Intramolecular Homolytic Displacements. 30. Functional Decarbonylative Transformations of Aldehydes via Homolytically Induced Decomposition of Unsaturated Peroxyacetals

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Received December 1, 1999

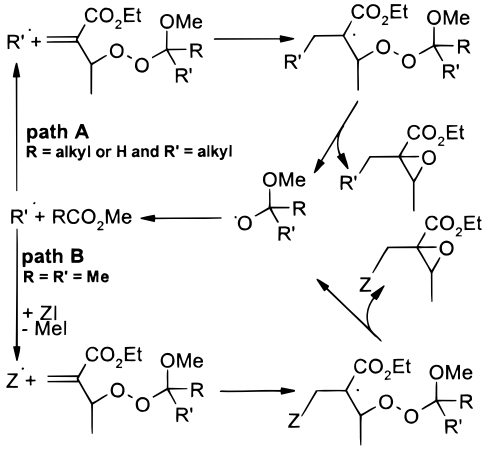
Homolytically induced decompositions of unsaturated peroxyacetals, synthesized from aldehydes, gave alkoxyalkoxyl radicals that yielded alkyl radicals by rapid β-scission. The latter radicals could react with several types of "transfer agents" to smoothly bring about homolytic decarbonylative functional group transformations of aldehydes into halides, hydrocarbons, xanthates, alkanenitriles, 2-alkyl-3-chloromaleic anhydrides, 1-phenylalk-1-ynes, and ethyl 2-alkylpropenoates.

Introduction

Free-radical chemistry has offered over the two past decades new paths for carbon−carbon and carbon−heteroatom bond formation. Barton and co-workers[1] particularly studied the decarboxylative homolytic functional transformations of carboxylic acids via thiohydroxamic esters. Such processes occur by free-radical chain mechanisms in which the key step is the decarboxylation of an acyloxyl radical. To our knowledge, no general study has been published on the decarbonylative functionalization of aldehydes. Recently, new chemistry, based on the fast alkoxyalkoxyl radical fragmentation to generate alkyl radicals, has been developed in our group. First, the free-radical decomposition of unsaturated peroxyacetals was used to synthesize glycidic esters[2] (Scheme 1, path A). The mechanism involved the addition of alkyl radicals, obtained from β-scission of alkoxyalkoxyl radicals, to the peroxyketal carbon−carbon double bond. However, this method has a limitation because it requires the synthesis of a specific peroxide to produce each glycidic ester. A more general pathway based on ethyl 2-[1-(1-methoxy-1-methylethylperoxy)ethyl]propenoate (Scheme 1, path B) was developed with the production of the alkyl radical Z$^{\cdot}$ by iodine abstraction from ZI by a methyl radical.[3]

The alkoxyalkoxyl radical, produced in the induced decomposition of the unsaturated peroxyacetal, originated from the aldehyde RCHO. The alkyl radical R$^{\cdot}$ is then generated by β-elimination; hence, this reaction may be considered as a dehydrodecarbonylation of the aldehyde. Thus, the combination of such an induced decomposition with the reaction of this radical R$^{\cdot}$ with a compound Z−X, to produce RX and a radical Z$^{\cdot}$, would allow the decarbonylative functionalization of the aldehyde, provided Z$^{\cdot}$ adds efficiently to the double bond of the peroxyketals to support a chain reaction mechanism (Scheme 2). In a preliminary communication,[4] we proved the validity of this approach. This paper reports evidence of the general character of this methodology.

Scheme 1



Results and Discussion

Free-radical chlorodecarbonylations of aldehydes have been extensively studied[5] by the generation of a radical in carbon tetrachloride solutions containing the aldehydes. All these studies showed that chlorine atom abstraction by acyl radicals competes with their decarbonylation, making this reaction inefficient for functional transformation of linear and α-alkyl-substituted aldehydes. In the preliminary study,[4] we showed that homolytically induced decomposition of unsaturated peroxyacetals in carbon tetrachloride (peroxyacetal/CCl_4 1/5), with triethylborane−dioxygen initiation, gave alkyl chlorides at room temperature. Thus, this indirect chlorodecarbonylation of dodecanal and 2-methylundecanal gave

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(1) See, e.g.: Crich, D. *Aldrichim. Acta* **1987**, *20*, 35. Crich, D.; Quintero, L. *Chem. Rev.* **1989**, *89*, 1413−1432. Barton, D. H. R. *Tetrahedron* **1992**, *48*, 2529−2544. Motherwell, W. B.; Crich, D. *Free Radical Chain Reactions in Organic Synthesis*; Academic Press: London, 1992.

(2) Colombani, D.; Maillard, B. *J. Org. Chem.* **1994**, *59*, 4765−4772.

(3) Ramon, F.; Degueil-Castaing, M.; Maillard, B. *J. Org. Chem.* **1996**, *61*, 2071−2074.

(4) Moutet, L.; Bonafoux, D.; Degueil-Castaing, M.; Maillard, B. *J. Chem. Soc., Chem. Commun.* **1999**, 139−140.

(5) Winstein, S. *J. Am. Chem. Soc.* **1947**, *69*, 2916−2917. Ol'dekop, Y. A.; Kalinima, A. M.; Shklyar, S. A. *Dokl. Akad. Nauk. S.S.S.R.* **1961**, *139*, 1383−1385; *Chem. Abstr.* **1962**, *56*, 400c. Ol'dekop, Y. A.; Kalinima, A. M. *Zh. Obshch. Khim.* **1964**, *34*, 3473−3478; *Chem. Abstr.* **1965**, *62*, 3972b. Applequist, D. E.; Kaplan, L. *J. Am. Chem. Soc.* **1965**, *87*, 2194−2200.

10.1021/jo9918495 CCC: $19.00
Published on Web 05/27/2000

Scheme 2

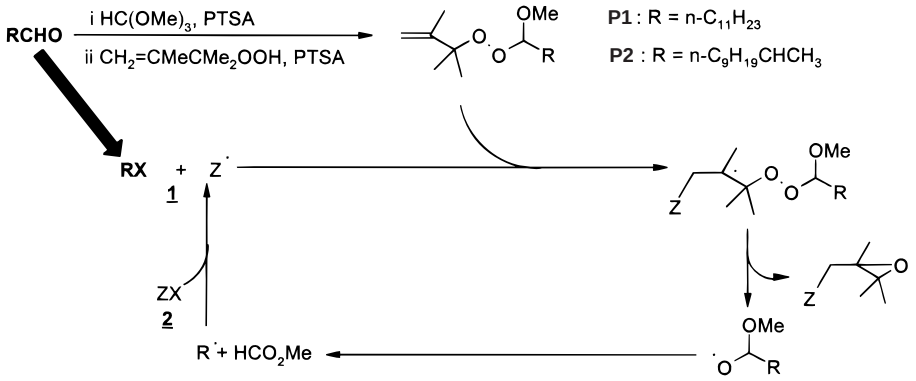
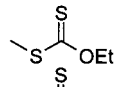
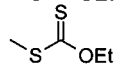
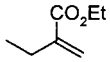
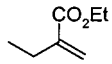
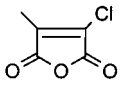
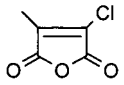


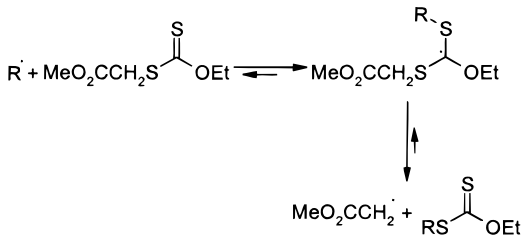
Table 1

	R	X	Z	Yield (%)
a	n-$C_{11}H_{23}$	Cl	Cl_3C	86
b	n-$C_9H_{19}CHCH_3$	Cl	Cl_3C	75
c	n-$C_{11}H_{23}$	Br	Cl_3C	75
d	n-$C_9H_{19}CHCH_3$	Br	Cl_3C	75
e	n-$C_{11}H_{23}$	I	MeO_2CCH_2	75
f	n-$C_9H_{19}CHCH_3$	I	MeO_2CCH_2	75
g	n-$C_{11}H_{23}$		MeO_2CCH_2	75
h	n-$C_9H_{19}CHCH_3$		MeO_2CCH_2	75
i	n-$C_{11}H_{23}$	H	n-$C_{12}H_{25}S$	75
j	n-$C_9H_{19}CHCH_3$	H	n-$C_{12}H_{25}S$	75
k	n-$C_{11}H_{23}$		Br	60
l	n-$C_9H_{19}CHCH_3$		Br	60
m	n-$C_{11}H_{23}$	CN	Br	78
n	n-$C_9H_{19}CHCH_3$	CN	Br	75
p	n-$C_{11}H_{23}$		Cl	50
q	n-$C_9H_{19}CHCH_3$		Cl	50
r	n-$C_{11}H_{23}$	C_6H_5	CF_3SO_2	40
s	n-$C_9H_{19}CHCH_3$	C_6H_5	CF_3SO_2	55

1-chloroundecane (**1a**) and 2-chloroundecane (**1b**) in 86 and 75% yields respectively (Table 1).

The observation of faster bromine abstraction from bromotrichloromethane than of chlorine from carbon tetrachloride[6] by the acyl radical indicated that the decarbonylation of the acyl radical could not compete with the bromine transfer. This showed that the direct bromodecarbonylation of aldehydes by radical production in a solution of the aldehyde and bromotrichloromethane could not be achieved. These observations prompted us to perform the induced decomposition of the unsaturated peroxyacetals **P1** and **P2**, obtained from dodecanal and 2-methylundecanal, respectively, in a solution of bromotrichloromethane in chloroform (peroxyacetal/$BrCCl_3$/$HCCl_3$ 1/1.1/5). The use of chloroform as diluent was necessary to avoid the possible trapping of the adduct radical by the bromotrichloromethane.[7] 1-Bromoundecane (**1c**) and 2-bromoundecane (**1d**) were isolated after each reaction achieved in 75% yield (Table 1). Similarly, the iododecarbonylation of these aldehydes was easily realized using methyl iodoacetate as halogenating agent and cyclohexane as diluent (peroxyacetal/$ICH_2CO_2CH_3$/C_6H_{12} 1;1.1;5 BEt_3/O_2 rt). 1-Iodoundecane (**1e**) and 2-iodoundecane (**1f**) were each produced in 75% yield (Table 1).

Scheme 3



Zard[8] identified a reaction of alkyl radicals with xanthates to produce new xanthates via their addition to the carbon−sulfur double bond. This reaction is reversible, but it appears that the β-elimination is governed by the stability of the eliminated radical. Taking into account these factors, a reaction cascade (combination of the induced decomposition of the unsaturated peroxyketal with the reaction of the alkyl radical with methyl (ethoxythiocarbonyl)thioethanoate (**2g**) was designed to transform aldehydes RCHO into *O*-ethyl alkylsulfanylcarbothioates. Reduction of the latter could then provide thiols RSH. Indeed, methoxycarbonylmethyl radical formation is favored because it is more stabilized than an alkyl radical (Scheme 3). Thus, peroxyacetals synthesized from dodecanal and 2-methylundecanal each gave xanthates (peroxyacetal/**2g**/C_6H_{12} 1;1.1;5 BEt_3/O_2, rt) in 75% yield (**1g** and **1h**, Table 1).

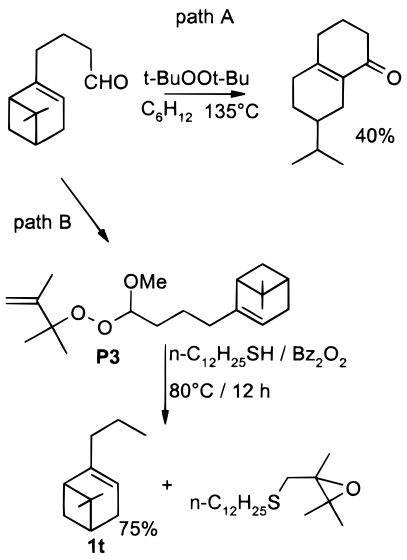
The direct free-radical decarbonylation of aldehydes was developped by Berman.[9] The drastic conditions (high temperature, catalytic amounts of thiol, UV irradiation)

(6) Brown, C. E.; Neville, A. G.; Rayner, D. M.; Lusztyk, J.; Ingold, K. U. *Aust. J. Chem.* **1995**, *48*, 363−379.

(7) Bourgeois, M. J.; Maillard, B.; Montaudon, E. *Tetrahedron* **1986**, *42*, 5309−5320.

(8) Forbes, J. E.; Tailhan, C.; Zard, S. Z. *Tetrahedron Lett.* **1990**, *31*, 2565−2568.

Scheme 4



of this reaction led us to apply the unsaturated peroxyacetal method as a milder alternative. Under triethylborane−dioxygen initiation, peroxyacetal (**P1** or **P2)** and dodecanethiol reacted, at room temperature, in cyclohexane as diluent (peroxyacetal/*n*-$C_{12}H_{25}SH$/C_6H_{12} 1/1.1/5) to yield undecane **1i** (75%, Table 1). A consideration of the mechanism of the direct free-radical decarbonylation also shows it is limited to aldehydes that afford acyl radicals that decarbonylate faster than they react by alternative pathways. This is the case of 7,7-dimethyl-2-(3-formylpropyl)bicyclo[3.1.1]hept-2-ene since its treatment under free-radical conditions produced essentially the ketone obtained from acyl radical cyclization in 40% yield[10] (Scheme 4, path A). The acyclic and decarbonylated product (**1t**), which could not be synthesized directly from the aldehyde, was isolated in good yield using the peroxyacetal method (Scheme 4, path B). The acyl radical is not an intermediate in this reaction, so there is no possibility of cyclization.

Ethyl 2-alkylpropenoates are required as starting materials for various syntheses and as monomers for polymer chemistry. Two free-radical methods were developed to produce them from ethyl 2-bromomethylpropenoate (**2k**). The free-radical reactions involved are based on the reaction of ethyl 2-tributylstannylmethylpropenoate and an alkyl bromide[11] or on that of a thiohydroxamic ester with ethyl 2-alkylthiomethylpropenoate.[12] The induced decomposition of peroxyacetals in the presence of **2k** would offer another alternative for access to such a family of products, the starting materials being an aldehyde and the ethyl 2-bromomethylpropenoate. The reaction performed with **P1** and **P2**, using initiation with AIBN, with cyclohexane as diluent, (peroxyacetal/**2k**/C_6H_{12}/AIBN 1/1.2/6/0.12) afforded **1k** and **1l** (Table 1) in 60% yield. Alkyl radicals reacted with the bromide derivative via an addition−elimination reaction with generation of a bromine atom that added to the peroxyacetal carbon−carbon double bond. This is analogous to Tanko's mechanism[13] for allylation with allyl bromide.

The addition reaction of alkyl radicals to isonitriles has been used for a long time as a way to produce nitriles.[14] The production of alkyl radicals in the induced decomposition of peroxyacetals **P1** and **P2** led us to envisage their reaction with isonitriles to achieve the functional transformation of an aldehyde into a nitrile by the mechanism given in Scheme 2. However, the necessity to prepare a specific isonitrile, liberating an electrophilic radical in its reaction with the alkyl radical, and the commercialy availability of cyanogen bromide (**2m**) prompted us to perform the induced decomposition of the peroxyacetals in the presence of cyanogen bromide, initiated with 1,1-dimethylethyl peracetate (DMEPA), cyclohexane being the diluent (peroxyacetal/**2m**/C_6H_{12}/DMEPA 1/1.8/5/0.12). Undecyl cyanide and 2-methyldecyl cyanide were obtained in 78 (**1m**) and 75% (**1n**) yields, respectively.

Minisci and co-workers[15] achieved the alkylmonodechlorination of dichloromaleic anhydride (**2p**) by an addition−elimination mechanism involving alkyl radicals. Hence, it appeared to us that combination of such a process with the induced decomposition of a peroxyacetal could be another means of production of 2-alkyl-3-chloromaleic anhydrides. This was verified in heating a mixture of peroxyacetal **P1** or **P2**, dichloromaleic anhydride, and DMEPA in cyclohexane (peroxyacetal/**2p**/C_6H_{12}/ DMEPA 1/1.1/5/0.1), which gave the chloromaleic anhydrides **1p** and **1q** in yields of 50%.

In the decomposition of an initiator in a mixture of an aldehyde and trifluoromethylsulfonylphenylacetylene (**2r**), Gong et al.[16] observed the formation of a mixture of an α,β-alkynone and an alkyne. They attributed these products to the involvement of addition−elimination processes of alkyl and acyl radicals with **2r**. Such a mixture proved the existence of a competition between the trapping of the acyl radical by the alkyne and its decarbonylation. To offer a selective alternative to produce the alkyne from the aldehyde, we decided to combine the addition elimination process with the induced decomposition of the peroxyacetal **P1** and **P2** (peroxyacetal/**2r**/CH_3CN/AIBN 1/1.1/5/0.2). These reactions produced 1-phenyltridec-1-yne (**1r**) in a yield of 40% and 3-methyl-1-phenyldodec-1-yne (**1s**) in a 55% yield.

The induced decomposition of the unsaturated peroxyketals were performed in different conditions of reaction. AIBN and DMEPA were used to increase the reaction temperature, when the initiating system BEt_3/O_2 failed.

Conclusion

The induced decomposition of peroxyacetals deriving from aldehydes RCHO and 1,1-dimethylprop-2-enylhydroperoxide functions as a good method for decarbonylative functionalization of aldehydes having a primary or a secondary alkyl group as R. This methodology was applied to generate alkyl halides, alkyl xanthates, alkyl-

(9) Berman, J. D.; Stanley, J. H.; Sherman, W. V.; Cohen, S. G. *J. Am. Chem. Soc.* **1963**, *85*, 4010−4013.
(10) Chatzopoulos, M.; Montheard, J. P. *Rev. Roum. Chim.* **1981**, *26*, 275−282.
(11) Baldwin, J. E.; Adlington, R. M.; Birch, D. J.; Crawford, J. A.; Sweeney, J. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1339−1344.
(12) Barton, D. H. R.; Crich, D. J. *Chem. Soc., Perkin. Trans. 1* **1986**, 1613−1619.
(13) Tanko, J., Sudeghipour, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 159−161.
(14) For recent uses of this reaction, see, e.g.: Curran, D. P.; Ko, S. B.; Josien, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2683−2684. Kim, S. S.; Yang, K. W.; Lee, C. S. *J. Org. Chem.* **1996**, *61*, 4827−4829.
(15) Araneo, S.; Arrigoni, R.; Bjorsvik, H. R.; Fontana, F.; Liguori, L.; Minisci, F.; Recupero, F. *Tetrahedron Lett.* **1996**, *37*, 6897−6900.
(16) Gong, J.; Fuchs, P. L. *Tetrahedron Lett.* **1997**, *38*, 787−790.

nitriles, 2-alkyl-3-chloromaleic anhydrides, 1-phenylalkynes, and ethyl 2-alkylpropenoates in 40−86% yield under mild conditions.

Experimental Section

General Procedure and Materials. ^{1}H NMR spectra were recorded at 250 or 200 MHz, and the ^{13}C NMR data were obtained at 62.9 or 50.3 MHz. The solvent was $CDCl_3$, and chemical shifts are reported relative to tetramethylsilane; *J* values are quoted in Hz. GC was performed with a silica capillary column DB5 (25 m by 0.3 mm by 1.5 μm) on a Varian 3300 apparatus. Microanalysis were performed by CNRS, Vernaison, France. Flash column chromatographic purifications were carried out on SDS silica gel (200−400 mesh) and monitored by TLC using Schleider and Schuell precoated silica gel F1500/LS254 (0.25 mm thickness) plastic-backed plates. The plates were visualized under UV or iodine vapor. Mixtures of light petroleum ether (bp 45−55 °C) and diethyl ether were used as eluant. Other types of purifications were performed by a bulb-to-bulb distillation under reduced pressure using a Büchi oven. Benzene was dried over sodium. Dodecanal and 2-methylundecanal were purchased from Aldrich and were redistilled before use. The other products were commercially available and used without any further purification. α,α′-Azobisisobutyronitrile was obtained from Fluka. Solution (1 M) of triethylborane in hexanes, benzoyl peroxide (Bz_2O_2), cyanogen bromide, and dichloromaleic anhydride were purchased from Aldrich.

Methyl iodoacetate,[17] methyl (ethoxythiocarbonyl)thioethanoate,[18] ethyl 2-bromomethylpropenoate,[19] 1,1-dimethylethylperacetate,[20] phenyltrifluoromethylsulfonylethyne,[21] and 7,7-dimethyl-2-(3-formylpropyl)bicyclo[3.1.1]hept-2-ene[22] were obtained according literature methods.

Preparation of Peroxyacetals. They were synthesized from a dimethylacetal and 1,1-dimethyl-prop-2-enylhydroperoxide[3] with a catalytic amount of PTSA using the method described by Colombani and Maillard[2] and used with no further purification.

2,3-Dimethyl-2-(1-methoxydodecyl)peroxybut-3-ene (P1): 80%; ^{1}H NMR δ 4.88 (s, 1H), 4.8 (s, 1H), 4.72 (t, J = 6 Hz, 1H), 3.4 (s, 3H), 1.76 (s, 3H), 1.6−1 (m, 26H), 0.8 (t, J = 6 Hz, 3H); ^{13}C NMR δ 148.8, 111.1, 107.4, 83.2, 55.8, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 24.9, 24.5, 22.7, 18.6, 18.5, 14.1.

2,3-Dimethyl-2-(1-methoxy-2-methylundecyl)peroxybut-3-ene (P2): 80%; ^{1}H NMR δ 4.9 (s, 1H), 4.8 (s, 1H), 4.56 and 4.52 (d, J = 6 Hz, 1H), 3.52 (s, 3H), 1.8 (s, 3H), 1.6−1 (m, 23H), 0.88 (d, J = 6 Hz, 3H), 0;84 (t, J = 6 Hz, 3H); ^{13}C NMR δ 148.7, 111.1, 110.6, 110.4, 83.3, 57.3, 57.2, 36.2, 36.1, 32.1, 32.0, 31.9, 29.8, 29.6, 29.4, 27.0, 26.9, 24.5, 24.4, 22.7, 18.6, 14.9, 14.5, 14.1.

7,7-Dimethyl-2-[4-methoxy-4-(1,1,2-trimethylprop-2-enyl)peroxybutyl]bicyclo[3.1.1]hept-2-ene (P3): 70%; ^{1}H NMR δ 5.1 (s, 1H), 4.9 (s, 1H), 4.8 (s, 1H), 4.7 (t, J = 6 Hz, 1H), 3.4 (s, 3H), 2.4−1.8 and 1.6−1.3 (m, 12H), 1.8 (s, 3H), 1.3 (s, 6H), 1.2 (s, 3H), 0.8 (s, 3H); ^{13}C NMR δ 148.7, 147.9, 116.1, 111.2, 107.3, 107.2, 83.2, 55.9, 55.8, 45.6, 40.8, 37.9, 36.5, 31.7, 31.6, 31.2, 29.0, 26.3, 24.5, 22.1, 18.6.

General Procedures for the Induced Decomposition of the Peroxyacetals. - BEt_3/O_2 Initiating System. A 1 M solution of triethyborane in hexanes was added dropwise at room temperature directly in a mixture of peroxyacetal, "transfer agent", and the solvent. The reaction was monitored by NMR by following the disappearance of the peroxyacetal. The solvent was evaporated under vacuum, and the product was isolated by flash chromatography or distilled.

Initiation by the Thermal Decomposition of an Initiator. The mixture of peroxyacetal, "transfer agent", initiator, and solvent was heated for 12 h at 80 °C (for AIBN and Bz_2O_2) or 110 °C (for DMEPA) in a glass autoclave.

The solvent was evaporated after the reaction under vacuum, and the product was isolated by flash chromatography or distilled. When the reaction product was known it was identified by comparison with an authentic sample (NMR and GC); unknown ones were characterized by ^{1}H and ^{13}C NMR and microanalysis.

Products. Chloroalkanes: peroxyacetal (**P1** or **P2**, 10 mmol), carbon tetrachloride (50 mmol), BEt_3/O_2. Eluant: petroleum ether. **Chloroundecane**[23] **(1a)**: 86%. **2-Chloroundecane**[24] **(1b)**: 75%.

Bromoalkanes: peroxyacetal (**P1** or **P2**, 10 mmol), bromotrichloromethane (11 mmol), trichloromethane (50 mmol), BEt_3/O_2. Eluant: petroleum ether. **Bromoundecane**[25] **(1c)**: 75%. **2-Bromoundecane**[24] **(1d)**: 75%.

Iodoalkanes: peroxyacetal (**P1** or **P2**, 10 mmol), ethyl iodoacetate (11 mmol), cyclohexane (50 mmol), BEt_3/O_2. Eluant: petroleum ether. **Iodoundecane**[25] **(1e)**: 75%. **2-Iodoundecane**[24] **(1f)**: 75%.

Alkanes. Reaction at room temperature: peroxyacetal (**P1** or **P2**, 10 mmol), dodecanethiol (11 mmol), cyclohexane (50 mmol), BEt_3/O_2. Eluant: petroleum ether. **Undecane**[25] **(1i)**: 75%.

Reaction at 80 °C: peroxyacetal (**P3**, 10 mmol), dodecanethiol (11 mmol), cyclohexane (50 mmol), and benzoyl peroxide (1 mmol). Eluant: petroleum ether.

7,7-Dimethyl-2-propylbicyclo[3.1.1]hept-2-ene (1t): 75%; ^{1}H NMR δ 5.2 (s, 1H), 2.4−1.9 and 1.5−1.3 (m, 10H), 1.3 (s, 3H), 0.9 (t, J = 7 Hz, 3H), 0.9 (s, 3H); ^{13}C NMR δ 148.5, 115.7, 45.8, 41.0, 39.2, 37.9, 31.7, 31.3, 26.4, 21.2, 20.4, 14.0. Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.40; H, 12.40.

Xanthates: peroxyacetal (**P1** or **P2**, 10 mmol), methyl-(ethoxythiocarbonyl)thioethanoate (**2g**, 11 mmol), cyclohexane (50 mmol), BEt_3/O_2. Eluant: 80% of petroleum ether−20% of diethyl ether.

***O*-Ethyl undecylsulfanylcarbothioate (1g):** 75%; ^{1}H NMR δ 4.56 (q, J = 7.1 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H), 1.74−1.02 (m, 21H), 0.8 (t, J = 6.2 Hz, 3 H); ^{13}C NMR δ 215.0, 69.6, 35.9, 31.9, 29.6, 29.5, 29.4, 29.2, 28.9, 28.4, 22.7, 14.1, 13.8. Anal. Calcd for $C_{14}H_{28}OS_2$: C, 60.81; H, 10.21; S, 23.19. Found: C, 60.73; H, 10.04; S, 23.25.

***O*-Ethyl 2-undecylsulfanylcarbothioate (1h):** 75%; ^{1}H NMR δ 4.56 (q, J = 7 Hz, 2H), 3.64 (sx, J = 7 Hz, 1H), 1.7−1.1 (m, 22H), 0.8 (t, J = 6.2 Hz, 3H); ^{13}C NMR δ 214.8, 69.5, 46.0, 36.0, 32.0, 29.6, 29.5, 29.4, 27.1, 22.8, 20.6, 14.2, 13.9. Anal. Calcd for $C_{14}H_{28}OS_2$: C, 60.81; H, 10.21; S, 23.19. Found: C, 60.36; H, 10.27; S, 23.27.

Ethyl 2-alkylpropenoates: peroxyacetal (**P1** or **P2**, 10 mmol), ethyl 2-bromomethylpropenoate (**2k**, 12 mmol), cyclohexane (60 mmol), AIBN (1.2 mmol).

Ethyl 2-dodecylpropenoate (1k): 60% (lit.[26]); eluant: petroleum ether 94%−diethyl ether 6%; ^{1}H NMR δ 6.0 (s, 1H), 5.4 (s, 1H), 4.1 (q, J = 8 Hz, 2H), 2.2 (t, J = 7 Hz, 2H), 1.5−1.1 (m, 23H), 0.8 (t, J = 7 Hz, 3H); ^{13}C NMR δ 166.9, 140.8, 123.7, 60.1, 31.6, 31.5, 29.4, 29.3, 29.1, 29.0, 28.9, 28.1, 22.3, 13.8, 13.7.

Ethyl 2-(2-methylundecyl)propenoate (1l): 60%; eluant: petroleum ether 95%−diethyl ether 5%; ^{1}H NMR δ 6.1 (s, 1H), 5.4 (s, 1H), 4.1 (q, J = 7.1 Hz, 2H), 2.32−2.25 (m, 1H), 1.98−1.9 (m, 1H), 1.9−1.6 (m, 1H), 1.42−1.1 (m, 19H), 0.8 (t, J = 6.6 Hz, 3H), 0.76 (d, J = 6.6 Hz, 3H); ^{13}C NMR δ 167.2, 140.0, 125.2, 60.3, 36.8, 31.8, 29.9, 29.7, 29.6, 29.3, 27.0, 22.6,

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19.2, 14.1, 14.0. Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.05; H, 12.02. Found: C, 76.30; H, 12.11.

Nitriles: peroxyacetal (**P1** or **P2**, 10 mmol), BrCN (18 mmol), cyclohexane (50 mmol), DMEPA (1.2 mmol). **Dodecanenitrile**[27] **(1m)**: 78%. **2-Methylundecanenitrile**[28] **(1n)**: 75%.

Substituted maleic anhydrides: peroxyacetal (**P1** or **P2**, 10 mmol), dichloromaleic anhydride (**2p**, 11 mmol), dried benzene (50 mmol), DMEPA (1 mol).

2-Chloro-3-undecylmaleic anhydride (1p): 50%; eluant: petroleum ether 70%−diethyl ether 30%; ^{1}H NMR δ 2.5−2.3 (m, 2H), 1.8−1.1 (m, 18H), 0.8 (t, J = 6 Hz, 3H); ^{13}C NMR δ 202.3, 144.5, 135.0, 31.7, 29.6, 29.5, 29.4, 29.3, 29.1, 26.7, 24.9, 24.6, 22.6, 14.0. Anal. Calcd for $C_{15}H_{23}ClO_3$: C, 62.80; H, 8.09; Cl, 12.37. Found: C, 63.01; H, 8.15; Cl, 12.24.

2-Chloro-3-(1-methyldecyl)maleic anhydride (1q): 50%; eluant: petroleum ether 90% − diethyl ether 10%; ^{1}H NMR δ 2.9−2.8 (m, 1H), 1.8−1.1 (m, 16H), 1.0 (d, J = 7 Hz, 3H), 0.8 (t, J = 6.7 Hz, 3H); ^{13}C NMR δ 204.7, 147.6, 135.0, 46.2, 31.8, 30.5, 29.6, 29.5, 29.3, 27.6, 27.2, 26.7, 22.6, 17.4, 14.0. Anal. Calcd for $C_{15}H_{23}ClO_3$: C, 62.8; H, 8.09; Cl, 12.37. Found: C, 62.88; H, 8.23; Cl, 12.53.

Alkynes: peroxyacetal (**P1** or **P2**, 10 mmol), phenyltrifluoromethylacetylene (**2r**, 11 mmol), acetonitrile (50 mmol), AIBN (2 mmol).

1-Phenyltridec-1-yne (1r): 40%; eluant: petroleum ether 95%−diethyl ether 5%; ^{1}H NMR δ 7.4−7 (m, 5H), 2.4 (t, J = 7 Hz, 2H), 1.6−1.2 (m, 18H), 0.9 (t, J = 6.5 Hz, 3H); ^{13}C NMR δ 131.6, 128.3, 127.3, 124.3, 90.5, 80.7, 32.1, 32.0, 29.8, 29.6, 29.4, 29.1, 28.8, 23.0, 22.8, 19.5, 14.1. Anal. Calcd for $C_{19}H_{28}$: C, 88.99; H, 11.01. Found: C, 88.78; H, 11.02.

1-Phenyldodec-1-yne (1s): 55%; eluant: petroleum ether 95%−diethyl ether 5%; ^{1}H NMR δ 7.3−7.2 (m, 5H), 2.6 (sx, J = 6.5 Hz, 1H), 1.4−1.2 (m, 19H), 0.8 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ 131.6, 128.2, 127.4, 124.0, 95.0, 82.0, 37.1, 32.0, 29.7, 29.6, 29.4, 27.5, 22.8, 21.2. Anal. Calcd for $C_{19}H_{28}$: C, 88.99; H, 11.01. Found: C, 89.24; H, 10.54.

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