Article

Preparation of Propargyl Hydroperoxides by Regioselective Oxidation of Allenic Zinc Reagents with Molecular Oxygen

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Treatment of allenic zinc reagents ($R^1R^2C=C=C(R^3)ZnL$), generated by the reaction of propargyl derivative $(R^1R^2C(X)C \equiv CH)$ with triorganozincates (R^3_3ZnLi) , under oxygen atmosphere in the presence of ZnCl₂ and chlorotrimethylsilane afforded propargyl hydroperoxides (R¹R²C(OOH)- $C = CR^3$) regioselectively. In this reaction, the use of $ZnCl_2$ and chlorotrimethylsilane as additives is essential for the transformation of the initially generated allenic reagents to more reactive chlorozinc species.

Organozinc compounds have been well-known to react with molecular oxygen to provide hydroperoxides and/or alcohols (Scheme 1).^{1,2} Depending on the reaction conditions, such as solvents, temperatures, and O₂ concentration, initially produced zinc peroxides often serve as oxidizing reagent to afford zinc alkoxides.³ The oxidation reaction is of less synthetic utility when the zinc organometallics are prepared from an alky iodide or bromide, derived from the corresponding alcohol. On the other hand, oxidation of organozinc intermediates generated by homologation reaction of organozinc precursors is a synthetically useful transformation, as demonstrated by Knochel et al. in their report of alcohol synthesis from zinc organometallics prepared by hydro- and carbozincation.1c

We previously reported the reaction of triorganozincates with propargylic derivatives 1 leading to the efficient generation of homologated allenic zinc reagents 2 (Scheme 2).⁴ The zinc reagents react with a variety of electrophiles regioselectively at the γ position to give three component coupling products 3. Although organozinc compounds with a $C(sp^2)$ –Zn bond, such as vinyl and arylzincs, are reported to show reduced reactivity toward molecular oxygen in comparison with highly reactive alkylzincs,^{1b} oxidation of allenic zinc reagents 1, if it proceeds in an $S_E 2'$ manner, would provide us with a method for the preparation of propargyl hydroperoxides⁵ and/or alcohols. In the present study, we investi-

SCHEME 1



SCHEME 2

$$\xrightarrow{\mathbf{C}=\mathbf{C}=\mathbf{C}'}_{\mathbf{Zn}(\mathbf{L})} \xrightarrow{\mathbf{E}I^+}_{\substack{\mathbf{E}I=\mathsf{RCHO},\mathsf{RCOCI}\\\mathsf{R}_3\mathsf{SiCI},\mathsf{I}_2,\mathsf{H}_3\mathsf{O}^+}} \xrightarrow{\mathbf{C}=\mathbf{C}=\mathbf{C}=\mathsf{R}}_{\mathbf{S}}^{\mathsf{I}}$$

gated the oxidation of allenic zinc reagents generated by organozincate homologation.

Results and Discussion

Allenic zinc species **2a** was prepared by treatment of propargyl mesylate **1a** with 2 equiv of Bu₃ZnLi in THF at temperatures from -85 to 0 °C (eq 1). The yield of **2a**



is estimated to be 89% by a D₂O quench experiment.^{4a} When the resulting mixture was treated under oxygen

^{(1) (}a) Nützel, K. In Methoden der Organischen Chemie; Thieme: Stuttgart, Germany, 1973; Vol. 13/2a, p 700. (b) Chemla, F.; Normant, J. F. *Tetrahedron Lett.* **1995**, *36*, 3157. (c) Klement, I.; Lütjens, H.; Knochel, P. *Tetrahedron Lett.* **1995**, *36*, 3161–3164. (d) Klement, I.; Knochel, P. *Synlett* **1995**, 1113.

⁽²⁾ For the reaction of organometallics with molecular oxygen, see: Meher-Detweiler, M. *Medhoden der Organischen Chemie*; Thieme,

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(4) (a) Harada, T.; Katsuhira, T.; Osada, A.; Iwazaki, K.; Maejima, K. Oku, A. J. Am. Chem. Soc. 1996, 118, 11377. (b) Harada, T.; Oku, A. In Organozinc Reagents. A Practical Approach; Knochel, P., Jones, P., Eds.; Oxford University Press: Oxford, NY, 1999; Chapter 6.</sup>

TABLE 1. O_2 -Oxidation of Allenic Zinc ReagentGenerated by the Reaction of Propargyl Mesylate 1awith Bu_3ZnLi

	ZnCl ₂ (equiv)	TMSCl (equiv)	temp (°C)	yield (%) ^a	
entry				3a	4a
1			-85	36	13
2			-40	6	34
3	0.5		-40	6	22
4	3		-40	49	5
5^{b}		3	-40		
6	0.5	3	-40	54	7
7	0.5	3	-85	60	
8	0.5	6	-40	50	<2
9	3	3	-40	21	

atmosphere at $-85\ ^\circ C$ for 16 h, 2a underwent S_E2' type reaction with O_2 to give propargyl hydroperoxide 3a and alcohol 4a in 36% and 13% yield, respectively (Table 1, entry 1). The reaction of 2a with O_2 at $-40\ ^\circ C$, on the other hand, afforded alcohol 4a as a major product in 34% yield (entry 2).

In these reactions, 2 equiv of Bu_3ZnLi was employed for the efficient generation of 2a.^{4a} The resulting allenic zinc species, therefore, is an equilibrating mixture of triorganozincates **A** and diorganozinc **B** (eq 2).⁶ Addition



of 0.5 and 3.0 equiv of $ZnCl_2$ may lead to the formation of diorganozinc **B** and chlorozinc **C** species, respectively. To examine the reactivity of these allenic zinc species toward O_2 , reactions of **2a** were carried out in the presence of $ZnCl_2$ as an additive at -40 °C. While the reaction of diorganozincs **B** gave propargyl alcohol **4a** as a major product in low yield (entry 3), relatively clean reaction was observed for chlorozinc **C** affording hydroperoxides **3a** in 49% yield together with a small amount of alcohol **4a** (entry 4).

Chlorotrimethylsilane as a Lewis acidic additive has been reported to be effective in the reaction of organozinc reagents.⁸ To improve the efficiency of O_2 -oxidation of allenic zinc species, we examined the reaction in the





 a R = PhCH₂CH₂.

presence of chlorotrimethylsilane. While the reaction of **2a** without addition of $ZnCl_2$ gave propargylsilane 5^{4a} (entry 5), diorganozinc **B** generated in the presence of $ZnCl_2$ (0.5 equiv) reacted selectively with O_2 in the presence of chlorotrimethylsilane (3 equiv) to give hydroperoxide 3a (entries 6 and 7). The yields of 3a were comparable to that obtained in the reaction of chlorozinc C (entry 4). Further improvement was not obtained either when an increased amount of chlorotrimethylsilane was employed (entry 8) or when the additive was used in combination with 3.0 equiv of $ZnCl_2$ (entry 9). Since the use of a large amount of hygroscopic $ZnCl_2$ for the generation of chlorozinc C often led to some difficulties in reproducing the yield, the reaction conditions with chlorotrimethylsilane (3 equiv) in combination with 0.5 equiv of ZnCl₂ were chosen as a standard method in the following study.

The effect of chlorotrimethylsilane as an additive in the reaction of diorganozinc **B** is most simply rationalized by the in situ formation of chlorozinc reagent **C** (Scheme 3). Thus, if we assume that diorganozinc **B** undergoes reaction with O_2 at the more reactive butyl moiety, the resulting zinc hydroperoxide **6** might be trapped by chlorotrimethylsilane to give chlorozinc **C** with the formation of a trimethylsilylperoxide.

The results summarized in Table 1 suggest relatively higher reactivity of allenic chlorozinc reagents toward O_2 leading to the regioselective formation of propargylic hydroperoxides. Confirmation of this was obtained by the reaction of chlorozinc reagent **8** with O_2 (eq 3). Chlorozinc



8 was prepared by lithiation of allene **7** with butyllithium and transmetalation of the resulting allenic lithium with $ZnCl_2$.⁹ Treatment of **8** under O₂ atmosphere at -40 °C gave hydroperoxide **9** in 57% yield.

⁽⁵⁾ For the previous synthesis of propargyl hydroperoxides, see: (a) Milas, N. A.; Mageli, O. L. *J. Am. Chem. Soc.* **1952**, *74*, 1471. (b) Khan, N. A. *J. Org. Chem.* **1956**, *23*, 606.

⁽⁶⁾ Assuming a rapid ligand transfer,⁷ organozincates [RCH=C=C-(Bu)]_n(Bu)_{3-n}ZnLi (n = 2, 3), as well as diorganozinc [RCH=C=C(Bu)]₂Zn, should also present in the reaction mixture.

^{(7) (}a) Seitz, L. M.; Brown, T. L. J. Am. Chem. Soc. 1966, 88, 4140.
(b) Seitz, L. M.; Brown, T. L. J. Am. Chem. Soc. 1967, 89, 1602. (c) Seitz, L. M.; Little, B. F. J. Organomet. Chem. 1969, 18, 227.
(8) (a) Nakamura, E.; Kuwajima, I. J. Am. Chem. Soc. 1984, 106, (c) Seitz, L. M.; Little, S. F. J. Organomet. I. J. Am. Chem. Soc. 1984, 106, (c) Seitz, L. M.; Seitz, Seitz,

^{(8) (}a) Nakamura, E.; Kuwajima, I. J. Am. Chem. Soc. 1984, 106, 3368.
(b) Nakamura, E.; Aoki, S.; Sekiya, K.; Oshino, H.; Kuwajima, I. J. Am. Chem. Soc. 1987, 109, 8056.
(c) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Yoshida, Z. Angew. Chem., Int., Ed. Engl. 1987, 26, 1157.

⁽⁹⁾ Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, The Netherlands, 1981; p 33.

 TABLE 2.
 O2 Oxidation of Allenic Zinc Reagents 2a-g

 Generated by the Reaction of Propargyl Derivatives

 1a-c with Triorganozincates

R ¹ ↓	2 H	1) (R ³)₃ZnLi		2) 2	ZnCl ₂ , TM	ISCI, ≁			
X	ζ.			(L)	⊃ ₂ , -40 °C				
1a	-C		2a-g						
	R ¹	R^2 R^3	Zn, aq HCl	→ R ¹	\mathbb{R}^2	र ³ (4)			
		 0-ОН	Et ₂ O		он				
3a-g					4a-g				
entry	substrate	zincate	hydroperoxide	yield ^a (%)	alcohol	yield ^a (%)			
						, í			
1	Ph	Bu ₃ ZnLi	PhR ³	60	4 a	92			
	омs 1а		о-он 3а ; R ³ = Bu			56 ^b			
2		s-Bu ₃ ZnLi	3b ; $\mathbf{R}^3 = s$ -Bu	60	4b	54 ^b			
3		t-Bu ₃ ZnLi	$3\mathbf{c}; \mathbf{R}^3 = t - \mathbf{B}\mathbf{u}$	54	4c	81			
4		Bu ₃ ZnLi		60	4d	53 ^b			
	омs 1b		о́-он 3d ; R ³ = Bu						
5		s-Bu ₃ ZnLi	$3\mathbf{e}; \mathbf{R}^3 = s \cdot \mathbf{B}\mathbf{u}$	55	4 e	75			
6		t-Bu ₃ ZnLi	$\mathbf{3f}; \mathbf{R}^3 = t - \mathbf{Bu}$	63	4f	50 ^b			
7		Bu ₃ ZnLi	Bu	54	4g	84			
	1c		о́-он 3g						
^a Isolated yield. ^b Overall yield from 1 .									

Previously, Czernecki et al. reported that a crotylzinc bromide reacts smoothly with O₂ to give a 3:3:4 mixture of *trans*-crotyl alcohol, *cis*-crotyl alcohol, and 1-butene-3-ol in high yield.¹⁰ In contrast to nonregioselective reaction of the crotylzinc reagent, allenic chlorozinc reagents react regioselectively with O₂ in a S_E2' manner at the γ position. Organozinc compounds with a C(sp²)– Zn bond are reported to show low reactivity toward molecular oxygen.^{1b} The reduced reactivity of allenic zinc reagents at the sp² hybridized α carbon could be influential to the observed regioselctivity.

The scope of the present oxidation of allenic reagents generated from propargyl derivatives is shown by the results summarized in Table 2. Allenic zinc reagents **2b**,**c** bearing *sec*-butyl and *tert*-butyl groups at the α carbon were generated by the reaction of **1a** and the corresponding triorganozincates. These reagents gave propargylic hydroperoxides **3b**,**c** in yields comparable to that for the reaction with Bu₃ZnLi (entries 2 and 3). 1-Cyclohexyl-2-propynyl mesylate **1b** also underwent a similar reaction to give hydroperoxide **3d**-**f** in ca. 60% yield (entries 4–6). γ , γ -Disubstituted allenic zinc reagent **2g** can be prepared by the reaction of propargylic chloride **1c** with Bu₃ZnLi. **2g** also reacted with O₂ under the present reaction conditions to give *tert*-hydroperoxide **3g** in 54% yield (entry 7).

For the confirmation of the structure, hydroperoxides **3a**-**g** were converted to the corresponding alcohols **4a**-**g**

by treatment with zinc powder in a 1 N HCl–Et₂O twophase system at 0 °C (Table 2).^{1c} Under these conditions, for example, alcohol **4a** was obtained in 92% from **3a**. When the above transformation was carried out by using a crude reaction mixture obtained by O₂-oxidation of the corresponding allenic zinc reagent, alcohol **4a** was obtained in 56% overall yield from the starting propargylic mesylate **1a**. Hydroperoxides **3a**–**g** and alcohols **4a**–**g** exhibited considerably similar ¹H NMR spectra. However, in the spectra of **3a**–**g**, hydroperoxy proton appeared as a broad signal at 7.4–8.2 ppm. Downfield chemical shifts (ca. 0.3 ppm) were observed in the proton on the α carbon atom of hydroperoxides **3a**–**f** compared with that in the corresponding alcohols **4a**–**f**.¹¹

In summary, we have shown that allenic zinc reagents generated by the reaction of propargylic derivatives 1 and triorganozincates react regioselectively at the γ position with a molecular oxygen to give the corresponding hydroperoxides. To our knowledge, the reaction represents the first example of selective $S_{\rm E}2'$ type O_2 oxidation of organometallics. The use of $ZnCl_2$ and chlorotrimethylsilane as additives was found to be essential to this reaction for the transformation of the initially generated allenic reagents to more reactive chlorozinc species.

Experimental Section

Caution: Although no problems were encountered handling the propargyl hydroperoxides employed in this study, they are potentially explosive. Standard precautions (use of safety shields, avoidance of heat, light, or metal salts, and performance of reactions on minimal scale) should be faithfully observed.¹²

General Procedure for the Preparation of Propargylic Hydroperoxides 3a-g. Zinc chloride (0.28 g, 1.0 mmol) was dissolved in THF (6.6 mL) in a dry Schlenk flask under nitrogen. The resulting solution was cooled at 0 °C. A solution of an alkyllithium (6.0 mmol) (BuLi (1.6 M in hexane), sec-BuLi (0.97 M in cyclohexane, hexane), t-BuLi (1.6 M in pentane)) was added dropwise via syringe. To the resulting solution of triorganozincates (2.0 mmol) at -85 °C was added a solution of propargyl derivative $1a-c^{4a}$ (0.50 mmol) in THF (0.70 mL). After being stirred at -85 °C for 15 min, the mixture was allowed to warm immediately to 0 °C. To the resulting solution of allenic zinc 2 was successively added a solution of ZnCl₂ (34 mg, 0.25 mmol) in THF (1.0 mL) at 0 °C and chlorotrimethylsilane (0.19 mL, 1.5 mmol) at -85 °C. Then, the nitrogen line was exchanged by a thick wall, natural latex rubber balloon filled with oxygen. The mixture was allowed to warm to -40 °C during 1 h and stirred further for 15-20 h. The mixture was poured into aqueous 1 N HCl and extracted with ethyl acetate. The organic layer was washed successively with aqueous 5% Na₂S₂O₃ and water, dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash chromatography (SiO₂, 5% ethyl acetate in hexane) to give hydroperoxide 3a-g and a small amount of alcohols 4a-g(2-7%).

1-Phenyl-4-nonyn-3-yl Hydroperoxide (3a): ¹H NMR δ 0.97 (3H, t, J = 7.2 Hz), 1.47 (2H, m), 1.57 (2H, m), 2.04 (1H, m), 2.13 (1H, m), 2.31 (2H, dt, J = 1.8 and 7.2 Hz), 2.82 (2H, t, J = 7.9 Hz), 4.66 (1H, br t, J = ca. 6 Hz), 7.2–7.3 (5H, m), 8.20 (1H, br); ¹³C NMR δ 13.6, 18.4, 21.9, 30.6, 31.3, 34.8, 75.8,

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77.3, 88.0, 126.0, 128.41, 128.44, 141.1; IR (liquid film) 3425 (br), 2235, 1340, 750, 695 cm⁻¹.

6-Methyl-1-phenyl-4-octyn-3-yl Hydroperoxide (3b): ¹H NMR δ 1.04 (3H, t, J = 7.4 Hz), 1.22 (3H, d, J = 7.0 Hz), 1.50 (2H, m), 1.97–2.17 (2H, m), 2.47 (1H, m), 2.80 (2H, t, J = 6.3 Hz), 4.67 (1H, br t, J = ca. 6 Hz), 7.2–7.3 (5H, m), 8.15 (1H, br); ¹³C NMR (125.8 MHz, CDCl₃) δ 11.7, 20.6, 27.5, 29.7, 31.4, 34.9, 75.9, 77.4, 92.3, 126.0, 128.42, 128.44, 141.1; IR (liquid film) 3400 (br), 2220, 1325, 740, 690 cm⁻¹.

6,6-Dimethyl-1-phenyl-4-heptyn-3-yl Hydroperoxide (3c): ¹H NMR δ 1.17 (9H, s), 1.85–2.15 (2H, m), 2.66 (2H, t, J = 6.6 Hz), 4.54 (1H, t, J = 6.7 Hz), 7.1–7.25 (5H, m), 7.80 (1H, br); ¹³C NMR δ 27.5, 31.0, 31.4, 34.8, 75.5, 75.9, 96.4, 126.0, 128.45, 128.49, 141.1; IR (liquid film) 3420 (br), 2225, 1355, 740, 690 cm⁻¹.

1-Cyclohexyl-2-heptynyl Hydroperoxide (3d): ¹H NMR δ 0.90 (3H, t, J = 7.4 Hz), 1.05–1.25 (5H, m), 1.45 (2H, m), 1.54 (2H, m), 1.65–1.85 (6H, m), 2.29 (2H, dt, J = 1.9 and 7.0 Hz), 4.44 (1H, br d, J = 6.4 Hz), 8.12 (1H, br); ¹³C NMR δ 13.6, 18.4, 22.0, 25.76, 25.80, 26.3, 28.4, 29.0, 30.7, 40.6, 76.5, 81.4, 88.3; IR (liquid film) 3420 (br), 2210, 1325 cm⁻¹.

1-Cyclohexyl-4-methyl-2-hexynyl Hydroperoxide (3e): ¹H NMR δ 0.99 (3H, t, J = 7.0 Hz), 1.1–1.3 (8H, m), 1.45–1.5 (2H, m), 1.65–1.80 (6H, m), 2.43 (1H, m), 4.45 (1H, br d, J = ca. 6.5 Hz), 8.10 (1H, br); ¹³C NMR δ 11.8, 20.7, 25.77, 25.81, 26.3, 27.6, 28.3, 29.0, 29.8, 40.6, 76.6, 77.3, 81.4; IR (liquid film) 3400 (br), 2225, 1330 cm⁻¹.

1-Cyclohexyl-4,4-dimethyl-2-pentynyl Hydroperoxide (**3f**): ¹H NMR δ 1.0–1.3 (14H, m, including s (9H) at 1.27), 1.65–1.85 (6H, m), 4.45 (1H, d, J = 6.0 Hz), 8.10 (1H, br); ¹³C NMR δ 25.79, 25.82, 26.3, 27.5, 28.3, 29.1, 31.0, 40.6, 74.7, 81.4, 96.7; IR (liquid film) 3420 (br), 2240, 1450, 1260 cm⁻¹.

1-Hexynylcyclohexyl Hydroperoxide (3g): ¹H NMR δ 0.94 (3H, t, J = 7.3 Hz), 1.45–1.7 (12H, m), 1.91 (2H, m), 2.28 (2H, t, J = 7.2 Hz), 7.40 (1H, br); ¹³C NMR δ 13.6, 18.3, 21.9, 22.7, 25.4, 30.8, 35.2, 80.09, 81.40, 86.9; IR (liquid film) 3420 (br), 2240, 1340 cm⁻¹.

General Procedure for Conversion of Hydroperoxides 3a-g into Alcohols 4a-g. Aqueous 1 N HCl (5.0 mL) was added to a solution of propargylic hydroperoxide 3a-g (0.5 mmol) in ether (10 mL). To the vigorously stirred mixture at 0 °C was added zinc powder (0.30 g, 0.46 mmol). After being stirred for 30 min the reaction mixture was filtered and the filtrate was extracted with ether. The organic layer was dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash chromatography (SiO₂, 5% ethyl acetate in hexane) to give alcohol 4a-g.

hexane) to give alcohol **4a**–g. **1-Phenyl-4-nonyn-3-ol (4a):** bp 150 °C/0.06 mmHg (Kugel rohr); ¹H NMR δ 0.92 (3H, t, J = 7.3 Hz), 1.4–1.45 (2H, m), 1.5–1.55 (2H, m), 1.95–2.05 (3H, m), 2.23 (2H, m), 2.82 (2H, t, J = 7.9 Hz), 4.36 (1H, m), 7.2–7.3 (5H, m); ¹³C NMR (125.8 MHz, CDCl₃) δ 13.6, 18.3, 21.9, 30.7, 31.5, 39.6, 62.0, 80.9, 86.0, 125.9, 128.4, 128.5, 144.5; IR (liquid film) 3350 (br), 2225, 1030, 745, 695 cm⁻¹; MS *m*/*z* (rel intensity) 216 (M⁺, 14), 141 (20), 91 (100); HRMS calcd for C₁₅H₂₀O 216.1514, found 216.1513.

6-Methyl-1-phenyl-4-octyn-3-ol (4b): ¹H NMR δ 0.99 (3H, t, J = 7.5 Hz), 1.16 (3H, d, J = 6.9 Hz), 1.45–1.50 (2H, m), 1.80 (1H, br), 1.95–2.05 (2H, m), 2.41 (1H, m), 2.78 (2H, t, J = 7.9 Hz), 4.38 (1H, br t, J = ca. 6.5 Hz), 7.15–7.30 (5H, m); ¹³C NMR δ 11.8, 20.7, 27.5, 29.8, 31.5, 39.8, 62.0, 81.2, 90.3, 125.9, 128.4, 128.5, 141.5; IR (liquid film) 3320 (br), 2220, 1050, 1030, 1010, 745, 695 cm⁻¹; MS m/z (rel intensity) 216 (M⁺, 18), 159 (100), 91 (90); HRMS calcd for C₁₅H₂₀O 216.1514, found 216.1514.

6,6-Dimethyl-1-phenyl-4-heptyn-3-ol (4c): ¹H NMR δ 1.24 (9H, s), 1.74 (1H, br), 1.95–2.05 (2H, m), 2.79 (2H, t, J= 7.9 Hz), 4.35 (1H, t, J = 6.5 Hz), 7.15–7.3 (5H, m); ¹³C NMR

 δ 27.3, 31.0, 31.5, 39.7, 62.0, 79.3, 94.3, 125.9, 128.4, 128.5, 141.6; IR (liquid film) 3320 (br) 2225, 1145, 740, 690 cm^{-1}; MS m/z (rel intensity) 216 (M⁺, 8), 183 (87), 91 (100); HRMS calcd for $C_{15}H_{20}O$ 216.1514, found 216.1514.

1-Cyclohexyl-2-heptyn-1-ol (4d): ¹H NMR δ 0.89 (3H, t, J = 5.0 Hz), 1.00–1.25 (5H, m), 1.35–1.55 (5H, m), 1.65–1.85 (6H, m), 2.20 (2H, dt, J = 1.8 and 7.0 Hz), 4.12 (1H, d, J = 5.0 Hz); ¹³C NMR δ 13.6, 18.4, 21.9, 25.89, 25.92, 26.4, 28.1, 28.6, 30.8, 44.4, 67.5, 80.1, 86.3; IR (liquid film) 3350 (br), 2225, 1005 cm⁻¹; MS m/z (rel intensity) 194 (M⁺, 4), 137 (65), 111 (100); HRMS calcd for C₁₃H₂₂O 194.1671, found 194.1672.

1-Cyclohexyl-4-methyl-2-hexyn-1-ol (4e): ¹H NMR δ 0.96 (3H, t, J = 7.4 Hz), 1.0–1.3 (9H, m, including d (3H, J = 6.9 Hz) at 1.14), 1.41–1.55 (3H, m), 1.65–1.85 (5H, m), 2.38 (1H, m), 4.10 (1H, d, J = 5.9 Hz); ¹³C NMR δ 11.8, 20.7, 25.89, 25.93, 26.4, 27.5, 28.0, 28.6, 29.9, 44.4, 67.4, 80.3, 90.6; IR (liquid film) 3350 (br), 2225, 1010 cm⁻¹; MS m/z (rel intensity) 194 (M⁺, 7), 137 (73), 111 (100); HRMS calcd for C₁₃H₂₂O 194.1671, found 194.1676.

1-Cyclohexyl-4,4-dimethyl-2-pentyn-1-ol (4f): ¹H NMR δ 1.0–1.3 (14H, m, including s (9H) at 1.22), 1.75–1.9 (7H, m), 4.11 (1H, d, J = 6.0 Hz); ¹³C NMR δ 25.9, 26.0, 26.5, 27.4, 28.0, 28.6, 31.0, 44.4, 67.3, 78.46, 94.6; IR (liquid film) 3450 (br), 2225, 1020 cm⁻¹; MS *m*/*z* (rel intensity) 194 (M⁺, 4), 161 (67), 111 (100); HRMS calcd for C₁₃H₂₂O 194.1671, found 194.1676.

1-(1-Hexynyl)cyclohexanol (4g): ¹H NMR δ 0.92 (3H, t, J = 7.3 Hz), 1.22–1.28 (1H, m), 1.4–1.6 (9H, m), 1.68 (2H, m), 1.85–1.9 (3H, m), 2.22 (2H, t, J = 7.1 Hz); ¹³C NMR δ 13.6, 18.3, 21.9, 23.5, 25.3, 30.9, 40.3, 68.8, 83.8, 84.8; IR (liquid film) 3360 (br), 2225, 1060 cm⁻¹; MS *m/z* (rel intensity) 180 (M⁺, 15), 137 (100); HRMS calcd for C₁₂H₂₀O 180.1514, found 180.1514.

5-Phenyl-1-pentyn-3-yl Hydroperoxide (9). 5-Phenyl-1,2-pentadiene $^{13.14}$ (1.0 mmol) was dissolved in THF (3.0 mL) in a dry Schlenk flask under nitrogen. A solution of BuLi (0.63 mL, 1.0 mmol) was added dropwise via syringe at -80 °C. The resulting mixture was allowed to warm to -65 °C and stirred for 30 min. To the resulting solution of allenic lithium was added a solution of ZnCl₂ (0.14 g, 1.0 mmol) in THF (2.0 mL). After being stirred for 30 min at -65 °C, the mixture was cooled to -85 °C. Then, the nitrogen line was exchanged by a thick wall, natural latex rubber balloon filled with oxygen. The mixture was allowed to warm to -40 °C during 1 h and stirred further for 18 h. The mixture was poured into aqueous 1 N HCl and extracted with ether. The organic layer were washed successively with aqueous 5% Na₂S₂O₃ and water, dried over MgSO₄, and concentrated in vacuo. The residue was purified by flash chromatography (SiO₂, 10% ether in pentane) to give 89.8 mg (51% yield) of 9: ¹H NMR δ 2.0–2.2 (2H, m), 2.57 (1H, d, J = 2.0 Hz), 2.79 (2H, t, J = 7.5 Hz), 4.61 (1H, dt, J =2.0 and 7.0 Hz), 7.2–7.4 (5H, m), 8.22 (1H, br); $^{13}\mathrm{C}$ NMR δ 31.2, 34.3, 74.9, 75.2, 81.2, 126.2, 128.47, 128.52, 140.7; IR (liquid film) 3260 (br), 2110, 1335, 740, 690 cm⁻¹. Reduction of 9 by treatment with Zn powder in aqueous 1 N HCl-Et₂O gave 5-phenylpent-1-yn-3-ol.4a

Supporting Information Available: ¹³C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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^{(14) 5-}Phenyl-1,2-pentadiene was prepared in 63% yield by CuBrmediated reaction of methyl propargyl ether with PhCH₂CH₂MgCl.¹⁵ (15) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, The Netherlands, 1981; p 157.