Radicals from Aldehydes: A Convergent Access to Dienes and δ-Lactones

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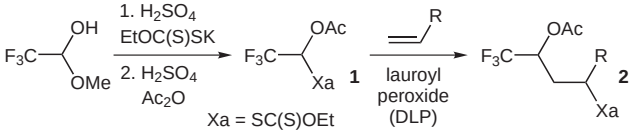
Abstract: A convenient method for the generation of *O*,*S*-acetal xanthates from aldehydes has been developed. The corresponding nucleophilic radicals undergo facile addition to unactivated olefins and the resulting adducts can be further elaborated to generate dienes and unsaturated δ-lactones.

Key words: aldehydes, xanthates, radical reactions, lactones, dienes

Aldehydes are considered as the epitome electrophilic partners in addition reactions of organometallic reagents, and thousands of carbinols have been prepared this way. Through conversion into protected cyanohydrins or dithianes aldehydes can acquire nucleophilic character, and such an umpolung has further expanded their synthetic utility.[1] In contrast, the use of aldehydes as radical precursors has remained somewhat limited, especially in terms of intermolecular radical reactions.[2]

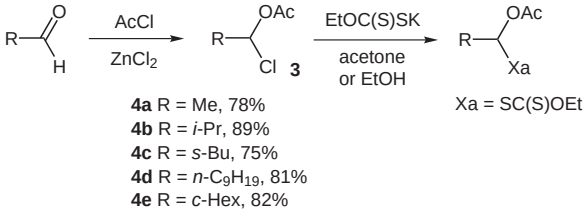
We have recently shown that the xanthate **1** derived from trifluoroacetaldehyde can be applied for the preparation of a wide variety of α-trifluoromethyl alcohol derivatives **2** by radical addition to unactivated olefins (Scheme 1).[3] The high yields of adduct **2** obtained (up to 92%) could be attributed to the strongly electron-withdrawing trifluoromethyl group which modifies the reactivity of the corresponding radical to give highly efficient propagation steps.



Scheme 1

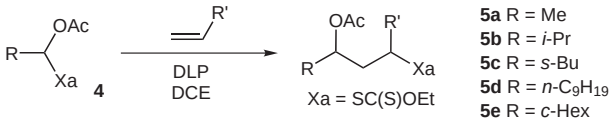
However, the question remained as to whether the presence of an electron-withdrawing group was essential for successful radical addition, or could parallel chemical transformations be accomplished with ordinary aldehydes.

Our initial target was the xanthate derived from acetaldehyde **4a** since it was analogous to the trifluorinated compound **1** (Scheme 2). To this end, a neat mixture of acetaldehyde and acetyl chloride was stirred in the presence of catalytic anhydrous zinc chloride to generate 1-chloroethyl acetate **3a**.[4] Treatment of the crude product mixture with potassium *O*-ethyl xanthate then cleanly furnished the desired radical precursor **4a** in an overall yield of 78%. This fast and efficient two-step protocol was then applied to additional aldehydes in order to assemble a group of radical precursors **4a**–**e** (Scheme 2).[15]



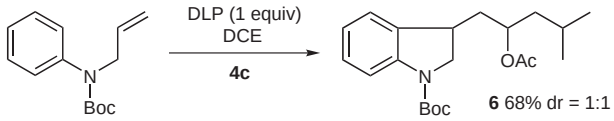
Scheme 2

With xanthates **4** in hand, we next investigated their ability to undergo group transfer radical addition. Pleasingly, when treated with a substoichiometric amount of lauroyl peroxide (DLP, 5–25%) and the corresponding olefin **A**–**F** (2 equiv) in refluxing 1,2-dichloroethane (DCE), xanthates **4** furnished good to excellent yields of olefin addition adducts **5** (Scheme 3, Table 1).[16]



Scheme 3

The adducts **5** were isolated as a mixture of diastereomers with low overall diasteroselectivity being observed during the radical addition step. In some cases interesting, separable minor products of double addition to olefin **B** could be isolated, e.g. **5bB′** and **5eB′** (entries 4 and 10). Moreover, one-pot radical addition to N-protected allyl-aniline followed by intramolecular cyclisation provided rapid access to the functionalised indoline **6** in excellent overall yield (Scheme 4).[5]



Scheme 4

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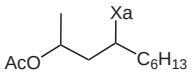
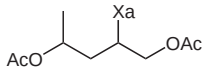
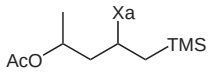
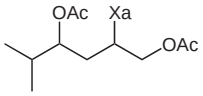
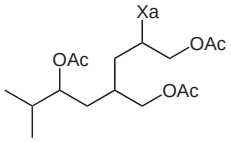
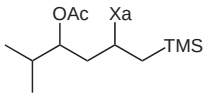
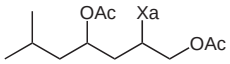
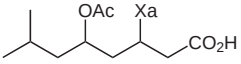
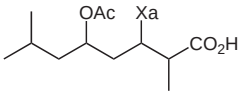
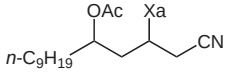
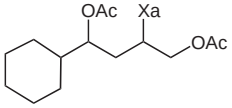
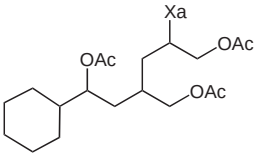
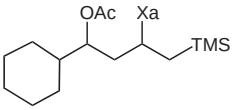
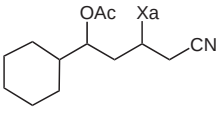
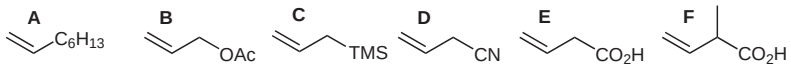
Table 1 Radical Addition of Xanthates **4a–e** to Olefins **A–F**[a]

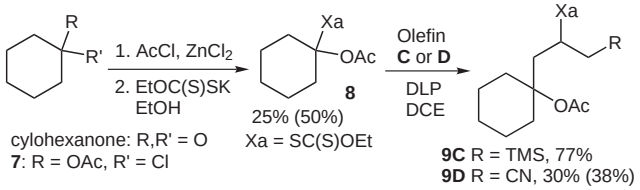
Entry	Substrate	Olefin **A–F**	Product(s) **5**	Xa = SC(S)OEt	Yield (%)[b]	dr[c]
1	**4a**	**A**	**5aA**		71	1:1
2	**4a**	**B**	**5aB**		78	1:1
3	**4a**	**C**[d]	**5aC**		74	1:1
4	**4b**	**B**	**5bB**		57	1:1
			5bB′		22	1:1:1:1
5	**4b**	**C**[d]	**5bC**		70	1:1
6	**4c**	**B**	**5cB**		91	1:1
7	**4c**	**E**	**5cE**		95	1:1
8	**4c**	**F**	**5cF**		81	1:1:1:1
9	**4d**	**D**	**5dD**		81	1:1
10	**4e**	**B**	**5eB**		50	1:1
			5eB′		26	1:1:1:1
11	**4e**	**C**[d]	**5eC**		81	1:1
12	**4e**	**D**	**5eD**		41 (52)[e]	1:1

Olefins **A–F**: 

[a] For general experimental procedures, see ref. 16.
[b] Reported yields are of isolated products.
[c] Diastereomeric ratio was measured after purification by NMR spectroscopy.
[d] Olefin was used as the reaction solvent due to its volatile nature.
[e] Reported yield is based upon recovered xanthate **4e**.

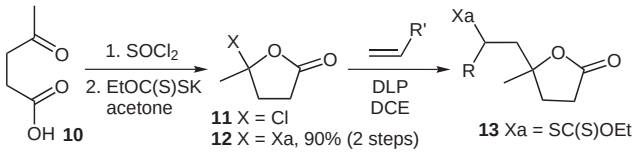
It may now be concluded that the presence of an electron-withdrawing group in the xanthate precursor (e.g. **1**) is unnecessary, and simple aldehyde derivatives **4a**–**e** are sufficiently reactive to undergo radical addition. In order to ascertain whether ketones could fulfill an analogous role as radical precursors, we briefly investigated the reactivity of cyclohexanone and levulinic acid (**10**).

Zinc chloride catalysed chloroacetylation of cyclohexanone to generate 1-chlorocyclohexyl acetate **7** followed by in situ treatment with potassium *O*-ethyl xanthate furnished the desired xanthate precursor **8** in reasonable overall yield (Scheme 5).[4,6] Radical addition to allyltrimethylsilane (olefin **C**) to afford **9C** was higher yielding than the corresponding transformation with allyl cyanide (olefin **D**), possibly due to a side reaction in which the corresponding radical was reduced.



Scheme 5[6,7]

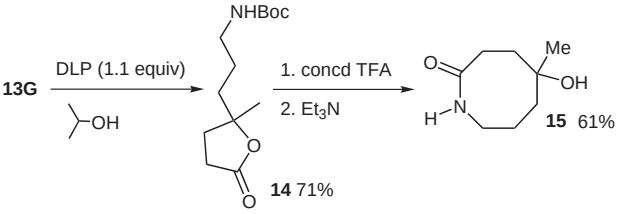
Levulinic acid (**10**) was transformed into xanthate **12** in 90% overall yield by initial thionyl chloride-mediated conversion to chlorolactone **11**, followed by nucleophilic substitution (Scheme 6).[8,17] To our delight, lauroyl peroxide (DLP, 5–25%) initiated radical addition of precursor **12** to olefins **B**–**J** afforded adducts **13B**–**J** in excellent yields (Table 2).[16,18]



Scheme 6

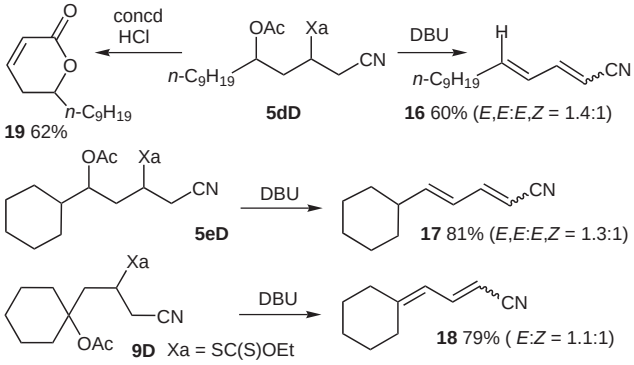
The product derived from (–)-β-pinene **13J** (entry 5) is particularly interesting since it was formed after initial radical addition followed by fragmentation of the cyclobutane ring. Furthermore, adduct **13G** (entry 2) provided facile access to the medicinally important azocin-2-one structural motif **15** through a rapid two-step reaction sequence.[9] Reductive dexanthylation followed by amine deprotection and subsequent base induced in situ cyclisation,[10] converted **13G** into the desired eight-membered lactam **15** in good overall yield (Scheme 7).[11]

Adducts generated by radical addition to allyl cyanide (olefin **D**) are of further significance since they provide new synthetic routes to the valuable building blocks: 1-cyanodienes and unsaturated six-membered lactones. Simply stirring adducts **5dD**, **5eD** (Table 1) and **9D** (Scheme 5) with DBU (2.2 equiv) in dichloromethane



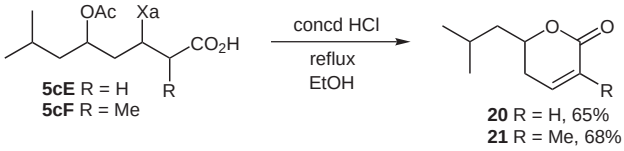
Scheme 7

or acetonitrile at room temperature, furnished the corresponding dienes **16**, **17**, and **18**, respectively, in high yields and with high *E*-selectivity for the γ,δ-double bond (Scheme 8).[19] In contrast, refluxing an ethanolic solution of **5dD** in the presence of concentrated hydrochloric acid afforded unsaturated δ-lactone **19**.[20]



Scheme 8

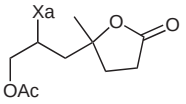
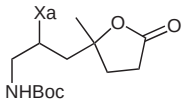
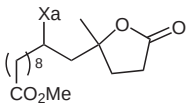
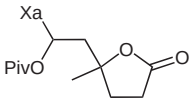
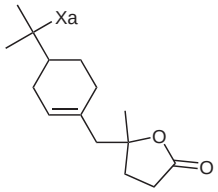
Facile entry into the δ-lactone domain was also obtained through similar thermal acidic treatment of adducts **5cE** and **5cF** (Table 1) to afford cyclisation products **20** and **21**, respectively (Scheme 9). The ready introduction of a methyl substituent is noteworthy since it is ubiquitous amongst natural products.[12,20]

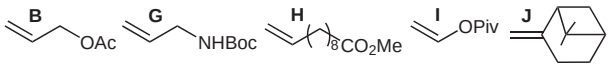


Scheme 9

More complex dienes can be assembled in a highly convergent and efficient manner by radical addition of a xanthate to vinyl pivalate (olefin **I**). The reaction product is a new radical precursor having an equivalent *O*,*S*-acetal moiety to the xanthates derived from aldehydes **4a**–**e**. Thus, xanthates **23**, **26**, and **13I** were prepared in exceptional yields from their corresponding precursors **22**,[13] **25**,[14] and **12** (Table 2, entry 4), respectively (Scheme 10). Radical addition of **23**, **26**, and **13I** to allyl cyanide (olefin **D**) to generate the corresponding addition adducts followed by base-induced elimination finally afforded the

Table 2 Radical Addition of Xanthate **12** to Olefins[a]

Entry	Olefin	Product(s) **13**	Xa = SC(S)OEt	Yield (%)[b]	dr[c]
1	**B**	**13B**		92	1:1
2	**G**	**13G**		89	1:1
3	**H**	**13H**		80	1:1
4	**I**	**13I**		85	1:1
5	**J**	**13J**		71	1:1

Olefins **B**–**J**: 

[a] For general experimental procedures, see ref. 16.
[b] Reported yields are of isolated products.
[c] Diastereomeric ratio was measured after purification.

structurally diverse cyanodienes **24**, **27**, and **28**, respectively, in good overall yields.[19] In line with our previous results (Scheme 8), a high selectivity for the *E* γ,δ-double bond was observed (Scheme 10).

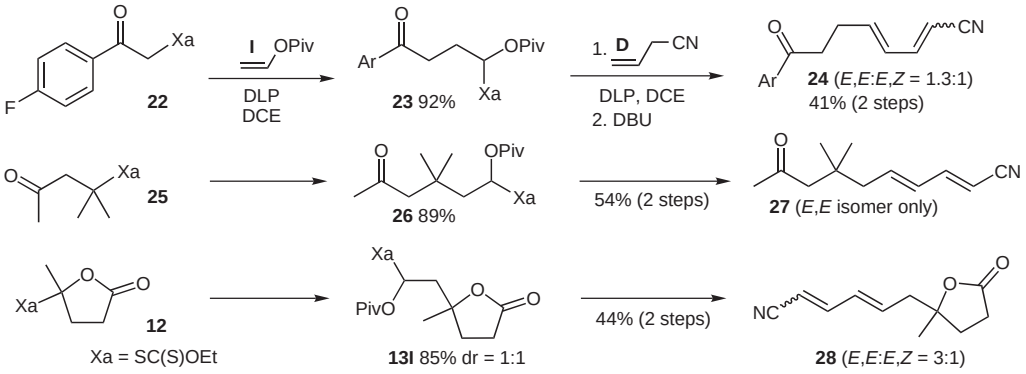
In summary, a facile and highly efficient method for the generation of radicals from aldehydes and their subsequent addition to unactivated olefins has been devised. The addition products have then been demonstrated as excellent precursors to cyanodienes and unsaturated δ-lactones. Since our approach represents an umpolung of the normal electrophilic reactivity of aldehydes, many of the key structural units prepared would be tedious to obtain through existing procedures.

Acknowledgment

We wish to thank Rhodia Chimie Fine for generous financial support to L.T. and Drs. Jean-Marc Paris and François Metz of Rhodia for friendly discussions.

References and Notes

(1) For an example of the use of protected cyanohydrins, see: (a) Stork, G.; Maldonado, L. *J. Am. Chem. Soc.* **1971**, *93*, 5286. (b) Stork, G.; Takahashi, T.; Kawamoto, I.; Suzuki, T. *J. Am. Chem. Soc.* **1978**, *100*, 8272. (c) For an example of the use of dithianes, see: Smith, A. B. III; Adams, C. M.; Barbosa, S. A. L.; Degnan, A. P. *J. Am. Chem. Soc.* **2003**, *125*, 350.



Scheme 10

(2) (a) Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Perkin Trans. 2* **1980**, *5*, 819. (b) Foulard, G.; Brigaud, T.; Portella, C. *J. Org. Chem.* **1997**, *62*, 9107. (c) Nishida, A.; Kawahara, N.; Nishida, M.; Yonemitsu, O. *Tetrahedron* **1996**, *52*, 9713. (d) Dondi, D.; Caprioli, I.; Fagnoni, M.; Mella, M.; Albini, A. *Tetrahedron* **2003**, *59*, 947. (e) Stojanovic, A.; Renaud, P. *Helv. Chim. Acta* **1998**, *81*, 353. (f) Giese, B.; Horler, H. *Tetrahedron* **1985**, *41*, 4025.

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(5) Ly, T. M.; Quiclet-Sire, B.; Sortais, B.; Zard, S. Z. *Tetrahedron Lett.* **1999**, *40*, 2533.

(6) The reaction yields reported are for preliminary studies and hence are unoptimised.

(7) Yields based upon recovered starting material are given in parentheses.

(8) Langlois, D. P.; Wolff, H. *J. Am. Chem. Soc.* **1948**, *70*, 2624.

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(11) Vedejs, E.; Stults, J. S. *J. Org. Chem.* **1988**, *53*, 2226.

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(13) Legrand, N.; Quiclet-Sire, B.; Zard, S. Z. *Tetrahedron Lett.* **2000**, *41*, 9815.

(14) Binot, G.; Quiclet-Sire, B.; Saleh, T.; Zard, S. Z. *Synlett* **2003**, 382.

(15) **General Procedure for Preparation of Xanthates 4a–e.**
To a flask containing freshly fused catalytic $ZnCl_2$ (ca. 5 mg) under argon was added acetyl chloride (2.4 mmol) and the mixture cooled to –5 °C to –10 °C. The aldehyde (1 mmol) was then added dropwise and the resulting reaction mixture stirred at r.t. for 1 h. The mixture was then concentrated under reduced pressure to afford crude chloride **3**. To a solution of crude chloride **3** in EtOH or acetone (1 M) at 0 °C under argon was added portionwise potassium *O*-ethyl xanthate (1.5 mmol) and the resulting mixture stirred at r.t. for 18 h overnight. The mixture was then concentrated under reduced pressure and diluted with H_2O and Et_2O. The aqueous layer was extracted with Et_2O and the organic layers were combined, washed with H_2O, brine, dried (Na_2SO_4), filtered and concentrated in vacuo. Purification by flash chromatography (silica gel) gave xanthates **4** as yellow oils. Note that in some cases, using 0.5 equiv of acetyl chloride gave higher product yields.
Data for (±)-Xanthate 4e.
R_f = 0.2 [PE (40–60)–Et_2O, 97:3]. IR (film): ν_{max} = 2929 (s), 2855 (s), 1753 (s), 1368 (s), 1221 (s), 1111 (s), 1051 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.93–1.30 (5 H, m), 1.40 (3 H, t, *J* = 7.0 Hz), 1.61–1.90 (6 H, m), 2.07 (3 H, s), 4.55–4.70 (2 H, m), 6.57 (1 H, d, *J* = 5.5 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.7 (CH_3), 20.9 (CH_3), 25.8 (2 CH_2), 26.0 (CH_2), 28.5 (CH_2), 28.9 (CH_2), 42.0 (CH), 70.1 (CH_2), 84.7 (CH), 169.3 (C), 210.7 (C). MS (CI): *m/z* (%) = 294 (10) [MNH_4^+], 277 (10) [MH^+], 217 (100). HRMS: *m/z* calcd for $C_{12}H_{20}O_3S_2$: 276.0854. Found: 276.0845 [M^+].

(16) **General Procedure for Radical Addition.**
A solution of xanthate (1 mmol) and the desired olefin (2 mmol) in 1,2-dichloroethane (DCE, 2 mL) was refluxed for 15 min under nitrogen. Lauroyl peroxide (DLP, 5% mol) was then added to the refluxing solution, followed by additional portions (5% mol) every 1.5 h until the xanthate was completely consumed. The mixture was then cooled to r.t., concentrated under reduced pressure and purified by flash chromatography (silica gel). A small layer of basic alumina was placed on top of the silica to remove any lauric acid present.
Data for (±)-Xanthate Adduct 5eD.
R_f = 0.2 [PE (40–60)–Et_2O, 4:1]. IR (film): ν_{max} = 2929 (s), 2855 (s), 2251 (w), 1735 (s), 1446 (s), 1234 (s), 1051 (s), 733 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.93–1.28 (10 H, m), 1.36–1.45 (6 H, m), 1.45–1.59 (2 H, m), 1.59–1.80 (10 H, m), 1.97–2.08 (4 H, m), 2.05 (3 H, s), 2.09 (3 H, s), 2.80–3.05 (4 H, m), 3.78–3.87 (1 H, m), 3.88–3.97 (1 H, m), 4.59–4.68 (4 H, m), 4.78–4.86 (1 H, m), 4.88–4.97 (1 H, m). ^{13}C NMR (100.6MHz, $CDCl_3$): δ = 13.8 (2 CH_3), 21.1 (2 CH_3), 22.6 (CH_2), 24.4 (CH_2), 25.9 (2 CH_2), 26.0 (2 CH_2), 26.2 (CH_2), 26.3 (CH_2), 27.9 (CH_2), 28.2 (CH_2), 28.5 (CH_2), 28.9 (CH_2), 33.8 (CH_2), 34.3 (CH_2), 41.5 (CH), 41.9 (CH), 43.1 (CH), 43.9 (CH), 70.5 (CH_2), 70.6 (CH_2), 74.4 (2 CH), 116.9 (C), 117.1 (C), 170.5 (C), 171.0 (C), 212.0 (C), 212.3 (C). MS (EI): *m/z* (%) = 343 (40) [M^+], 283 (100). HRMS: *m/z* calcd for $C_{16}H_{25}O_3NS_2$: 343.1276. Found: 343.1287 [M^+].

(17) **Procedure for Preparation of Xanthate 12.**
To a flask containing levulinic acid (**10**, 8 g, 69 mmol, 1 equiv) under nitrogen at 0 °C was added dropwise freshly distilled $SOCl_2$ (6 mL, 83 mmol, 1.2 equiv) and the resulting mixture stirred for 1 h. The reaction mixture was then allowed to warm to r.t. and concentrated in vacuo to afford crude chloride **11**. To a solution of crude chloride **11** in acetone (70 mL) at 0 °C under nitrogen was added portionwise potassium *O*-ethyl xanthate (13.3 g, 83 mmol, 1.2 equiv) and the resulting mixture stirred at r.t. for 18 h overnight. The mixture was then concentrated under reduced pressure and diluted with H_2O and Et_2O. The aqueous layer was extracted with Et_2O and the organic layers were combined, washed with brine, dried (Na_2SO_4), filtered and concentrated in vacuo. Purification by flash chromatography [PE (40–60)–EtOAc, 9:1] gave xanthate **12** as a yellow oil (13.7 g, 90%, 2 steps).
Data for (±)-Xanthate 12.
R_f = 0.1 [PE (40–60)–EtOAc, 9:1]. IR (film): ν_{max} = 2981 (s), 2933 (s), 1791 (s), 1241 (s), 1128 (s), 1040 (s), 896 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.50 (3 H, t, *J* = 7.0 Hz), 1.96 (3 H, s), 2.35–2.42 (1 H, m), 2.63–2.91 (3 H, m), 4.67–4.77 (2 H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.7 (CH_3), 28.6 (CH_3), 28.8 (CH_2), 35.2 (CH_2), 70.2 (CH_2), 94.4 (C), 175.1 (C), 209.4 (C). MS (CI): *m/z* (%) = 238 (100) [MNH_4^+], 221 (48) [MH^+]. HRMS: *m/z* calcd for $C_8H_{12}O_3S_2$: 220.0228. Found: 220.0234 [M^+].

(18) **Data for (±)-Xanthate Adduct 13H.**
R_f = 0.15 [PE (40–60)–Et_2O–CH_2Cl_2, 7.5:1.5:1]. IR (film): ν_{max} = 2829 (s), 2856 (s), 1774 (s), 1737 (s), 1444 (s), 1364 (s), 1216 (s), 1052 (s), 734 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23–1.50 (17 H, m), 1.46 (6 H, t, *J* = 7.0 Hz), 1.47 (3 H, s), 1.53 (3 H, s), 1.57–1.97 (9 H, m), 2.00–2.22 (8 H, m), 2.33 (4 H, t, *J* = 7.5 Hz), 2.36–2.46 (2 H, m), 2.54–2.75 (4 H, m), 3.69 (6 H, s), 3.78–3.96 (2 H, m), 4.67 (4 H, q, *J* = 7.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.8 (2 CH_3), 24.8 (CH_3), 24.9 (2 CH_2), 27.0 (CH_3), 27.0 (CH_2), 28.6 (CH_2), 29.0 (2 CH_2), 29.1 (3 CH_2), 29.2 (4 CH_2), 29.3 (CH_2), 32.5 (CH_2), 34.0 (2 CH_2), 34.7 (2 CH_2), 35.9 (CH_2), 44.3 (CH_2), 45.1 (CH_2), 46.7 (CH), 47.3 (CH), 51.3 (2 CH_3), 69.9 (CH_2), 70.0 (CH_2), 85.9 (C), 86.1 (C), 174.2 (2 C), 176.2 (C), 176.3 (C), 214.0 (C), 214.1 (C). MS (CI): *m/z* (%) = 436 (100) [MNH_4^+], 419 (44) [MH^+]. HRMS: *m/z* calcd for $C_{20}H_{34}O_5S_2$: 418.1848. Found: 418.1844 [M^+].

(19) **General Procedure for Diene Formation.**
To a solution of xanthate (1 mmol) in CH_2Cl_2 or MeCN (0.1 M) at r.t. under nitrogen was added DBU (2.2 mmol) dropwise and the resulting mixture stirred for 18 h overnight. The mixture was then concentrated under reduced pressure and diluted with H_2O and Et_2O. The aqueous layer was extracted with Et_2O and the organic layers were combined, washed several times with sat. aq NH_4Cl and then brine, dried (Na_2SO_4), filtered and concentrated in vacuo. Purification was performed by flash chromatography (silica gel).
Data for (±)-(2*E*,4*E*)- and (±)-(2*Z*,4*E*)-5-Cyclohexylpenta-2,4-dienenitrile (17).
Purification by flash chromatography [PE(40–60)–CH_2Cl_2, 7:3) gave diene **17** as a pale yellow oil (81%) and as a mixture of 2 diastereomers in a 2*E*,4*E*/2*Z*,4*E* ratio of 1.3:1. Only traces of the 2*E*,4*Z* and 2*Z*,4*Z* diastereomers could be detected in the NMR spectra.
R_f = 0.5 and 0.35 [PE (40–60)–CH_2Cl_2, 1:1]. IR (film): ν_{max} = 3039 (m), 2927 (s), 2856 (s), 2214 (s), 1637 (s), 1595 (s), 994 (s), 742 (s) cm^{-1}. MS (CI): *m/z* (%) = 179 (100) [MNH_4^+], 162 (1) [MH^+]. HRMS: *m/z* calcd for $C_{11}H_{15}N$: 161.1205. Found: 161.1207 [M^+]
NMR Data for (±)-(2*E*,4*E*)-Isomer.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08–1.43 (5 H, m), 1.59–1.86 (5 H, m), 2.07–2.26 (1 H, m), 5.28 (1 H, d, *J* = 16.0 Hz), 6.11–6.16 (2 H, m), 7.01 (1 H, dd, *J* = 16.0, 10.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.3 (CH_2), 24.4 (2 CH_2), 30.6 (2 CH_2), 41.2 (CH), 96.5 (CH), 115.4 (CN, very weak), 125.5 (CH), 151.4 (CH), 151.6 (CH).
NMR Data for (±)-(2*Z*,4*E*)-Isomer.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08–1.43 (5 H, m), 1.59–1.86 (5 H, m), 2.07–2.26 (1 H, m), 5.14 (1 H, d, *J* = 11.0 Hz), 6.11–6.20 (1 H, m), 6.55 (1 H, dd, *J* = 15.0, 11.0 Hz), 6.82 (1 H, t, *J* = 11.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.3 (CH_2), 24.5 (2 CH_2), 30.7 (2 CH_2), 41.1 (CH), 94.8 (CH), 117.1 (CN, very weak), 124.4 (CH), 150.2 (CH), 151.3 (CH).

(20) **General Procedure for Lactone Formation.**
To a solution of **5dD**, **5cE** or **5cF** (100 mg) in EtOH (10 mL) at r.t. under nitrogen was added concd HCl (1 mL) and the resulting mixture refluxed (EtOH) for 72 h. The mixture was then cooled to r.t., concentrated under reduced pressure and diluted with Et_2O (50 mL). The ethereal phase was washed with sat. aq K_2CO_3, dried ($MgSO_4$), filtered and concentrated in vacuo. Purification by flash chromatography (silica gel) gave lactones **19**, **20**, **21** as yellow oils.
Data for (±)-6-Isobutyl-3-methyl-5,6-dihydro-pyran-2-one (21).
R_f = 0.2 [PE (40–60)–EtOAc, 9:1]. IR (film): ν_{max} = 2959 (s), 2929 (s), 1726 (s), 1368 (s), 1113 (s), 786 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (6 H, d, *J* = 6.5 Hz), 1.26–1.37 (1 H, m), 1.65–1.75 (1 H, m), 1.77–1.92 (1 H, m), 1.86 (3 H, s), 2.17–2.28 (2 H, m), 4.34–4.46 (1 H, m), 6.49–6.58 (1 H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.0 (CH_3), 22.1 (CH), 23.0 (CH_3), 23.9 (CH_3), 30.3 (CH_2), 44.0 (CH_2), 76.4 (CH), 128.4 (C), 139.0 (CH), 166.2 (C). MS (CI): *m/z* (%) = 186 (100) [MNH_4^+], 169 (100) [MH^+].