Tetrahedron Letters 50 (2009) 121–123

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Singlet oxygen addition to homoallylic substrates in solution and microemulsion: novel secondary reactions

Axel G. Griesbeck *, Miyeon Cho

Department of Chemistry, University of Cologne, Greinstr. 4, 50939 Köln, Germany

ARTICLE INFO

Article history:
Received 22 September 2008
Revised 19 October 2008
Accepted 21 October 2008
Available online 1 November 2008

Keywords:
Ene reaction
Singlet oxygen
Homoallylic substrates
Rearrangement

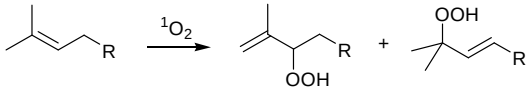
ABSTRACT

The photooxygenation of three homoallylic substrates, the γ,δ-unsaturated ketone **1a**, nitrile **2a**, and the γ,δ-unsaturated ester **3a** was investigated in homogeneous solution and in microemulsion (for **1a**). Two secondary reaction pathways were detected for the allylic hydroperoxides of type **b** and **c**, respectively. The cyclization reactions of **1b** and **2b** to the 1,2-dioxanes **1d** and **2d** followed well-known reaction patterns, whereas the base-catalyzed epoxide (**1e**–**3e**) formation from the tertiary allylic hydroperoxides **1c**–**3c** is a unprecedented reaction type.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

In the course of the singlet oxygen ene reaction, $^1O_2$ attacks one center of a CC double bond with abstraction of an allylic hydrogen atom and with simultaneous allylic shift of the double bond. As a result of this reaction, allylic hydroperoxides are formed. Since the first report, the $^1O_2$ ene reaction has attracted major interest not only in mechanistic photochemistry but also in modern organic synthesis. Several mechanisms have been postulated for this reaction with concerted or 'concerted two-stage' mechanisms,[1] as well as 1,4-biradicals,[2] 1,4-zwitterions,[3] perepoxide, dioxetane[4] or exciplex intermediates. Inter- and intramolecular isotope effect experiments[5] with isotopically labeled tetramethylethylenes provided evidence for the perepoxide intermediate. Also, the small negative activation enthalpies and highly negative activation entropies observed for the singlet oxygen ene reaction from kinetic measurements lead to the fact that the reaction of $^1O_2$ with electron-rich olefins proceed 10^3 times slower than the diffusion rate. This accounts for the presence of non-productive encounters between $^1O_2$ and the alkene favoring the participation of a reversibly formed exciplex as intermediate.[6] The *regiochemistry* of the ene reaction with substrates with multiple sites for allylic hydrogen transfer was extensively studied and several general effects can predict the regioselective introduction of the hydroperoxy group:[7] (a) the *cis*-effect[8] (*syn*-effect). In the reaction of $^1O_2$ with trisubstituted alkenes[9] or enol ethers,[10] the allylic hydrogen atoms on the more substituted side of the double bond are more reactive for H-abstraction by $^1O_2$; (b) the *gem*-effect,[11] that leads to highly selective abstraction of an allylic hydrogen atom from a substituent in α-position of an α,β-unsaturated carbonyl compound; (c) The large-group effect,[12] that leads to selective (moderate) abstraction of an allylic hydrogen from the substituent geminal to a large group. With exception of hydroxyl groups, substituents in allylic positions do not exhibit appreciable effects on the regioselectivity of the $^1O_2$ ene reaction and ca. 1:1 mixtures of secondary and tertiary allylic hydroperoxides are formed (Scheme 1).



Scheme 1.

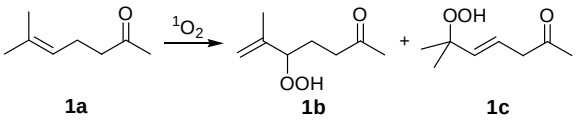
The influence of substituents that are weakly interacting with the π-system such as homoallylic groups has not been systematically investigated. The γ,δ-unsaturated ketone **1a** was recently described as a sensitive substrate for the study of environmental effects on the ene reaction. In zeolite NaMBY, the secondary allylic hydroperoxide is formed preferentially (**1b**:**1c** = 85:15) whereas under isotropic solvent conditions a 53:47 mixture of **1b**:**1c** was reported (Scheme 2).[13]

2. Results and discussion

We became interested in this substrate because of recent experiments performed in microemulsions that show interesting selectivity pattern.[14] Useful sensors for the microenvironment

* Corresponding author. Tel.: +49 221 470 3083; fax: +49 221 470 5057.
E-mail address: griesbeck@uni-koeln.de (A. G. Griesbeck).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.10.094

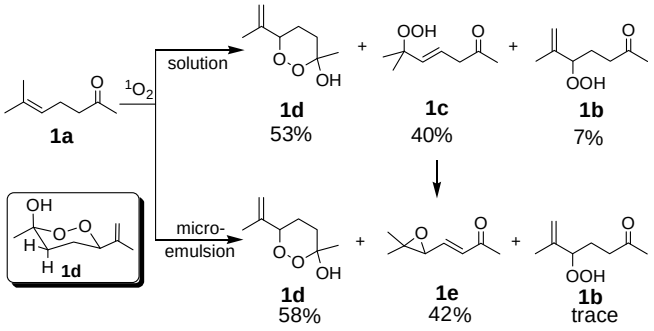


Scheme 2.

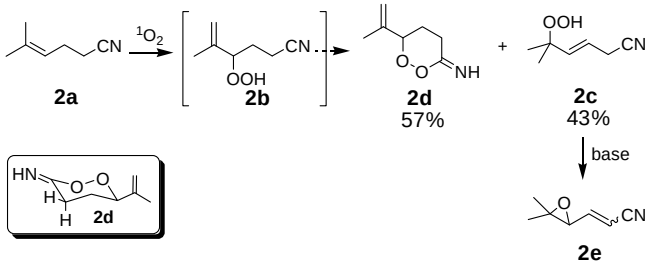
are allylic alcohols that have been widely used to pattern the polarity and hydrogen-bonding situation in isotropic and non-isotropic media, for example, in solution phase,[15] microemulsions,[16] or polymer networks.[17] When testing **1a** as substrate in isotropic media (acetonitrile/rose bengal as sensitizer) in comparison with SDS microemulsions, we discovered two new products **1d**,**e** besides the hydroperoxide mixture **1b**/**1c**. The photooxygenation of **1a** in homogeneous solution (CH_3CN or acetone) gave the 3-hydroxy-1,2-dioxane **1d** and the tertiary hydroperoxide **1c** as the major products, while **1d** and **1e** were obtained in SDS microemulsion. **1d** was formed as a 85:15 diastereoisomeric mixture.[18] The NOESY data indicate the cis isomer (hydroxyl in axial position) as the major diastereoisomer. More interesting was the fate of the tertiary hydroperoxide **1c**: after chromatography on silica, a complete conversion into the epoxy enone **1e**, which was also observed in the microemulsion, took place. From the best of our knowledge, this is a new conversion of allylic hydroperoxides.

We suspected this reaction to be base-induced and actually, treatment of a **1d**/**1c** mixture with sodium acetate in methanol resulted in the corresponding **1d**/**1e** mixture.[19] Epoxy enones of type **1e** are not easily accessible by selective epoxidation of the corresponding dienones[20] (Scheme 3).

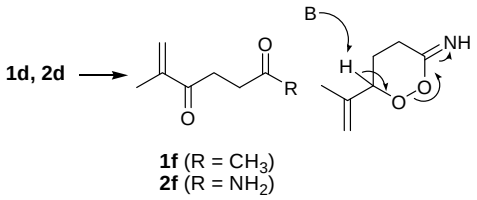
If our procedure is generally applicable, other acceptor-substituted homoallylic substrates should depict similar reactivity in the presence of bases. Indeed, the γ,δ-unsaturated nitrile **2a** gave a comparable reaction picture (Scheme 4). The secondary hydroperoxide **2b** was not observed in the ^1H NMR spectrum but rapidly cyclized to **2d** with an unusual iminoperester structure. The more



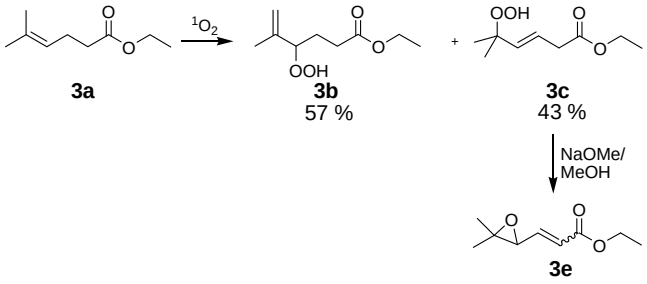
Scheme 3.



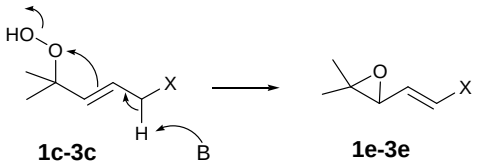
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

stable hydroperoxide **2c**, when treated with base (sodium acetate in methanol), rearranged quantitatively into a *E*/*Z*-mixture of epoxy acrylonitrile derivatives **2e**.[21]

Both the iminoperester **2d** as well as the hydroxydioxane **1d** did ring-open under the basic chromatographic conditions (Al_2O_3, PE–EE) to give the enones **1f** and **2f**, respectively, by a Kornblum–DeLaMare rearrangement (Scheme 5).[22]

The γ,δ-unsaturated ethyl ester **3a** was investigated in order to elucidate the mechanism of the epoxides formation. Dioxane ring formation was not expected from the corresponding secondary hydroperoxide **3b** and actually, this product was isolated as the major regioisomer.[23] The minor product, the tertiary hydroperoxide **3c** was stable under the photooxygenation conditions. When however treated with sodium acetate in methanol, **3c** was slowly converted into the diastereoisomeric epoxides **3e**[24] but full conversion could not be achieved. Quantitative conversion was achieved by using sodium methoxide in methanol indicating the lower acidity of the ester hydroperoxide **3c** in comparison with **1c** and **2c**, respectively (Scheme 6).

In summary, we report a new secondary reaction of allylic hydroperoxides initiated by deprotonation in the α-position of a δ-hydroperoxy β,γ-unsaturated carbonyl compound (or carbonyl analogue). In principle, this process resembles the Kornblum–DeLaMare rearrangement in that deprotonation is followed by heterolytic cleavage of the peroxy bond (Scheme 7).

Acknowledgment

This research was supported by the Deutsche Forschungsgemeinschaft (DFG).

References and notes

1. Singleton, D. A.; Hang, C.; Szymanski, M. J.; Meyer, M. P.; Leach, A. G.; Kuwata, K. T.; Chen, J. S.; Greer, A.; Foote, C. S.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 1319–1328.
2. Maranzana, A.; Canepa, C.; Ghigo, G.; Tonachini, G. *Eur. J. Org. Chem.* **2005**, 3643–3649.
3. Jefford, C. W.; Kohmoto, S.; Boukouvalas, J.; Burger, U. *J. Am. Chem. Soc.* **1983**, *105*, 6498–6500.
4. Gollnick, K.; Kuhn, H. J. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic press: New York, 1979; pp 287–427.
5. Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 1417–1418.
6. Hurst, J. R.; Wilson, S. L.; Schuster, G. B. *Tetrahedron* **1985**, *41*, 2191–2197.
7. Stratakis, M.; Orfanopoulos, M. *Tetrahedron* **2000**, *56*, 1595–1615.
8. Adam, W.; Prein, M. *Angew. Chem., Int. Ed.* **1996**, *35*, 477–494.
9. (a) Orfanopoulos, M.; Gardina, M. B.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 275–276; (b) Rautenstrauch, V.; Thommen, W.; Schulte-Elte, K. H. *Helv. Chim. Acta* **1986**, *69*, 1638–1643.
10. (a) Rousseau, G.; Le Perchec, P.; Conia, J. M. *Tetrahedron Lett.* **1977**, *18*, 2517–2520; (b) Jefford, C. W. *Tetrahedron Lett.* **1979**, *20*, 985–988.
11. (a) Adam, W.; Griesbeck, A. G. *Synthesis* **1986**, 1050–1052; (b) Orfanopoulos, M.; Foote, C. S. *Tetrahedron Lett.* **1985**, *26*, 5991–5994.
12. (a) Clennan, E. L.; Chen, X. *J. Am. Chem. Soc.* **1989**, *111*, 5787–5792; (b) Orfanopoulos, M.; Stratakis, M.; Elemis, Y. *J. Am. Chem. Soc.* **1990**, *112*, 6417–6419.
13. (a) Clennan, E. L.; Sram, J. P.; Pace, A.; Vincer, K.; White, S. *J. Org. Chem.* **2002**, *67*, 3975–3978; (b) Pace, A.; Clennan, E. L. *J. Am. Chem. Soc.* **2002**, *124*, 11236–11237.
14. Aubry, J.-M.; Adam, W.; Alsters, P. L.; Borde, C.; Queste, S.; Marko, J.; Nardello, V. *Tetrahedron* **2006**, *62*, 10753–10761.
15. (a) Griesbeck, A. G.; Adam, W.; Bartoschek, A.; El-Idreesy, T. T. *Photochem. Photobiol. Sci.* **2003**, *2*, 877–881; (b) Bartoschek, A.; El-Idreesy, T. T.; Griesbeck, A. G.; Höinck, L.-O.; Lex, J.; Miara, C.; Neudörfl, J. M. *Synthesis* **2005**, 2433–2444.
16. Nardello, V.; Caron, L.; Aubry, J.-M.; Adam, W.; Bouttemy, S.; Wirth, T.; Saha-Möller, R. C.; Adam, W. *J. Am. Chem. Soc.* **2004**, *126*, 10692–10700.
17. (a) Griesbeck, A. G.; El-Idreesy, T. T.; Bartoschek, A. *Adv. Synth. Catal.* **2004**, *346*, 245–251; (b) Griesbeck, A. G.; Schäfer, M.; Uhlig, J. *Adv. Synth. Catal.* **2008**, *350*, 2104–2108.
18. *General procedure for the photooxygenation in homogeneous solution*: A 0.1 M solution of substrate with the sensitizer (rose bengale) was irradiated with two external 150 W halogen or sodium street lamps. During the irradiation, a stream of air was bubbled through the solution. After complete consumption of the starting material the solvent was removed by rotary evaporation under reduced pressure. The mixture of **1c** and **1d** was chromatographed on silica gel (eluent: PE/EE = 2:1 for **1c**/**1d**, dichloromethane for **2c**/**2d**, dichloromethane/EE = 4:1 for **3b**/**3c**) or neutral aluminium oxide (for **1f** and **2f**, eluent: *c*-hexane/EE = 3:1 for **1f**, *c*-hexane/EE = 2:1 for **2f**).
19. *5-Hydroperoxy-6-methylhept-6-ene-2-one* (**1b**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.12 (s, 3H, CH_3C=O), 2.50 (t, J = 7.0 Hz, 2H, CH_2C=O), 4.26 (t, J = 6.5 Hz, 1H, *H*COO) other signals could not be assigned because of overlap with **1d**; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 17.8 (CH_3C_q), 23.8 ($OCCH_2CH_2$), 29.9 ($OCCH_3$), 39.2 (CH_2CH_2CO), 87.6 (C_qCOO), 113.6 (CH_2), 144.1 (C_q), 209.5 (C=O). *3-Hydroxy-3-methyl-6-(prop-2-enyl)-1,2-dioxane* (**1d**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.34 (s, 3H, OC_qCH_3), 1.73 (s, 3H, C_qCH_3), 1.65–1.83 (m, 2H, CH_2CO), 1.86–2.00 ($C_qCH_2CH_2$), 3.62 (br s, 1H, O*H*), 4.39 (dd, 1H, OOCC*H*), 4.91 (s, 1H, C_q=CH_2), 4.94 (s, 1H, C_q=CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.5 (CH_3C_q), 23.9 ($CHCH_2$), 25.5 (CH_3C_qO), 32.9 (CH_2C_q), 83.0 (CHOH), 99.0 (OOC_qO), 113.5 (CCH_2), 141.9 (C_q=C). *3-Hydroxy-3-methyl-(6-prop-2-enyl)-1,2-dioxane* (diastereoisomer **1d′**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.39 (s, 3H, OC_qCH_3), 1.76 (s, 3H, C_qCH_3), 1.65–1.83 (m, 2H, CH_2CO), 1.86–2.00 ($C_qCH_2CH_2$), 3.73 (br s, 1H, O*H*), 4.39 (dd, 1H, OOCC*H*), 4.91 (s, 1H, C_qCH_2), 4.94 (s, 1H, s, 1H, C_qCH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 20.9 (CH_3C_q), 23.6 ($CHCH_2$), 23.8 (CH_3C_qO), 31.6 (CH_2C_q), 81.8 (CHOOH), 100.6 (OOC_qO), 112.4 (C=CH_2), 142.8 (C_q=C). MS (EI, mixture) *m/z*: 140, 125, 112, 97, 83, 69, 55. IR (film, mixture) ν 3438, 2937, 1446, 1374, 1227, 1141, 1105, 942, 904 cm^{-1}. *(E)-6-Hydroperoxy-6-methylhept-4-ene-2-one* (**1c**): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.29 (s, 6H, 2 × CH_3), 2.13 (s, 3H, CH_3), 3.16 (d, J = 6.8 Hz, 2H, CH_2), 5.63 (d, J = 16.0 Hz, 1H, OOCC*H*=CH), 5.73 (dt, J = 6.8, 16.0 Hz, 1H, =C*H*CH_2), 8.56 (s, 1H, OO*H*); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 24.1 (2 × CH_3), 29.5 (C_qCH_3), 46.9 (CH_2), 81.7 (CHOOH), 122.8 (CH), 138.1 (C_q), 207.6 (C=O). *(3E)-5,6-Epoxy-6-methylhept-3-ene-2-one* (**1e**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 2.16 (s, 3H, $OCCH_3$), 3.22 (d, J = 6.5 Hz, 1H, C*H*=CH_2), 6.23 (d, J = 16.0 Hz, 1H, CH=C*H*), 6.5 (dd, J = 6.5, 16.0 Hz, 1H, C*H*=CH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.5 (C_qCH_3), 24.4 (C_qCH_3), 27.1 ($COCH_3$), 61.5 (OCH), 62.0 (C_q), 133.2 (CHCHC=O), 141.3 ($OCCHCH_q$), 197.0 (C=O). *6-Methylhept-6-ene-2,5-dione* (**1f**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.80 (s, 3H, CH_3C_q), 2.15 (s, 3H, CH_3CO), 2.68 (t, J = 6.5 Hz, 2H, $CH_2CH_2C_q$), 2.93 (t, J = 6.5 Hz, 1H, $OCCH_2CH_2$), 5.72 (s, 1H, H_2CC_q), 5.97 (s, 1H, H_2CC_q); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 17.4 (CH_3C_q), 29.9 (CH_3CO), 31.2 ($OCCH_2CH_2$), 36.9 (CH_2CH_2CO), 124.7 (CH_2C_q), 143.8 (C_q), 199.8 (C_qCO), 207.2 ($COCH_3$).
20. Bougioukou, D. J.; Smonou, I. *Tetrahedron Lett.* **2002**, *43*, 4511–4514.
21. *6-(Prop-2-enyl)-1,2-dioxane-3-imine* (**2d**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.72 (s, 3H, C_qCH_3), 1.82–2.01 (m, 2H, $CHCH_2CH_2$), 2.36–2.54 (m, 2H, CH_2C_q), 4.38 (m, 1H, CHOO), 5.03 (m, 2H, C_qCH_2), 8.75 (br s, 1H, N*H*); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.5 (CH_2CN), 17.4 (CH_3), 26.5 ($OOCCH_2$), 86.5 (COO), 114.8 (CH_2=C_q), 119.3 (C_qCN), 141.9 (CN). MS (EI) *m/z*: 123, 82, 69, 54. IR (film) ν 3361, 2946, 1652, 1438, 1422, 1377, 910 cm^{-1}. *(E)-5-Hydroperoxy-5-methylhex-3-enenitrile* (**2c**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (s, 6H, 2 × CH_3), 3.13 (d, J = 5.3 Hz, 2H, $HCCH_2$CN), 5.56 (dt, J = 5.3, 15.8 Hz, 1H, =C*H*CH_2), 5.91 (d, J = 15.8 Hz, 1H, OOCC*H*=CH), 8.24 (br s, 1H, OO*H*); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 20.1 (CH_2CN), 24.0 (2 × CH_3), 81.5 (COO), 117.3 (CN), 118.0 (=$CHCH_2$), 139.0 (OOCCH=). *5-Methyl-4-oxohex-5-enamide* (**2f**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.93 (s, 3H, CH_3C_q), 2.66 (t, J = 7.5 Hz, 2H, $CH_2CH_2C_q$), 3.11 (t, J = 7.5 Hz, 1H, $OCCH_2CH_2$), 5.90 (s, 1H, H_2CC_q), 6.01 (s, 1H, H_2CC_q), 7.43, 7.90 (br s, NH_2). *(E/Z)-3-(3,3-Dimethyl-oxiran-2-ylacrylonitrile (diastereoisomeric mixture)* (**2e**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (s, 3H, CH_3) 1.29 (s, 3H, CH_3) 1.37 (s, 3H, CH_3) 1.39 (s, 3H, CH_3), for C*H* of diastereoisomer A; 3.29 (d, J = 5.5 Hz, 1H, OC*H*), 5.58 (d, J = 16.2 Hz, 1H, =C*H*CN), 6.65 (dd, J = 5.5, 16.2 Hz, 1H, *H*C=CH), for C*H* of diastereoisomer B; 3.58 (d, J = 8.3 Hz, 1H, OC*H*), 5.57 (d, J = 11.5 Hz, 1H, =C*H*CN), 6.28 (dd, J = 8.3, 11.5 Hz, 1H, *H*C=CH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 24.0 (2 × CH_3), 24.4 (2 × CH_3), 62.4 (C_q), 61.7 (C_q), 61.9 (OCCH), 60.9 (OCCH), 102.6 (CHCN), 103.1 (CHCN), 116.5 (CN), 117.9 (CN), 149.2 (CHCH=), 149.6 (CHCH=).
22. Staben, S. T.; Linghu, X.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 12658–12659.
23. *Ethyl 4-hydroperoxy-5-methylhex-5-enoate* (**3b**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.76 (s, 3H, C_qCH_3), 1.94 (q, J = 6.9 Hz, 2H, $OOCCH_2$), 2.39 (t, J = 7.2 Hz, 2H, $CHCH_2C$=O), 4.15 (q, J = 7.1 Hz, 2H, OCH_2CH_3), 4.33 (t, J = 6.3 Hz , 1H, C_qCHOO), 4.98 (s, 1H, H_2CC_q), 5.02 (s, 1H, H_2CC_q), 8.53 (br s, OO*H*); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.0 (CH_2CH_3), 17.7 (CH_3C_q), 25.3 ($CHCH_2C$=O), 30.1 ($OOCCH_2$), 60.6 (OCH_2CH_3), 87.6 (COOH), 113.8 (CH_2C_q), 143.0 (CH_3C_q), 173.9 (OC=O). IR (film) ν 3396, 2981, 1713, 1373, 1254, 1174, 1028, 902, 858. *(E)-Ethyl 5-hydroperoxy-5-methylhex-3-enoate* (**3c**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (s, 6H, 2 × CH_3), 3.05 (d, J = 6.1 Hz, 2H, $HCCH_2C$=O), 4.10 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 5.63–5.80 (m, 2H, *H*C=C*H*), 8.26 (br s, 1H, OO*H*); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.0 (CH_2CH_3), 24.1 (2 × CH_3), 37.7 ($CHCH_2C$=O), 60.8 (OCH_2CH_3), 81.7 (COO), 122.8 (CHCH$_2$), 137.6 (OOCCH=), 171.9 (OC=O). IR (film) ν 3405, 2975, 1732, 1370, 1261, 1158, 1025, 971, 846. *(E/Z)-Ethyl 3-(3,3-dimethyloxiran-2-yl)acrylate (diastereoisomeric mixture)* (**3e**): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.40 (s, 6H, 2 × *E*-CH_3), 1.41 (s, 6H, 2 × *Z*-CH_3), 3.31 (d, J = 6.4 Hz, 1H, OC*H*), 4.20 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 6.04, 6.05 (dd, J = 1.0, 16.0 Hz, 1H, $CHCO_2$), 6.77, 6.78 (dd, J = 6.5, 16.0 Hz, 1H, CHC*H*=CH); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.1 (CH_2CH_3), 24.5 (2 × CH_3), 60.5 ($CO_2CH_2CH_3$), 61.6 (C_qO), 62.0 ($OCHCH_2$=), 124.2, 124.7 (HCC=O), 142.7, 143.0 (HC=CHC=O), 165.6, 166.0 (O=CO).
24. Marschall, H.; Penninger, J.; Weyerstrahl, P. *Liebigs Ann.* **1982**, 49–67.