Xanthic Anhydrides: A Novel and Convenient Source of Alkoxythiocarbonyl and Alkyl Radicals.

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Abstract: Upon irradiation with visible light, xanthic anhydrides 14 undergo a chain reaction leading to xanthates 17 and involving β -scission of the intermediate alkoxythiocarbonyl radical.

The importance of xanthates in radical chemistry became strongly manifest when, in 1975, Barton and McCombie¹ described a novel method for deoxygenating secondary alcohols based on the reaction of tributyltin hydride with their S-methyl xanthate derivatives. This process was later extended to other precursors containing a thiocarbonyl group such as thiocarbonyl imidazolides² and, more recently, to Oarylthiocarbonates.³ This radical deoxygenation became widely popular, especially in the carbohydrate field where effecting such a transformation using classical ionic chemistry was often fraught with considerable difficulty. Moreover, it highlighted the extraordinary potential of radical reactions and thus helped usher in the golden era of radical based methodologies which was to illuminate the organic synthesis scene soon after.

The initial mechanism proposed by Barton and McCombie¹ for the deoxygenation using xanthates is outlined in Scheme 1, path A. The essential feature is that attack of the tin radicals occurs on the thiono sulfur atom. Almost a decade later, Barker and Beckwith⁴ put forward an alternative sequence starting with an S_H^2 substitution on the sulfide sulfur of the xanthate and proceeding along pathway B in Scheme 1. This step leads to the hitherto unknown alkoxythiocarbonyl radical 3 which was postulated to fragment into carbon oxysulfide and R°. As no straightforward and unambiguous method for generating these species existed at the time, their susceptibility to such a β -scission could not be assessed. We have recently reported,⁵ in preliminary form, a simple solution to this problem involving some novel radical chemistry of xanthic anhydrides. We now wish to present a full account of this work.

This article is dedicated with affection and respect to Professor Sir Derek Barton on the occasion of his 75th birthday.



The appearance of Barker and Beckwith's alternative proposal triggered a more thorough mechanistic investigation by the Barton group.⁶ The results of this study, based essentially on a series of competition experiments, strongly supported the original mechanism which was however modified to include a *reversible* attack of the tin radicals on the thiono sulfur. Further compelling evidence in favour of the Barton-McCombie pathway was provided by an elegant experiment done by Bachi and Bosch⁷ who treated compound 6 with tributyl stannane and found that lactone 7 was obtained in good yield (Scheme 2). If attack on the sulfide sulfur had taken place, one would have expected sulfide 8 to form instead. This compound or others derived from it were not observed.



Scheme 2

Surprisingly, the clear-cut conclusions of Bachi and Bosch were almost immediately challenged by Crich⁸ who claimed that the outcome of the experiment could still be explained by considering that attack took place on the sulfide sulfur and that the ensuing alkoxythiocarbonyl radical added to the olefin before diffusing out of the cage (Scheme 3). Alternatively, it was further proposed, carbon-sulfur bond breaking and carbon-carbon bond formation could be synchronous.



These contentions, put forward without the customary accompaniment of experimental or theoretical evidence, are in fact quite specious, not bearing even a superficial scrutiny. Thus, the cage variant implies a rate of *intramolecular* addition of the alkoxythiocabonyl radical onto the olefin certainly greater than that of diffusion, and this is beyond the reach of any known combination of a carbon centered radical and an olefin.⁹⁴ As for a concerted bond breaking and bond forming process, taking place in what must be a very highly organised transition state and without the formation of a full-fledged intermediate radical, it is not at all obvious why this should occur in the case of a xanthate such as 6 and not in other related systems such a 5-hexenyl bromide (or iodide, sulfide, selenide etc..). As is well known, these, on reaction with stannyl radicals, give well defined 5-hexen-1-yl radicals which cyclise at a measurable rate *several orders of magnitude slower than diffusion*.^{9b}



Scheme 4

In this somewhat controversial context,¹⁰ finding an unambiguous source of alkoxythiocarbonyl radicals in order to study their reactivity, and especially their tendency to β -scission, became an interesting problem. For comparison purposes, it is worth mentioning that alkoxycarbonyl radicals **10** have been studied before and found not to rupture so readily.¹¹ These oxygen analogues are accessible by a number of ways,¹² most commonly by the action of stannyl radicals on a suitable alkyl carbonate derivative **9** (usually a selenocarbonate, **9**, X = SePh) as depicted on the left of Scheme 4.

Such an approach, however, is not easily applicable to alkoxythiocarbonyl radicals for reasons that will become immediately clear on inspection of the right hand reaction manifold in Scheme 4. In this instance, the attack of the stannyl radical can take place either on the X group of the corresponding thiono precursor 11 (path b, the Barker-Beckwith mode) to give the desired alkoxycarbonyl radical and methyl tributyltin sulfide or, alternatively, on the thiono sulfur (path a, the Barton-McCombie mode) to give an intermediate radical 12. The latter can evolve in at least two different ways depending on its lifetime in the medium.

One possibility for it is to undergo β -scission (path d) to an alkyl radical and a tin dithiocarbonate 13 which can be unstable,⁶ rupturing into carbon oxysulfide and Bu₃SnX. The second possibility is for the intermediate radical 12 to loose methyl tributyltin sulfide (path c) giving the desired alkoxythiocarbonyl radical by a more circuitous route. One can speculate at this stage that it is possibly through this route that small but detectable amounts of alkoxythiocarbonyl radicals were produced in Barker and Beckwith's experiment.⁴ It must be remembered that this experiment was done using hexamethyl ditin with irradiation at low temperature thus giving the putative intermediate 12 perhaps sufficient lifetime to fragment; loss of COS would finally provide radical R^o. The same end products are obtained by all three different routes and one cannot be certain whether alkoxythiocarbonyl radicals are indeed major intermediates in the process.





To lift this inherent ambiguity, we decided to examine the behaviour of xanthic anhydrides 14 towards tributyl tin hydride. Our reasoning behind this conjecture is outlined in Scheme 5. Thus, as a direct consequence of the symmetry of the xanthic anhydride, no matter which sulfur the stannyl radical chooses to attack, the products will be the same, namely the desired alkoxythiocarbonyl radical 3 and the tin xanthate 15 which will hydrolyse to the corresponding alcohol 16 upon work-up. If, as required by the mechanism of Barker and Beckwith,⁴ loss of COS is rapid, the ensuing radical R^{\bullet} can then either be reduced to the alkane R-H by the tin hydride or attack the starting xanthic anhydride 14. In the latter case, a chain reaction is triggered leading ultimately to xanthate 17, with the tin radicals acting merely as initiators. If, on

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the other hand, the expulsion of COS is not sufficiently rapid, the alkoxythiocarbonyl radical will abstract a hydrogen atom from the tin hydride to give first a thionoformate 18 which could then be reduced further to the thio-hemiacetal 19. A simple analysis of the products will therefore yield unambiguous information on the behaviour of alkoxythiocarbonyl radicals, at least as far as their propensity to fragmentation is concerned.

Xanthic anhydrides are easily made by treating xanthate salts with phosgene or a chloroformate.¹³ They are generally yellow substances which, although known for more than a century, have been little studied. Apart from some reports on their ionic chemistry, they main uses appear to be as vulcanizers or flotation agents in mineralogy. We selected for our study xanthic anhydride 20 derived from cholestanol because most of the expected products had already been described. In the event, heating 20 with one equivalent of tributyl tin hydride and a catalytic amount of AIBN in benzene for a few minutes resulted in the formation of three steroid derivatives: cholestane, cholestanol, and xanthate 21, isolated in comparable yields.



The outcome of this experiment is exceedingly interesting. It is clear that the loss of COS from the alkoxythiocarbonyl radical is significantly faster than hydrogen abstraction from the tin hydride. However, because the rate of the latter reaction is not known, it is not possible to estimate the minimun absolute rate of this fragmentation. Moreover, since xanthate 21 also reacts with tin hydride to give cholestane and cholestanol, the relative yield of the various products will depend on the exact experimental conditions. The fact that a 50% yield of 21 can be obtained indicates that the chain reaction leading to it is almost certainly the major process operating in the reaction medium. In this instance, the reaction of the cholestanyl radicals with the xanthic anhydride takes place from the α side of the steroid to give the unsymmetrical xanthate. Furthermore, this step must be extremely fast in order to be able to compete with hydrogen abstraction from tin hydride which has a rate constant¹⁴ of the order of $10^6 M^{-1}s^{-1}$.

Over and above answering the initial problem we set out to solve, this crucial experiment revealed a novel aspect of the chemistry of xanthic anhydrides. Thus exposing the same cholestanol derivative 20 to a small amount of AIBN and tributyltin hydride in refluxing hexane gave almost exclusively the unsymmetrical xanthate 21. Alternatively, the chain reaction could be initiated by visible light from a tungsten filament lamp or merely by heating in hexane which had not been degassed. In either case, the yield of 21 is nearly quantitative; moreover, the photochemical variant could be accomplished even below room temperature.

This process represents in fact a new way of generating radicals from alcohols via their xanthic anhydride derivatives, as illustrated by the following examples. The case of simple primary alcohols is represented by compounds **14a-c** which afforded the expected xanthates **17a-c** in 69, 89 and 97% yield respectively on irradiation in refluxing benzene or toluene.¹⁵ A further, perhaps more interesting, example is that of **22** derived from cyclopropylmethanol which gave a 93 % yield of **23** corresponding to the

rearrangement of the intermediate cyclopropylmethyl radical. This can be construed as another proof for the radical nature of the process. Unlike the cholestanyl case, xanthic anhydrides derived from primary alcohols required heating to 50-60°C in order to undergo this transformation in a reasonable time. Little or no change occured upon irradiation at room temperature or below, presumably because the unimolecular rupture of the primary alkoxythiocarbonyl radicals becomes relatively sluggish and, since their reaction with the starting xanthate is degenerate, no macroscopic modification of the system is apparent.



Two carbohydrate examples will further illustrate the scope of this method for the overall homolytic replacement of the carbon-oxygen bond in alcohols with a carbon sulfur bond. Thus, in the same way, both the glucose and galactose derivative 24 and 26 were smoothly converted into the corresponding complex xanthates 25 and 27 in 70 and 81 % yield respectively. These compounds had previously been prepared¹⁶ in low yield by photolysis (U.V. light) of the corresponding bis-xanthates.



Tertiary alcohols in general cannot be used as substrates because the corresponding xanthic anhydrides are quite susceptible to the Chugaev elimination in the same way as their normal xanthate derivatives. Special tertiary alcohols which are prevented from undergoing the elimination such as 1adamantanol or other compounds with a bridgehead hydroxy group should in principle be amenable to this transformation, although we have not so far examined such cases.

The bold assumption of Barker and Beckwith⁴ concerning the propensity of alkoxythiocarbonyl radicals to undergo B-scission turns out to be correct. However, the fact that even those radicals derived from primary alcohols fragment readily at temperatures where the xanthate deoxygenation process itself does not

work well^{1,2b} can be construed as evidence against the involvement of alkoxythiocarbonyl radicals in the main mechanistic pathway.

We next sought to obtain a more quantitative estimate for the rate of loss of carbon oxysulfide from alkoxythiocarbonyl radicals or at least be able to place them on a scale comparing them with other radicals capable of undergoing related fragmentations. The closest analogy is the expulsion of carbon dioxide from alkoxycarbonyl radicals for which some rate measurements have been recorded.¹⁰ We therefore attempted to compare both processes by using a competition experiment involving xanthic anhydrides and alkoxycarbonyl xanthates. We had shown¹⁸ that the latter were a convenient and synthetically useful source of alkoxycarbonyl radicals. Moreover, these substances are also yellow coloured and, in the same way, are sensitive to visible light. The rationale behind the competition experiment is displayed in Scheme 6 which is only superficially complex as it contains a number of symmetrical features and degenerate processes which make the analysis quite simple in fact.



Scheme 6

As we had mentioned earlier, the xanthic anhydride 14a derived from ethanol decomposes on irradiation to give O,S-diethylxanthate 17a in good yield. Under identical conditions, alkoxycarbonyl xanthate 28, easily made by the reaction of ethyl chloroformate and potassium ethyl xanthate, also gives this product, albeit this time through loss of CO_2 . The chain process for each of these processes run down the right and left hand sides respectively of the manifold in Scheme 6.

If a mixture of both is irradiated in the same flask, the ethoxythiocarbonyl radical generated from 14a can either extrude COS *irreversibly* to produce an ethyl radical or react *reversibly* with the other starting material 28 to give an ethoxycarbonyl radical and diethyl xanthic anhydride 14a. Similarly, the

ethoxycarbonyl radical derived from 28 can *irreversibly* fragment to CO_2 and an ethyl radical or it can react *reversibly* with the xanthic anhydride 14a to give an ethoxythiocarbonyl radical and ethoxycarbonyl xanthate 28. The ethyl radicals thus produced will react with either starting material to furnish O,S-diethyl xanthate 17a and propagate the chain process. Since the reaction of each the ethoxythiocarbonyl and ethoxycarbonyl radicals with their precursors (14a and 28 respectively) is degenerate and, as far as the whole system is concerned, their cross reaction with each other's precursor is also degenerate, *the only way evolution can occur is through the two irreversible fragmentation steps*. Thus, the relative rate of these two steps will determine to a large extent which of the two starting materials is depleted fastest. Conversely, by looking at the relative disappearance of the starting materials, information can be obtained regarding the relative rate of the two fragmentation steps (this is valid on the *a priori* reasonable assumption that the equilibrium shown in Scheme 6 is established rapidly and is not too heavily biased in either direction). The fact that both 14a and 28 give the same end product simplifies considerably the final analysis.

In the event, irradiation of a 1:2 mixture of 14a and 28 in refluxing benzene for 30 minutes resulted in the almost complete consumption of the former whereas only about 10% of the latter had reacted as can be easily judged by nmr.. A two-fold excess of the alkoxycarbonyl xanthate was used in order to compensate somewhat for the fact that it contains only one thiocarbonyl group. Clearly the alkoxythiocarbonyl radical undergoes β -scission at least an order of magnitude faster than its oxygen counterpart. In fact, the difference is almost certainly much greater since the comparison should have been done at low conversion to minimize the effect of changes in the concentration terms during the course of the reaction. Further work is needed in this respect; nevertheless, this preliminary experiment does give an idea of the reactivity of alkoxythiocarbonyl radicals which was hitherto not available. Why are these radicals so much more susceptible to fragmentation than their oxygen analogues is not clear at this point. A better overlap and energy correspondence between the SOMO of the radical and the σ^* of the carbon - oxygen bond being broken may be one explanation. A more complete answer will have to await some hard theoretical calculations in order to determine the relative importance of the various interactions involved.

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EXPERIMENTAL SECTION

All reactions were performed under an inert atmosphere (nitrogen or argon) in dry, purified solvents. Melting points were determined using a Reichert hot stage apparatus. ¹H spectra (200MHz) are for deuteriochloroform solutions with tetramethylsilane as internal standard (δ ppm) unless specified to the contrary. I.R. spectra are of Nujol mulls unless otherwise stated. Mass spectra (electron impact) were recorded on MS 50 or VG ZAB spectrometers. MATREX 60 (35-70 µm) silica gel was used for column chromatography. Solvents and reagents were purified according to standard laboratory techniques.

Xanthic anhydride 14a was prepared according to the literature^{13c} procedure; 14b-c, 20, 22, 24, and 26 were prepared according to the following general procedure given for the cholestanyl derivative 20:

Bis-(cholestan-36-yl) xanthic anhydride 20. To a solution of cholestanol (1.00g; 2.58 mmoles) in THF (50 ml) was added n-BuLi in hexane (2.58 mmoles) followed by carbon disulfide (0.99g; 13 mmoles) and the mixture stirred at room temperature for 20 minutes. Methyl chloroformate (0.12g; 1.29 mmoles) was then added and stirring continued for 22 hours in the dark (aluminum foil). The resulting mixture was then poured into saturated brine, extracted with dichloromethane and the combined organic layers dried over sodium sulfate and concentrated *in vacuo* to give an orange foam (1.14g; 98% crude yield). Recrystallisation from ether furnished derivative 20 as a yellow solid in 60-70% yiel; m.p. 166-167°C; $[\alpha]_D^{20} + 6.0^\circ$ (chloroform); v_{max} : 1247, 1235, 955 cm⁻¹; δ_H : 5.50 (m, 2H, 3α H). (Found: C, 75.00; H, 10.50; S, 10.69%. $C_{56}H_{94}O_2S_3$ requires: C, 75.17; H, 10.51; S, 10.74%.).

Bis-(2,2,2-trimethylethyl) xanthic anhydride 14c. This compound was obtained in 45% yield as a yellow oil following chromatography using petroleum ether as eluent (the corresponding amount of ethyl chloroformate was used in this case); v_{max} (film): 1280, 1250, 1033 cm⁻¹; δ_H : 4.33 (s, 4H), 1.03 (s, 18H). It was used without further purification.

Bis-cyclopropylmethyl xanthic anhydride 22. This compound was obtained as a yellow needles (93%) following recrystallisation from ether (the corresponding amount of phosgene, as a 20% solution in toluene, was used in this case in place of methyl chloroformate); m.p. 46-47°C; v_{max} : 1260, 1020 cm⁻¹; δ_H : 4.47 (d, J=7.4Hz, 4H), 1.24-1.42 (m, 2H), 0.64-0.73 (m, 4H), 0.37-0.45 (m, 4H). (Found: C, 45.82; H, 5.42 %. C₁₀H₁₄O₂S₃ requires: C, 45.80; H, 5.34 %.).

Bis-(1,2:5,6-di-O-isopropylidene-\alpha-D-glucofuranos-3-yl) xanthic anhydride 24. This compound was obtained as a yellow oil (96%) following chromatography using petroleum ether- dichloromethane (1:1) as eluent (the corresponding amount of phosgene, as a 20% solution in toluene, was used in this case in place of methyl chloroformate); v_{max} (film): 1250, 1155, 1070, 1025 cm⁻¹; $\delta_{\rm H}$: 5.93-5.97 (m, 4H), 4.68 (d, J=3.9Hz, 2H), 4.27 (m, 4H), 3.99-4.13 (m, 4H), 1.54 (s, 6H), 1.41 (s, 6H), 1.33 (s, 12H). It was used without further purification.

Bis-(1,2:3,4-di-O-isopropylidene-\alpha-D-galactopyranos-6-yl) xanthic anhydride 26. This compound was obtained as a yellow foam (65%) following chromatography using petroleum ether- ether (1:1) as eluent (the corresponding amount of phosgene, as a 20% solution in toluene, was used in this case in place of methyl chloroformate); v_{max} (film): 1250, 1205, 1155, 1060, 1010 cm⁻¹; δ_{H} : 5.56 (d, J= 4.9Hz, 2H), 4.62-4.91 (m, 6H), 4.23-4.40 (m, 6H), 1.51 (s, 6H), 1.46 (s, 6H), 1.36 (s, 6H), 1.32 (s, 6H). It was used without further purification.

General procedure for the photochemically initiated transformation of the xanthic anhydrides.

A degassed solution of the xanthic anhydride (1 mmole) in benzene or toluene (10 ml) was irradiated with a 500W tungsten halogen lamp until disappearance of the starting material (5 - 55 min.). The heat from the lamp caused the solution to reflux gently and the yellow color of the anhydride gradually faded. The toluene was then removed in vacuo and the residue purified by crystallisation in the case of solids or by flash chromatography for liquids.

O-(Cholestan-38-yl)-S-(cholestan-3 α -yl) dithiocarbonate 21. This compound was obtained from anhydride 20 in 83% yield after recrystallisation from ether; m.p.206-206.5°C; $[\alpha]_D^{20} + 32^\circ$ (chloroform); $v_{max} : 1265, 1055$ cm⁻¹; $\delta_H : 5.50$ (m, 1H, 3 α H), 4.13 (br. s, 1H, 3BH). (Found: C, 79.08; H, 11.14 %. C₅₅H₉₄OS₂ requires: C, 79.14; H, 11.27 %.).

O,S-Diethyl dithiocarbonate 17a. This compound was obtained from anhydride 14a in 69% yield and was identical to authentic material.¹⁹

O,S-Di-n-octadecyl dithiocarbonate 17b. This compound was obtained from anhydride 14b in 89% yield. It had a m.p. of 53.5-54°C (ether / methanol; lit.²⁰ m.p. 54.5°C) and was identical to authentic material prepared from potassium n-octadecyl xanthate and 1-bromooctadecane.

O,S-Di-(2,2,2-trimethylethyl) dithiocarbonate 17c. This compound was obtained from anhydride 14c in 97% yield as a colourless liquid; v_{max} (film): 1270, 1205, 1055, 1012 cm⁻¹; δ_{H} : 4.26 (s, 2H), 3.15 (s, 2H), 1.00 (s, 18H).

O-Cyclopropylmethyl S-(3-butenyl) dithiocarbonate 23. This compound was obtained from anhydride 22 in 88% yield as a colourless liquid after chromatography on silica using petroleum ether as eluent; v_{max} (film): 1210, 1160, 1055, 1000 cm⁻¹; $\delta_{\rm H}$: 5.63 (m, 1H), 5.12 (m, 2H), 4.42 (d, J=7.2Hz, 2H), 3.18 (t, J= 7Hz, 2H), 2.45 (m, 2H), 1.27 (m, 1H), 0.64 (m, 2H), 0.38 (m, 2H).

O,S-Di-(1,2:5,6-di-O-isopropylidene- α -D-glucofuranos-3-yl) dithiocarbonate 25. This compound was obtained from anhydride 24 in 70% yield as a colourless oil following chromatography using petroleum ether : ether (2:1) as eluent. This was recrystallised from hexane to give white needles (m.p. 133.5-135.5°C; $[\alpha]_D^{20}$ -63°, c=1 in acetone; lit.¹⁷ m.p. 133-135°C; $[\alpha]_D^{20}$ -56°).

O,S-Di-(1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) dithiocarbonate 27. This compound was obtained from anhydride 26 in 81% yield as a pale yellow oil following chromatography using petroleum ether : ether (4:1) as eluent. Its spectra were identical to those in the literature¹⁷ ($[\alpha]_{p^{20}}$ -58°, c=1.2 in chloroform ; lit.¹⁷ $[\alpha]_{p^{20}}$ -55°).

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