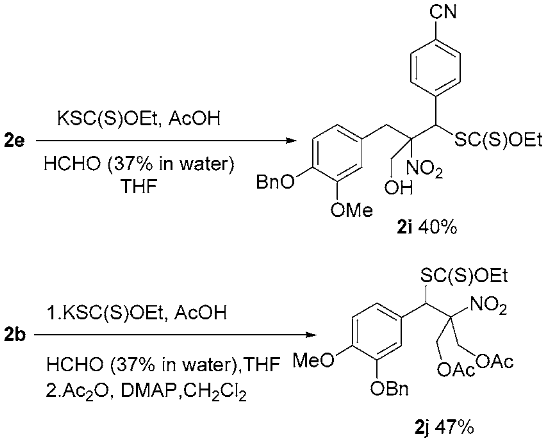


[a] Reagents and conditions: (a) isobutyraldehyde, Et_3N, TBAF, TBDMSCl, THF, 0 °C; (b) Ac_2O, DMAP, CH_2Cl_2, rt; (c) KSC(S)-OEt, MeCN, AcOH; (d) $MeNO_2$, Et_3N.

Not unexpectedly, β-nitro xanthates are sensitive to base and treatment with triethylamine regenerates the corresponding nitro-olefin. The reversibility of the addition of the xanthate salt can, however, be used to advantage by trapping the resulting Michael adduct with an electrophile.

Indeed, the resulting anion could be readily captured with formaldehyde, as illustrated by the transformations in Scheme 4. Unfortunately, we have not yet been successul in extending this multicomponent process to other less reactive electrophiles.

Scheme 4. Functionalization of β-Nitro Xanthate **2**



With a versatile approach to β-nitro xanthates in hand, we examined their behavior under the action of a radical

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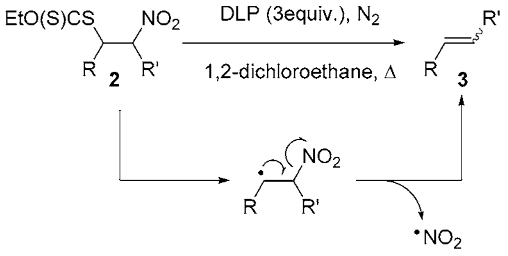
[8] Fernández, R.; Gasch, C.; Gómez-Sánchez, A.; Vílchez, J. E. *Tetrahedron Lett.* **1991**, *32*, 3225.

source, namely stoichiometric amounts of lauroyl peroxide (DLP). We found that this cheap and safe peroxide, with a half-life of 1−2 h at 80 °C, was quite convenient and effective in promoting radical xanthate transfer reactions.[5] The transformation we expected to accomplish is summarized in Scheme 5,

Scheme 5. General Scheme

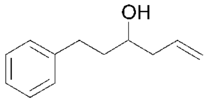
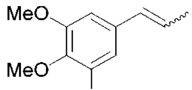
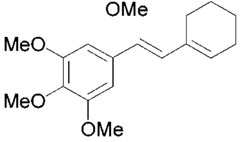
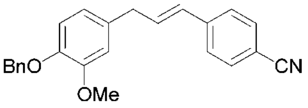
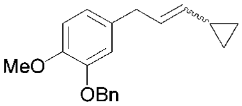
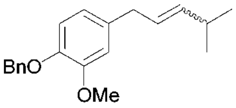
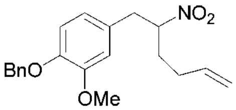
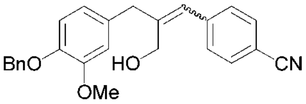
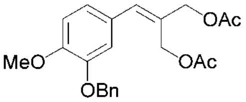


The process is not a chain mechanism because nitrogen dioxide is not a suitable chain carrier, and 3 equiv of initiator were needed for total consumption of the starting material. Presumably, the nitrogen dioxide produced in the process scavenges a portion of the undecyl radicals generated in the thermal decomposition of lauroyl peroxide. The results are compiled in Table 2. The reactions were generally quite clean and the yield good. Radical elimination of the nitrogen dioxide is not stereospecific and both diastereoisomers of the β-nitro xanthates give the thermodynamically most stable olefin with *E* geometry. In other words, bond rotation is faster than β-elimination of the nitrogen dioxide.

The reaction is efficient for the synthesis of mono-, di-, or trisubstituted olefins. As for most radical reactions, it is compatible with many functional groups (free alcohol, ethers, esters, cyano). More interestingly, the reaction is compatible with the presence of other nitro groups (compound **3h**) and with cyclopropane derivatives (compound **3f**). In the latter case, either the elimination of nitrogen dioxide is faster than ring opening of the cyclopropane or the opening of the cyclopropane is reversible under the reaction conditions. We favor the former hypothesis in view of the high rate of xanthate transfer. We would have expected this process to compete successfully with the reverse 3-*exo* ring closure. No ring-opened xanthate was observed. In any case, all these examples highlight once again the remarkable chemoselectivity of the xanthate-mediated radical chemistry. The synthesis of dienes (compound **3d**) is especially noteworthy in this respect.

In summary, these preliminary results demonstrate the potential of β-nitro xanthates as olefin precursors. These compounds are easy to prepare and the structures that one can construct can be quite complex. The olefination method thus efficiently combines the vast ionic chemistry of nitro compounds[9] with the generality and mildness of the xanthate radical fragmentation.

Table 2. Radical Elimination of β-Nitro Xanthates **2**

β–nitro xanthate **2**	olefin **3**	yield (*E*/*Z*)[a]
2a		**3a** 62%
2c		**3c** 75% (*Z*/*E* 1:10)
2d		**3d** 53%
2e		**3e** 75%
2f		**3f** 63% (*Z*/*E* 1:3)
2g		**3g** 57% (*Z*/*E* 1:7)
2h		**3h** 54%
2i		**3i** 82% (*Z*/*E* 4:1)
2j		**3j** 72%

[a] *E*/*Z* ratio determined by ^{1}H NMR.

Acknowledgment. This paper is dedicated with respect and affection to the memory of Professor Sylvestre Julia. We also thank Cécile Blachère for participating in this work as part of an undergraduate research project.

Supporting Information Available: Detailed experimental procedures and spectra data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL035027C

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(9) For general reviews on this chemistry see: (a) Barrett, A. G. M. *Chem. Soc. Rev.* **1991**, *20*, 95. (b) Ono, N. *The Nitro Group in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2001.