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XANTHATES AS A SOURCE OF STABILISED CARBON CENTERED RADICALS USING VISIBLE LIGHT[+]

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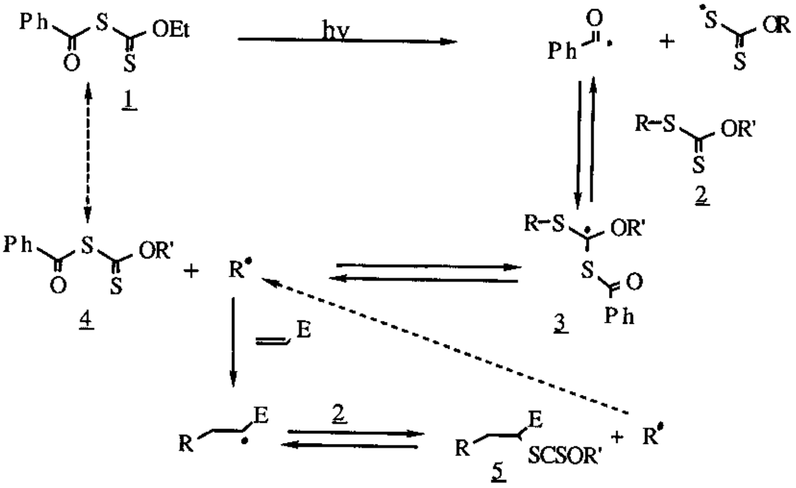
Abstract — Stabilised alkyl radicals can be generated and trapped in useful yields by irradiating the corresponding S-alkyl xanthates with visible light in the presence of catalytic amounts of O-ethyl S-benzoyl xanthate.

We have recently reported that alkyl and acyl xanthates can be induced into participating in a radical chain process whereby an alkyl or acyl radical is produced and captured by an appropriate olefin[1]. Ordinary alkyl xanthates require initiation by uv light whereas acyl xanthates are conveniently decomposed by visible light from a tungsten lamp.

In view of the rather unselective nature of uv irradiation, we considered the possibility of using small amounts of an acyl xanthate to trigger, with visible light, *the radical chain* sequence from an ordinary xanthate as shown by the reaction manifold displayed in scheme 1. Irradiation with visible light of O-ethyl S-benzoyl xanthate 1 produces benzoyl radicals which, unlike aliphatic analogues, are quite resistant to loss of carbon monoxide. In the presence of xanthate 2, a rapid but reversible addition to the thiocarbonyl group takes place leading to radical 3. This addition can then be followed by β-scission to give radical R$^\bullet$ and, concomitantly, a molecule of acylxantate 4. The formation of the latter regenerates the catalytic activity of 1. Finally irreversible addition of R$^\bullet$ onto the olefinic trap sets off the principal chain reaction leading ultimately to derivatives of structures 5.

The success of this contrivance hinges, to a large extent, on the efficiency of the fragmentation leading to R$^\bullet$ as compared with the collapse to give back the benzoyl radical. Clearly, the desired pathway will be favoured if R$^\bullet$ is a stabilised radical. These expectations were borne out in practice using a variety of *resonance stabilised carbon centered radicals.*

[+] This paper is dedicated with respect and gratitude to Professor Sir Derek Barton F.R.S. on the occasion of his seventieth birthday.

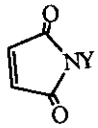


Scheme 1

Thus irradiation with visible light of a refluxing toluene solution of benzyl xanthate 2a (3 fold excess), N-methylmaleimide 6a, and a catalytic amount (ca 10%) of 1 gave cleanly the expected adduct 7a in 78% yield. No reaction is observed in the absence of the acylxanthate catalyst unless the tungsten lamp is replaced by a uv source, but then the yield drops to about 40%[1]. This procedure was extended to other benzylic xanthates as shown by the examples compiled in the Table (entries 1-3). Other stabilised nucleophilic radicals such as allyl and 2-thienomethyl could also be produced and captured with N-benzylmaleimide (entries 4 and 5). Yields are generally good, although no systematic effort was made to optimise the process.

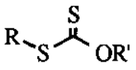
TABLE

Entry	Xanthate	Olefin	Product	Yield(%)
1	2a	6a	7a	78
2	2b	6b	7b	59
3	2c	6b	7c	66
4	2d	6b	7d	52
5	2e	6b	7e	72
6	2f	allyl acetate	8a	71
7	2g	" "	8b	55
8	7a	" "	9a	60
9	7b	" "	9b	67



6a, Y= Me

6b, Y=$PhCH_2$-



2

2a, R= PhCH$_2$-; R' = Me

2b, R= 4-F-C$_6$H$_4$-CH$_2$-; R' = Me

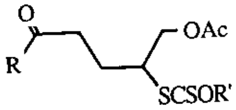
2c, R= 3-(MeO-)-4-(PhCH$_2$O)C$_6$H$_3$CH$_2$-; R' = Me

2d, R= allyl; R' = Me

2e, R= 2-thienylmethyl; R' = Et

2f, R= PhCO-CH$_2$-; R' = Me

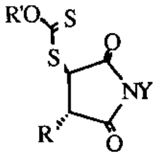
2g, R= MeCO-CH$_2$-; R' = Et



8

8a, R= Ph-; R' = Me

8b, R= Me-; R' = Et



7

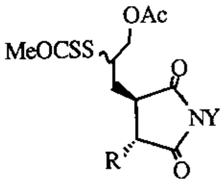
7a, R=PhCH$_2$-; R' = Me ; Y = Me

7b, R= 4-F-C$_6$H$_4$-CH$_2$-; R' = Me ; Y = PhCH$_2$-

7c, R= 3-(MeO)-4-(PhCH$_2$O)C$_6$H$_3$-CH$_2$-; R' = Me; Y = PhCH$_2$-

7d, R= allyl; R' = Me; Y = PhCH$_2$-

7e, R= 2-thienylmethyl; R' = Et ; Y = PhCH$_2$-



9

9a, R= PhCH$_2$-; Y = Me

9b, R = 4-F-C$_6$H$_4$-CH$_2$-; Y = PhCH$_2$-

From a synthetic standpoint, radicals stabilised by conjugation with a carbonyl group are perhaps more interesting. However these are electrophilic species and must be intercepted with an olefin of opposite polar characteristics[2]. For convenience, we have used allyl acetate (5-10 fold excess) as the olefinic trap in these cases. We have thus found, for example, that radicals generated from phenacyl- and acetonylxanthates 2f and 2g readily add to allyl acetate to give derivatives 8a and 8b in good yield (entries 6 and 7). This variant constitutes a simple and efficient procedure for branching the α-position of carbonyl derivatives under mild and essentially neutral conditions. These attractive features are frequently encountered in methods based on controlled radical chain reactions[3].

The process can be taken one step further by noting that adducts 7a-2 themselves are xanthates and therefore potential sources of electrophilic radicals. Indeed, starting from 7a and in the presence of allyl acetate, compound 9a is obtained in 60% yield as a mixture of diasterioisomers (approx. 1:1). Similarly, 9b was prepared from 7b, also in good yield (70%). Thus, simply by alternating the polar characteristics of the radicals and traps it is possible to create sequentially two carbon-carbon bonds at both ends of the olefinic linkage in the maleimide molecule. In fact the whole process leading to 9b (40% yield) can be performed in one pot[3,4] simply by irradiating a mixture of xanthate 2b, N-benzylmaleimide 6b, and allyl acetate in the presence of catalytic amounts of benzoylxanthate 1. The formation of intermediate 7b and its conversion into the final adduct 9b can be easily monitored by thin layer chromatography. The reversibility of the xanthate group transfer therefore makes it possible to pursue the initial reaction further with selectivity being controlled by the various polar factors involved. Overall, this procedure allows an expedient entry into otherwise inacessible derivatives.

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3. B. Giese, "Radicals in Organic Synthesis : Formation of Carbon-Carbon Bonds", Pergamon Press, 1986 ; D.P Curran, Synthesis, 1988, 417; idem, ibid, 1988, 489.
4. For other examples of multiple additions, see : K. Mizuno, M. Ikeda, S. Toda, and Y. Otsuji, J. Amer. Chem. Soc., 1988, 110, 288 ; D.H.R. Barton, E. Da Silva, and S.Z.Zard, J. Chem. Soc., Chem. Commun., 1988, 285 and references there cited.

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