Cyclization of 5-hexenyl radicals from nitroxyl radical additions to 4-pentenylketenes and from the acyloin reaction

Huda Henry-Riyad and Thomas T. Tidwell

Abstract: Photochemical Wolff rearrangements were used to form 5-substituted-4-pentenylketenes **1a**–**1d** ($RCH{=}CHCH_2X$-$CH_2CH{=}C{=}O$: **1a** R = H, X = CH_2; **1b** R = Ph, X = CH_2; **1c** R = *c*-Pr, X = CH_2; **1d** R = H, X = O), which were observed by IR at 2121, 2120, 2119, and 2126 cm^{-1}, respectively, as relatively long-lived species at room temperature in hydrocarbon solvents. These reacted with the nitroxyl radical tetramethylpiperidinyloxyl (TEMPO, TO·) forming carboxy-substituted 5-hexenyl radicals **3**, which were trapped by a second nitroxyl radical forming 1,2 diaddition products **4a**–**4d**. On thermolysis, **4a**–**4d** underwent reversible reformation of the radicals **3**, which underwent cyclization forming cyclopentanecarboxylic acid derivatives **6** or **11** as the major products. However, in the case of **1b**, the cyclopentane derivative was formed reversibly and on prolonged reaction times the only product isolated was $PhCH{=}CH$-$(CH_2)_4CO_2H$ (**8b**) from hydrogen transfer to C_β and cleavage of the TEMPO group. Cyclopropylcarbinyl radical ring opening in the cyclized radical **5c** from **1c** led to the 2-(4-*N*-tetramethylpiperidinyloxybut-1-enyl)cyclopentane derivative **11** as the major product. In a test for 5-hexenyl radical ring closure in the radical anion intermediate of the acyloin condensation, the ester $CH_2{=}CH(CH_2)_3CO_2Et$ (**12a**) gave the acyloin **13a** (76%) as the only observed product, while $PhCH{=}CH(CH_2)_3CO_2CH_3$ (**12b**) with Na in toluene gave 21% of the acyloin product **13b** and 42% of 2-benzylcyclopentanol (**15**) from cyclization of the intermediate radical anion.

Key words: ketenes, free radical cyclization, TEMPO, acyloin condensation.

Résumé : On a utilisé les réarrangements photochimiques de Wolff pour produire des 4-penténylcétènes substitués en position **5 1a**–**1d** ($RCH{=}CHCH_2XCH_2CH{=}C{=}O$: **1a** R = H, X = CH_2 ; **1b** R = Ph, X = CH_2 ; **1c** R = c-Pr, X = CH_2 ; **1d** R = H, X = O). On a observé ces produits en IR à 2121, 2120, 2119 et 2126 cm^{-1} respectivement, comme étant relativement des espèces à longue durée de vie dans des solvants hydrocarbonés à la température ambiante. Ces produits substitués réagissent avec le radical nitroxyle tétraméthylpipéridinoxyle (TEMPO, TO·) en formant des radicaux 5-hexényles portant un substituant carboxy **3**, qui sont piégés par un deuxième radical nitroxyle pour donner des produits de diaddition 1,2 **4a**–**4d.** Par thermolyse, ces produits **4a**–**4d** redonnent de façon réversible le radical **3** qui par cyclisation forme les dérivés de l'acide cyclopentanecarboxylique **6** ou **11** comme produits majoritaires. Toutefois dans le cas du composé **1b** le dérivé cyclopentane se forme de façon réversible, et en prolongeant les temps de réaction le seul produit obtenu est le : $PhCH{=}CH(CH_2)_4CO_2H$ (**8b**) résultant du transfert d'hydrogène sur C_β et du clivage du groupe TEMPO. L'ouverture du cycle du radical cyclopropylcarbinyle dans le radical cyclisé **5c** obtenu à partir du composé **1c** conduit au dérivé 2-(4-*N*-tétraméthylpipéridinyloxybut-1-ényl)cyclopentane **11** comme produit majoritaire. Dans un essai de cyclisation du radical 5-hexényle de l'anion radicalaire intermédiaire de la condensation acyloïne, l'ester $CH_2{=}CH(CH_2)_3CO_2Et$ (**12a**) donne l'acyloïne **13a** (76%) comme seul produit observé, tandis que le composé $PhCH{=}CH(CH_2)_3CO_2CH_3$ (**12b**) avec le Na dans le toluène donne 21% de l' acyloïne **13b** et 42% de 2-benzylcyclopentanol (**15**) à partir de la cyclisation de l'anion radicalaire intermédiaire.

Mots clés : cétènes, radical libre, cyclisation, TEMPO, condensation acyloïne.

[Traduit par la Rédaction]

Introduction

As part of our studies of the reactions of ketenes with aminoxyl radicals (1), we have examined the reactivity of 4-pentenylketenes **1a**, **1b** with TEMPO (TO·) (1*a*). For **1a** (R = H, X = CH_2) and **1b** (R = Ph, X = CH_2) generated from diazo ketones **2** (eq. [1]) these reactions were found to proceed by radical attack at the carbonyl carbon forming enolic radicals **3** which then were trapped by a second TEMPO giving the 1,2-diaddition products **4** (eqs. [2] and [3]). Cyclization of the intermediate 5-hexenyl radicals **3** forming cyclopentylmethyl radicals **5** and capture as cyclopentanes **6** was

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This paper is dedicated to Professor Don Arnold in recognition of his many achievements in chemistry.

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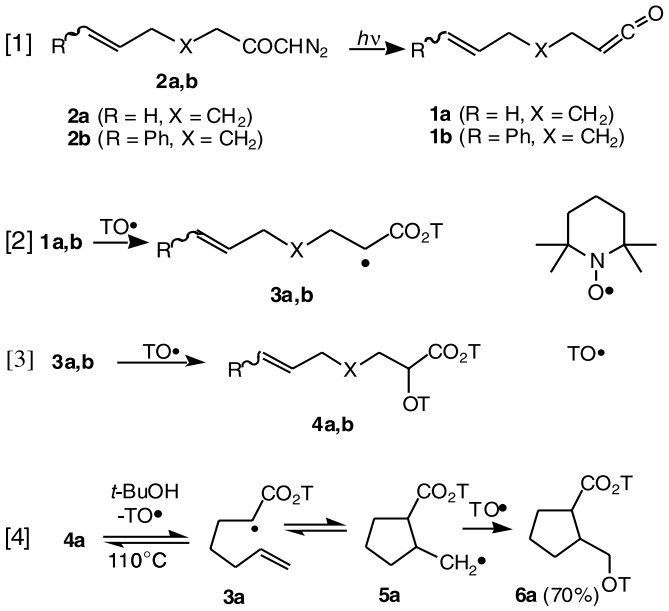
evidently too slow to compete with capture of **3** by TEMPO at these concentrations. However, on thermolysis of **4a** in *tert*-butyl alcohol according to the protocol of Studer (2*a*) cyclization forming **6a** was successful, indicating that upon equilibration of **3a** and **4a** cyclization to **5a** was followed by capture by TEMPO forming **6a** as a *cis–trans* mixture (eq. [3]).



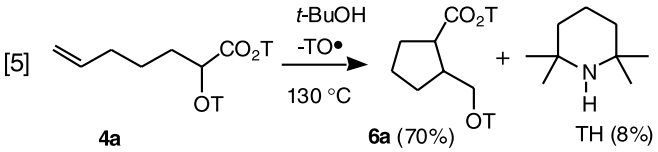
However, when the 1, 2-bis(TEMPO) addition product **4b** from 5-phenyl-4-pentenylketene (**1b**) was heated as in eq. [4], the corresponding cyclization product **6b** was not observed, and other reactions appeared to be taking place (1*a*). Further investigations have now been carried out to elucidate the behavior of **4b**, and the reactivity of 5-cyclopropyl-4-pentenylketene **1c** as well as the 2-oxa-4-pentenylketene analogue **1d** have been studied, and the results are reported here.

The reactions of ketenes with TEMPO and the reactions of these substrates are of interest because of current studies of the reactions of TEMPO with free radicals and the chemistry of the adducts (2, 3), especially in living free radical polymerization (4). Free radical rearrangements are also of wide applicability in organic synthesis (5, 6). In other recent studies designed to examine the formation and reaction of TEMPO esters, we have reported the thermal reactivity of Ph_3CCO_2T (1*j*) and the addition of TEMPO to the unreactive ketenes CH_2=C=O and $PhMe_2SiCH$=C=O (1*k*).

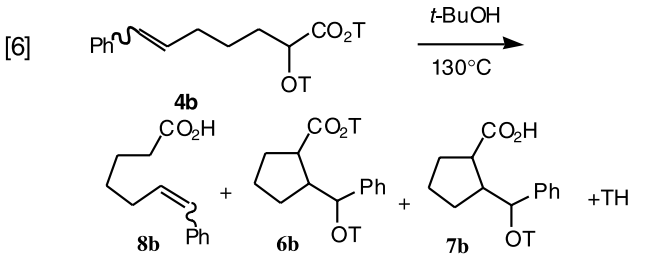
Results

The thermolysis reaction of the bis(TEMPO) adduct **4a** (1*a*) from **1a** in *tert*-butyl alcohol by the protocol of Studer (2*a*) was reexamined, and, in addition to the cyclized TEMPO ester **6a** (70%), tetramethylpiperidine (TH, 8%) was also identified (eq. [5]). The presence of carboxylic acid absorption in the IR was also detected in the crude product, but the acid was not isolated.

Heating the bis(TEMPO) adduct **4b** (1*a*) of 5-phenyl-4-pentenylketene **1b** at 130°C for 18 h in *tert*-butyl alcohol



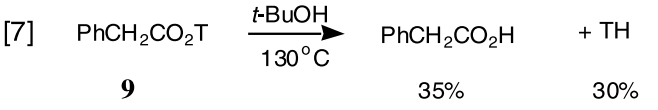
gave no detectable cyclized product, but instead the carboxylic acid **8b** was isolated (54%), along with TH (14%). Experiments at shorter time intervals revealed that **8b** was not the first formed product, but the cyclized ester **6b** (mixture of stereoisomers) was present early in the reaction, as well as the cyclized acid **7b** (eq. [6]).



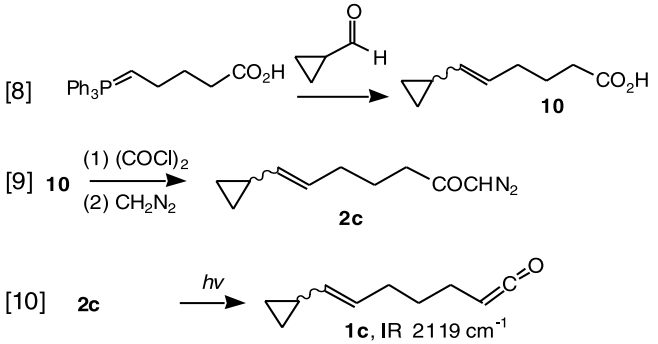
Time (h)				
2.5	-	32%	10%	
5	-	22%	12%	
10	34%	-	7%	
18	54%	-	-	14%

As a test of the source of carboxylic acids and TH in these reactions, the thermolysis of the ester **9** of phenylacetic acid and 2,2,6,6-tetramethylpiperidinol under Studer's conditions was examined. This reaction was found to give phenylacetic acid (35%) and TH (30%) after 7 days at 130°C (eq. [7]).

The cyclopropyl group serves as a useful clock for investi-



gating the presence of free radicals and so the new 5-cyclopropyl-substituted 4-pentenyl diazomethyl ketone **2c** was prepared as shown (eqs. [8] and [9]). Photolysis of **2c** gave the ketene **1c** as identified by the IR absorption at 2119 cm^{-1} (eq. [10]), and addition of TEMPO to the preformed ketene gave the 1,2-diaddition product **4c** in 71% yield (eq. [11]). Thermolysis of **4c** resulted in the formation of the cyclized ester **11** (mixture of stereoisomers) in 65% yield, along with TH in 15% yield (eq. [11]).



[11] **1c** $\xrightarrow{TO\bullet}$ **4c** (71%)

4c $\xrightarrow[130°C,\ 5\ h]{t\text{-BuOH}}$ **11** (R = T, 65%) + TH (15%)

The incorporation of hetero atoms in 5-hexenyl radical chains is a method to enhance their propensity for cyclization to cyclopentylmethyl radicals (4), and so the ketene precursor 2-oxa-4-pentenyl diazomethyl ketone **2d** was prepared from 3-oxa-5-hexenoic acid (7*h*) by conversion to the acyl chloride and reaction with diazomethane. Photolysis of **2d** in pentane at room temperature gave the ketene **1d**, as identified by its ketenyl IR absorption at 2126 cm^{-1} (eq. [12]), and upon reaction with TEMPO this gave the product **4d** of 1,2-addition of two molecules of TEMPO to the ketenyl moiety (eq. [13]). Thermolysis of **4d** in *tert*-butanol at 130°C gave the cyclized product **6d** (*cis–trans* mixture) in 67% yield (eq. [13]).

[12] **2d** $\xrightarrow{h\nu}$ **1d**, IR 2126 cm^{-1}

[13] **1d** $\xrightarrow{TO\bullet}$ **4d** (73%) $\xrightarrow[130°C,\ 5\ h]{t\text{-BuOH}}$ **6d** (67%)

The acyloin condensation (8) is a reaction proposed to involve radical anion intermediates formed by electron transfer from sodium to esters, but we are unaware of examples of radical cyclization under these conditions. As a further test of the cyclization of 5-hexenyl radicals, the acyloin condensations of ethyl 5-hexenoate (**12a**) (7*j*) and methyl 6-phenyl-5-hexenoate (**12b**) (7*b*, 7*i*) were investigated. Reaction of **12a** with sodium in toluene gave the acyloin **13a** in 76% yield as the only isolated product (eq. [14]), and for further characterization this was oxidized to the diketone **14a** (45%). Similar reaction of **12b** gave the cyclized product *cis*-2-benzylcyclopentane **15** (42%) along with the acyloin **13b** (21%) (eq. [15]). Oxidation of **13b** formed the corresponding α-diketone **14b** (52%). The stereochemistry of **15** was assigned by comparison with the reported spectra (7*j*).

[14] **12a** $\xrightarrow[130°C]{Na,\ toluene}$ **13a** (76%)

13a $\xrightarrow[CH_2Cl_2]{PCC}$ **14a** (45%)

[15] **12b** $\xrightarrow[toluene]{Na}$ **15** (42%) + **13b** (21%)

13b $\xrightarrow{PCC}$ **14b** (52%)

Discussion

As already reported (1*a*), the formation of the cyclized product **6a** (eq. [4]) is in accord with the mechanism in which the initially formed product **4a** of 1,2-diaddition of TEMPO reforms the radical **3a** upon heating, and this undergoes cyclization leading to **6a**, which is stable to ring opening. The formation of carboxylic acids and TH as observed from **4a**–**4c** and from $PhCH_2CO_2T$ (**9**) under these conditions is however unusual, and this reaction is under further investigation.

2-Oxa-4-pentenylketene (**1d**) reacted similarly to **1a** with TEMPO (eq. [12]), and formed the cyclized product **6d** upon thermolysis in an analogous manner (eq. [13]). However, no improved efficiency of cyclization was observed compared to the carbon analogue **1a**.

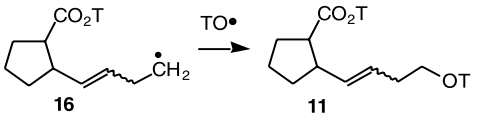
The initial 1,2-diaddition of TEMPO to 5-phenylpentenylketene **1b** (eqs. [2] and [3]) was also reported previously (1*a*). Upon heating this is also found to form the cyclized product **6b** at short reaction time, analogously to the previously observed formation of **6a** (eq. [4]). However, **6b** is reactive under these conditions, and is gradually converted to **8b**, evidently by reforming the intermediate radical **5b** which reopens to **3b**, which abstracts hydrogen and also undergoes loss of the TEMPO group as found for $PhCH_2CO_2T$ (eqs. [16] and [17]).

[16] **6b** $\rightleftharpoons$ **5b** $\rightarrow$ **3b**

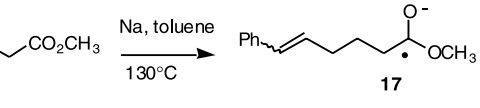
[17] **3b** $\xrightarrow[(-T)]{(H\bullet)}$ **8b**

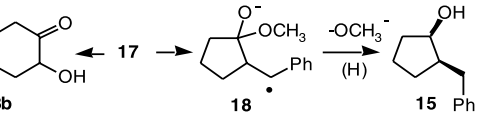
The formation of **11** (eq. [11]) in the reaction of TEMPO with 5-cyclopropyl-4-pentenylketene (**1c**) indicates that radical **3c** is formed by TEMPO dissociation from **4c**, and then undergoes cyclization to **5c** (eq. [18]). Ring opening of **5c** gives **16** which is captured by TEMPO forming **11** (eq. [19]).

[18] **4c** $\rightleftharpoons$ **3c** $\rightleftharpoons$ **5c**

[19] 

The possibility of 5-hexenyl radical cyclization during the acyloin condensation does not appear to have been previously examined, but acyloin reactions of linoleic and oleic esters gave the normal acyloin products, and did not undergo the potential radical cyclization which would form 10-membered rings (8*a*). In this study, ethyl 5-hexenoate (**12a**), which could form a five-membered ring by radical cyclization, gave the normal acyloin product (eq. [14]). However, when the double bond is activated with a phenyl substituent cyclization does occur with the formation of **15** from **12b** (eq. [15]). Evidently the intermediate radical anion **17** from single electron transfer to **12b** (eq. [20]) undergoes competitive acyloin condensation, forming **13b**, and cyclization leading to **15** via **18** (eq. [21]). Related radical cyclizations of radical anions from ketones are known (5*b*). The scope and mechanism of this interesting reaction are under further study.

[20] 

[21] 

In summary, radical cyclization of the 5-hexenyl radicals **3** resulting from TEMPO addition to 4-pentenylketenes **1** does not compete with the addition of a second TEMPO forming the 1,2-diaddition products **4**. However, upon heating under the conditions of Studer (2*a*) the products **4** reversibly reform **3**, which cyclize to cyclopentylmethyl radicals **5** which are captured by TEMPO for **1a** and **1d**, and for **1b** are in equilibrium with **3b**, which eventually reacts by hydrogen abstraction. The cyclopropyl derivative **5c** undergoes cyclopropylcarbinyl radical ring opening forming **11** after addition of TEMPO. Degradation of TEMPO esters to carboxylic acids and TH is noted, and is under further study. 5-Hexenyl radical cyclization is observed in the radical ion intermediate of the acyloin condensation when the double bond is activated with a phenyl substituent.

Experimental

Chromatography was carried out on silica gel. Solutions for reactions of TEMPO products were degassed and kept under argon or nitrogen. Gas chromatography (GC) was carried out with a flame ionization detector and a Simplicity 5 column (poly-5% diphenylsiloxane – 95% dimethylsiloxane). The disubstituted alkenes studied were *cis–trans* isomers that were not separated but the NMR spectra were assigned from the mixtures.

Lithium hexamethyldisilazide was prepared, by addition to a solution of 1,1,1,3,3,3-hexamethyldisilazane (1.04 equiv) in 1 to 2 mL THF cooled in an ice water bath, of a hexane solution of *n*-butyllithium (1.0 equiv) via syringe, followed by stirring the mixture at room temperature for 15–30 min prior to use (7*d*).

(4-Carboxybutyl)triphenylphosphonium bromide (7*c*, 7*f*, 7*g*) was prepared by addition of Ph_3P (5.06 g, 19.3 mmol) to a solution of 5-bromovaleric acid (3 g, 16.6 mmol) in acetonitrile (7.5 mL). The resulting mixture was stirred at 80°C under reflux for 24 h, concentrated, and the residue was washed with benzene, hexane, and ether and dried giving (4-carboxybutyl)triphenylphosphonium bromide (6.75 g, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.70 (m, 2, $CH_2CH_2CH_2$), 1.91 (m, 2, $CHCH_2CH_2$), 2.90 (t, 2, CH_2CO, J = 6.9 Hz), 3.68 (m, 1, Ph_3PCH), 7.73–7.78 (m, 15, Ar).

Thermolysis of 4a

The bis-TEMPO adduct **4a** (20 mg, 0.047 mmol) in degassed *t*-BuOH (4 mL) was heated 24 h in a sealed ampoule at 130°C, and GC analysis indicated the presence of 2,2,6,6-tetramethylpiperidine (8 ± 1%). The solvent was removed under reduced pressure and chromatography ($CHCl_3$–MeOH, 9:1) gave a product containing carboxylic acid based on the IR spectrum ($CDCl_3$) 3516, 1745, 1700 cm^{-1}. Base extraction and rechromatography ($CHCl_3$–MeOH, 9:1) afforded **6a** (14 mg, 70%, *E*:*Z* (45:55)) (1*a*). The carboxylic acid product was not recovered from the aqueous layer.

Thermolysis of *N*-2,2,6,6-tetramethylpiperidinyl 2-(*N*-2,2,6,6-tetramethyl piperidinyloxy)-7-phenyl-5-heptenoate (4b)

The bis-TEMPO adduct **4b** (20 mg, 0.040 mmol) under nitrogen in degassed *t*-BuOH (4 mL) was sealed in an ampoule and heated 18 h at 132–135°C in a refluxing xylene bath. Gas chromatography showed the presence of TH (14 ± 2%). The solvent was removed under reduced pressure and chromatography ($CHCl_3$–MeOH, 9:1) gave the known (7*b*) uncyclized acid **8b** $PhCH{=}CH(CH_2)_4CO_2H$ (54%). IR ($CDCl_3$) (cm^{-1}): 1703, 3518. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.54–1.83 (m, 4, $CH_2CH_2CO_2H$), 2.23 (m, 2, $CHCH_2CH_2$), 2.42 (m, 2, $CH_2CH_2CO_2H$), 5.66 (m, 1, *cis*-PhCH=CH), 6.18 (m, 1, *trans*-PhCH=CH), 6.37 (m, 1, PhCH=CH),), 7.33 (m, 5, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.5, 28.9, 32.8, 33.9, 126.2, 127.1, 128.7, 128.8, 128.9, 129.6, 130.4, 130.5, 131.3, 132.5, 137.6, 137.9, 178.8 (*C*O). EI-MS (*m*/*z*): 204 (M^+), 186, 157, 144, 130, 117, 104, 91, 77, 65. HR-EI-MS (*m*/*z*) calcd. for $C_{13}H_{16}O_2$: 204.1143; found: 204.1150.

Heating of **4b** with shorter reaction times gave *N*-2,2,6,6-tetramethyl-piperidinyl 2-(phenyl-*N*-2,2,6,6-tetramethylpiperidinyloxymethyl)cyclo pentanecarboxylate (**6b**) which was purified by chromatography (CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.66–2.85 (m, 44), 3.25–3.28 (m, 1, $CHCO_2T$), 4.76 (d, 1, C*H*PhOT, J = 6.8 Hz), 7.22–7.39 (m, 5, Ar). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.2, 17.3, 20.5, 20.6, 23.4, 24.8, 28.7, 29.1, 29.7, 31.1, 31.9, 32.1, 32.2, 32.3, 32.7, 39.0, 39.1, 39.2, 39.25, 45.7, 47.3, 59.8, 60.1, 87.7 *C*H(OT)Ph, 126.0, 127.2, 127.5, 128.5, 128.9, 131.0, 137.7, 140.9, 175.5 (*C*O). EI-MS (*m*/*z*): 499 (M^+), 326, 187, 157, 140, 117, 91, 69, 55. HR-EI-MS (*m*/*z*) calcd. for $C_{31}H_{51}N_2O_3$: 499.3907; found: 499.3900. IR ($CDCl_3$) (cm^{-1}): 1751. Further chromatography (EtOAc–MeOH, 3:7) gave 2-(phenyl-*N*-2,2,6,6-tetramethylpiperidinyloxymethyl)cyclo-

pentane carboxylic acid (**7b**). IR ($CDCl_3$) (cm^{-1}): 3513, 1701. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.06–2.38 (m, 24), 2.78–2.80 (m, 1, C*H*CHOTPh), 2.98–3.02 (m, 1, C*H*CO_2H), 4.80 (d, 1, C*H*OTPh) *J* = 8.9 Hz), 7.23–7.36 (m, 5, Ar). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.4, 21.5, 22.9, 25.4, 30.3, 31.8, 38.5, 40.0, 46.9, 47.7, 53.7, 61.2, 88.8 (*C*HOTPh), 126.5, 127.6, 128.0, 128.6, 129.1, 130.1, 130.4, 139.7, 178.9 (*C*O). EI-MS (*m*/*z*): 360 (M^+), 293, 239, 203, 185, 157, 142, 125, 91, 69, 55. HR-EI-MS (*m*/*z*) calcd. for $C_{22}H_{34}NO_3$: 360.2534; found: 360.2539.

6-Cyclopropyl-5-hexenoic acid (10)

4-Carboxy-*n*-butyltriphenylphosphonium bromide (5 g, 11.3 mmol) in THF (15 mL) was treated with lithium hexamethyldisilazide (23.7 mmol) in THF (4 mL) at 25°C with stirring. After 15 min, cyclopropanecarboxaldehyde (0.79 g, 11.3 mmol) in THF (5 mL) was added at 25°C, rapidly decolorizing the red-orange mixture. After 15 min, water (25 mL) and ether (25 mL) were added. The organic phase was rinsed with 20 mL of water. The combined aqueous solution was washed with EtOAc (25 mL), acidified with 10% HCl, and extracted with EtOAc. The united EtOAc extracts were rinsed with H_2O, dried with Na_2SO_4, and concentrated. Kugelrohr distillation gave **10** (1.12 g, 64%) (*E*/*Z* isomers, 1:1). ^1H NMR (400 MHz, $CDCl_3$) δ: 0.30–0.32 (m, 2), 0.63–0.67 (m, 2, *E*-isomer), 0.69–0.73 (m, 2, *Z*-isomer), 1.49–1.58 (m, 1), 1.65–2.41 (m, 6), 4.80 (dd, 1, *J* = 10.6, 9.8 Hz, *c*-PrHC*H*=CH, Z-isomer), 5.02 (dd, 1, *J* = 15.2, 8.2 Hz, *c*-PrHC*H*=CH, *E*-isomer), 5.30 (dt, 1, *J* = 10.6, 6.2 Hz, CH=C*H*CH_2, *Z*-isomer), 5.45 (dt, 1, *J* = 15.2, 6.4 Hz, CH=C*H*CH_2, *E*-isomer).

6-Cyclopropyl-5-hexenoyl chloride

Oxalyl chloride (1.05 g, 8 mmol) was added dropwise to a stirred solution of 6-cyclopropyl-5-hexenoic acid (**10**, 0.76 g, 4 mmol) in CCl_4 (10 mL) and stirred for 2 h. The solvent was removed in vaccuo to give 6-cyclopropyl-5-hexenoyl chloride as a dark brown oil (1.20 g, 92%) containing *E*/*Z* (50:50), used subsequently without further purification. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.31–0.32 (m, 2), 0.71–0.73 (m, 2, *E*-isomer), 0.74–0.79 (m, 2, *Z*-isomer), 1.52–1.6 (m, 1), 1.90 (distorted q, 2, $CH_2CH_2CH_2$), 2.32 (dt, 2, $CHCH_2CH_2$), 3.05 (t, 2, *J* = 7.2 Hz, CH_2COCl), 4.84 (dd, 1, *J* = 10.5, 8.4 Hz, *c*-PrHC*H*, *Z*-isomer), 5.20 (dd, 1, *J* = 13.2, 7.7 Hz, *c*-PrHC*H*=CH, *E*-isomer), 5.35 (dt, 1, *J* = 9.4, 7.5 Hz, CH=C*H*CH_2, *Z*-isomer), 5.50 (dt, 1, *J* = 11.4, 8.5 Hz, CH=C*H*CH_2, *E*-isomer).

1-Diazo-7-cyclopropyl-6-hepten-2-one (2c)

6-Cyclopropyl-5-hexenoyl chloride (1.20 g, 7.0 mmol) in ether (5 mL) was added dropwise over a period of 0.5 h to a stirring cooled solution of 0.018 mol of diazomethane (3 equiv) in ether (60 mL) which the solution was stirred at 0°C for 2 h. Excess diazomethane was removed by evacuating with a water aspirator through an empty Erlenmeyer flask and quenched in acetic acid, and the solution was concentrated. Chromatography (EtOAc–hexane, 3:7) gave **2c** (0.92 g, 5.2 mmol, 74%) as a yellow oil containing *E*/*Z* isomers (47:53). IR (pentane) (cm^{-1}): 2102, 1662. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.29–0.32 (m, 2), 0.63–0.66 (m, 2, *E*-isomer), 0.69–0.74 (m, 2, *Z*-isomer), 1.32–1.34 (m, 1, *E*-isomer), 1.48–1.53 (m, 1, *Z*-isomer), 1.73 (distorted q, 2, $CH_2CH_2CH_2$), 2.00–2.35 (m, 4), 4.80 (dd, 1, *J* = 10.6, 6.3 Hz, *c*-PrHC*H*=CH, *Z*-isomer), 4.98 (dd, 1, *J* = 12.3, 8.2 Hz, *c*-PrHC*H*=CH, *E*-isomer), 5.23 (s, 1, COC*H*N_2), 5.28 (dt, 1, *J* = 10.4, 9.9 Hz, CH=C*H*CH_2, Z-isomer), 5.45 (dt, 1, *J* = 13.2, 6.4 Hz, CH=C*H*CH_2, *E*-isomer). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 7.2, 10.0, 13.9, 25.4, 27.2, 32.2, 126.9 (CH=*C*HCH_2), 135.3 (*c*-Pr*C*H=CH), 195.2 (*C*O). EI-MS *m*/*z*: 179 (MH^+), 149 ($M^+ - N_2$), 135, 121, 107, 91. HR-EI-MS *m*/*z* calcd. for $C_{10}H_{14}N_2O$: 179.1186; found: 179.1184.

5-Cyclopropyl-4-pentenylketene (1c) and reaction with TEMPO

1-Diazo-7-cyclopropyl-6-hepten-2-one (**2c**, 100 mg, 0.56 mmol) in pentane (75 mL) was photolyzed for 30 min with 250-nm light to give ketene **1c** (IR: 2119 cm^{-1}). TEMPO (183 mg, 1.18 mmol, 2.1 equiv) was added to the preformed ketene and the solution was left stirring at room temperature for 24 h. Chromatography with CH_2Cl_2 gave **4c** (191 mg, 0.40 mmol, 71%) *E*/*Z* isomers (50:50). IR ($CDCl_3$) (cm^{-1}): 1770. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.28–0.31 (m, 2), 0.62–0.65 (m, 2, *E*-isomer), 0.68–0.72 (m, 2, *Z*-isomer), 1.08–2.20 (m, 43), 4.48 (distorted t, 1, CH_2CHOT), 4.75 (dd, 1, *J* = 10.2, 7.3 Hz, *c*-PrHC*H*=CH, *Z*-isomer), 4.92 (dd, 1, *J* = 9.4, 8.2 Hz, C*H*=$CHCH_2$, *E*-isomer), 5.31 (dt, 1, *c*-PrHCH=C*H*, *Z*-isomer), 5.45 (dt, 1, *J* = 13.9, 7.5 Hz, CH=C*H*CH_2, *E*-isomer). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 6.6, 7.1, 9.8, 13.7, 17.2, 17.4, 20.8, 20.9, 24.7, 24.9, 27.8, 32.1, 32.3, 32.4, 32.6, 34.8, 39.5, 40.7, 60.2, 60.5, 83.7 (*C*HOT), 127.6, 127.7 (CH=*C*HCH_2), 134.6, 134.7 (*c*-Pr*C*H=CH), 171.9 (CO_2T). EI-MS *m*/*z*: 464 (MH^+), 448 ($M^+ - CH_3$), 322 ($M^+ - T$), 306, 278, 182, 156 (TO^+), 140 (T^+), 126, 83, 55. HR-EI-MS *m*/*z* calcd. for MH^+ $C_{28}H_{51}N_2O_3$: 463.3869; found: 463.3899.

Thermolysis of 4c

The bis-TEMPO adduct **4c** (50 mg, 0.108 mmol) in degassed *t*-BuOH (5 mL) was heated in a sealed ampoule at 130°C for 18 h. GC analysis indicated the presence of 2,2,6,6-tetramethylpiperidine (15 ± 2%). Concentration and chromatography ($CHCl_3$–MeOH, 9:1) afforded the cyclized ester **11** containing carboxylic acid. IR ($CDCl_3$) (cm^{-1}): 3512, 1740, 1702. Base extraction and chromatography (CH_2Cl_2–MeOH, 9:1) afforded ester **11** (32 mg, 0.069 mmol, 65%). IR ($CDCl_3$) (cm^{-1}): 1750. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.08–2.00 (m, 42), 2.22 (dt, 2, CH_2CH_2OT), 2.51 (m, 1, *Z*-C*H*CO_2T), 2.79 (m, 1, *E*-$CHCO_2T$), 3.71–3.74 (t, 2, *J*= 6.71 Hz, CH_2OT), 5.43–5.48 (m, 1, *c*-PnC*H*=CH), 5.52–5.56 (m, 1, *c*-PnCH=C*H*). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.4, 20.4, 20.8, 24.2, 24.8, 25.0. 30.0, 30.4, 31.5, 32.2, 33.3, 33.6, 39.8, 47.7, 50.4, 56.0, 76.5 (CH_2OT), 127.5 (CH=*C*HCH_2), 133.9 (*c*-Pn*C*H=CH), 180.6 (CO_2T). EI-MS *m*/*z*: 463 (MH^+), 447 ($M^+ - CH_3$), 306 ($M^+ - OT$), 278 ($M^+ - CO_2T$), 182, 156 (TO), 140 (T), 126, 109, 93, 83, 69, 55. HR-EI-MS *m*/*z* calcd. for $C_{28}H_{50}N_2O_3$: 462.3816; found: 462.3821.

Allyloxyacetyl chloride

Oxalyl chloride (3.99 g, 2.7 mL, 0.03 mol) was added dropwise to a stirred solution of allyloxyacetic acid (7 h, 1.75 g, 0.015 mol) in dichloromethane (20 mL) followed by

stirring at room temperature for 2 h. The solvent was removed in vacuo to give allyloxyacetyl chloride as a yellow oil (1.85 g, 0.0137 mol, 92%) used subsequently without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.12–4.23 (m, 4, CH_2OCH_2COCl), 5.26–5.39 (m, 2, CH_2=CH), 5.85–5.98 (m, 1, CH_2=CH).

1-Diazo-4-oxa-6-hexen-2-one (2d)

Allyloxyacetyl chloride (1 g, 7 mmol) was dissolved in ether (5 mL) and added dropwise over 0.5 h to a stirring cooled solution of of diazomethane (0.018 mol, 2.5 equiv) in ether (100 mL), and the solution was stirred cold for 2 h. The excess diazomethane was removed by evacuating with a water aspirator pump and quenched into acetic acid. Concentration and chromatography (EtOAc–hexane, 1:3) gave **2d** (0.71 g, 5.1 mmol, 69%) as a yellow oil. IR (pentane) (cm^{-1}): 2107, 1661. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.95–4.04 (m, 4, $CH_2OCH_2COCHN_2$). 5.17–5.37 (m, 2, CH_2=CH), 5.73 (s, 1, $COCHN_2$), 5.79–5.92 (m, 1, CH_2=CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 53.3, 57.3, 67.2, 76.4, 118.1 (CH=CHCH$_2$), 133.7 (CH=CH), 193.9 (CO). EI-MS *m*/*z*: 141 (MH^+), 84, 69, 55. HR-EI-MS *m*/*z* calcd. for MH^+ $C_6H_9N_2O_2$: 141.0657; found: 141.0664.

(2-Oxa-4-pentenyl)ketene (1d) and reaction with TEMPO

1-Diazo-3-allyloxy-2-propanone (**2d**, 250 mg, 1.8 mmol) in 75 mL of pentane was photolyzed for 60 min with 250-nm light to give the corresponding ketene (IR: 2126 cm^{-1}). TEMPO (585 mg, 3.8 mmol, 2.1 equiv) was added to the preformed ketene and the solution was stirred at room temperature for 6 h. Concentration and chromatography (CH_2Cl_2) gave the bis-adduct **4d** (562 mg, 1.32 mmol, 73%). IR ($CDCl_3$) (cm^{-1}): 1773. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.22–1.82 (m, 36), 3.94–4.05 (m, 2, OCH_2CHOT), 4.11 (d, 2, *J* = 4.2 Hz, CH_2=$CHCH_2O$), 4.68 (t, 1, *J* = 5.5 Hz, CHOT), 5.15–5.31 (m, 2, CH_2=CH), 5.83–5.94 (m, 1, CH_2=CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.4, 17.5, 20.6, 20.8, 21.0, 21.1, 32.4, 34.0, 34.4, 39.6, 39.7, 40.8, 60.5, 60.7, 70.1, 72.8, 83.6 (CHOT), 117.7 (CH_2=CH), 135.0 (CH_2=CH), 170.5 (CO_2T). EI-MS *m*/*z*: 410 ($MH^+ - CH_3$), 308, 285 ($M^+ - T$), 268 ($M^+ - TO$), 240 ($M^+ - CO_2T$), 156 (TO^+), 140 (T), 126, 83, 69, 58. ES-MS *m*/*z* 425 (MH^+), 447 (MNa^+), 463 (MK^+).

The bis-TEMPO adduct **4d** (100 mg, 0.23 mmol) in degassed *t*-BuOH (5 mL) was heated for 5 h at 135°C in a refluxing xylene bath. After concentration chromatography ($CHCl_3$–MeOH, 9:1) gave the cyclized product **6d** (67 mg, 0.16 mmol, 67%). IR ($CDCl_3$) (cm^{-1}): 1756. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.04–1.70 (m, 36), 2.74–2.97 (m, 2), 3.72–4.10 (m, 6, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 17.3, 17.5, 20.2, 20.3, 20.4, 20.9, 23.0, 30.0, 32.2, 32.4, 32.5, 33.4, 33.5, 39.3, 39.4, 39.9, 41.5, 43.2, 46.1, 59.9, 60.2, 60.3, 74.9 (CH_2OT), 172.9 (CO_2T). EI-MS *m*/*z*: 341, 311, 270, 216, 156, 142, 126, 83, 69. ES-MS *m*/*z*: 447 (MNa^+), 463 (MK^+).

6-Phenyl-5-hexenoic acid (7*b*)

4-Carboxybutyltriphenylphosphonium bromide (2.0 g, 4.5 mmol) in dry THF (6 mL), under nitrogen, was treated with lithium hexamethyldisilazide (1.8 mL, 9.48 mmol). After 15 min, water and ether were added, the organic phase was rinsed with water (20 mL) and the combined aqueous solution was washed with EtOAc (25 mL), acidified with 10% HCl, and extracted with EtOAc. The united EtOAc extracts were rinsed with H_2O, dried with Na_2SO_4, and concentrated. Kugelrohr distillation gave 6-phenyl-5-hexenoic acid (0.68 g, 80%) containing *trans*/*cis* isomers (87:13). ^{1}H NMR (400 MHz, $CDCl_3$) *trans*-isomer δ: 1.70–2.56 (m, 6), 6.15 (m, 1, PhCH=CH), 6.45 (m, 1, PhCH=CH), 7.20 (m, 5, Ar), 10.65 (br s, 1, CO_2H); *cis*-isomer δ: 1.70–2.56 (m, 6), 5.60 (m, 1, PhCH=CH), 6.45 (m, 1, PhCH=CH), 7.20 (m, 5, Ar), 10.65 (br s, 1, CO_2H).

6-Phenyl-5-hexenoyl chloride (7*b*)

Oxalyl chloride (1.05 g, 8 mmol) was added dropwise to a stirred solution of 6-phenyl-5-hexenoic acid (0.76 g, 4.0 mmol) in CCl_4 (10 mL) followed by stirring at room temperature for 2 h. The solvent was removed in vaccuo to give 6-phenyl-5-hexenoyl chloride as a yellow oil (0.81 g, 3.9 mmol, 97%) containing *E*/*Z* isomers (85:15), used subsequently without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.89 (distorted q, 2, $CH_2CH_2CH_2$), 2.29 (dt, 2, $CHCH_2CH_2$), 2.95 (t, 2, *J* = 6.8 Hz, CH_2COCl), 6.16 (m, 1, PhCH=CH, *Z*-isomer), 5.61 (m, 1, PhCH=CH, *E*-isomer), 6.41 (m, 1, PhCH=CH, *E* and *Z* isomers), 7.31–7.36 (m, 5H, Ar).

Methyl 6-phenylhex-5-enoate (12b) (7*i*)

To a stirred mixture of methanol (0.2 mL, 4.9 mmol) and triethylamine (0.62 mL, 4.9 mmol) in CH_2Cl_2 (30 mL) at 0°C was added of 6-phenyl-5-hexenoyl chloride (1 g, 4.9 mmol). The reaction mixture was stirred for 20 min then 2 M HCl (10 mL) was added. The organic layer was washed with $NaHCO_3$ and brine, dried, and concentrated. Chromatography (CH_2Cl_2) yielded **12b**, (0.90 g, 4.4 mmol, 90%) as a yellow oil (*E*/*Z* isomers, 93:7). ^{1}H NMR (400 MHz, $CDCl_3$) *trans*-**12b** δ: 1.82–1.88 (q, 2, $CH_2CH_2CH_2$), 2.25–2.32 (dt, 2, $CHCH_2CH_2$), 2.37–2.42 (t, 2, *J* = 4.9 Hz, 2, $CH_2CO_2CH_3$), 3.69 (s, 3, *E*-OCH_3), 3.94 (s, 3, *Z*-OCH_3), 6.22 (m, 1, PhCH=CH), 6.39 (m, 1, PhCH=CH), 7.31–7.36 (m, 5, Ar).

Acyloin reaction of 12a

Sodium metal (0.64 g, 28 mmol) and toluene (100 mL) were refluxed for 1 h with vigorous stirring, and ethyl hex-5-enoate (7*j*) (**12a**, 0.20 g, 20 mmol) in toluene (10 mL) was added dropwise over 20 min, and stirred a further 2 h. The solution was cooled and MeOH (15 mL) was added, the mixture was poured into water–EtOAc and acidified with 10% HCl, extracted with EtOAc, washed with water and $NaHCO_3$, dried, and concentrated. Chromatography (hexane–EtOAc, 7:3) gave **13a** (7-hydroxydodeca-1,11-diene-6-one, 2.08 g, 76%). IR ($CDCl_3$) (cm^{-1}): 1707, 3519. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.61–1.82 (m, 6, $CH_2CH_2CH_2$ and $CHOHCH_2$), 2.04–2.18 (m, 4 C=$CHCH_2$), 2.40 (t, 2, *J* = 7.4 Hz, CH_2CO), 4.96–5.09 (m, 4, CH_2=C), 5.75–5.85 (m, 2 CH_2=CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.0, 23.9, 33.2, 33.5, 33.9, 38.9, 77.6 (CHOH), 115.1, 115.8, 137.7, 138.5, 180.1 (CO). EI-MS *m*/*z*: 196 (M^+), 182, 169, 167, 149, 125, 107, 99, 97, 81, 69, 55. HR-EI-MS *m*/*z* calcd. for C_6H_9O: 97.0656; found: 97.0653.

Oxidation of 13a

Pyridinium chlorochromate (1.6 g, 7 mmol) and **13a** (1.0 g, 5.1 mmol) in CH_2Cl_2 (20 mL) were heated at reflux for 1.5 h. The mixture was filtered through Celite, washed with ether, and the filtrate was concentrated. Chromatography (hexane–EtOAc, 7:3) gave dodeca-1,11-diene-6,7-dione (**14a**) as a yellow oil (0.44 g, 2.3 mmol, 45%). IR ($CDCl_3$) (cm^{-1}): 1711. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.63–1.78 (m, 4, $CH_2CH_2CH_2$), 2.08–2.19 (m, 4, $CHCH_2$), 2.37 (t, 4, J = 7.2 Hz, CH_2CO), 4.98–5.12 (m, 4, CH_2=CH), 5.77–5.83 (m, 2, CH_2=CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24,6, 34.5, 52.0, 115.8, 138.7, 200.0 (*C*O). EI-MS *m*/*z*: 195 (MH^+), 167, 153, 149, 140, 125, 97, 81, 69, 55. HR-EI-MS *m*/*z* calcd. for $C_{12}H_{19}O_2$: 195.1380; found: 195.1385.

Acyloin reaction of 12b

Sodium metal (0.2 g, 8.6 mmol) and toluene (20 mL) were heated to reflux with vigorous stirring for 1 h. To this was added methyl 6-phenylhex-5-enoate (**12b**, 0.88 g, 4.3 mmol) in toluene (10 mL) dropwise over 20 min. Stirring was continued for a further 2 h. The solution was cooled and MeOH (2 mL) was added. The mixture was poured into water–EtOAc and acidified with 10% HCl, extracted with EtOAc, washed with water and $NaHCO_3$, dried, and concentrated. Chromatography (hexane–EtOAc, 7:3) afforded the cyclized product *cis*-**15** (7*j*) as a colourless oil (0.32 g, 1.8 mmol, 42%). IR ($CDCl_3$) (cm^{-1}): 3608. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.25–2.14 (m, 8, 3C*H*$_2$, C*H*CH_2Ph, and O*H*), 2.52–2.57 (m, 1, CH*H*Ar), 2.74–2.79 (m, 1, C*H*HAr), 3.90–3.93 (m, 1, C*H*OH), 7.28–7.37 (m, 4, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.7, 30.1, 34.4, 40.0, 50.1, 78.8 (*C*HOH), 126.2, 128.5, 128.6, 129.1, 141.3. EI-MS *m*/*z*:176 (M^+), 158 ($M^+ - H_2O$), 143, 129, 117, 104, 98, 85, 67, 57. HR-EI-MS *m*/*z* calcd. for $C_{12}H_{16}O$: 176.1199; found: 176.1201. 1,12-Diphenyl-7-hydroxy-dodeca-1,11-dien-6-one (**13b**) was obtained as a yellow oil (0.31 g, 21%) 78:22 double bonds of *E*/*Z* isomers. IR ($CDCl_3$) (cm^{-1}): 1705, 3522. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.79–1.84 (m, 6, 2$CH_2CH_2CH_2$ and $CHOHCH_2$), 2.24–2.28 (m, 2, CH_2CH_2CO), 2.33–2.36 (m, 4, 2$CHCH_2CH_2$), 5.59–5.63 (m, *Z*-PhC*H*=CH), 6.17–6.23 (m, *E*-PhC*H*=CH), 6.38–6.44 (m, 2, 2PhCH=C*H*), 7.21–7.39 (m, 10, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.5, 27.4, 28.7, 32.4, 33.5, 37.5, 50.2, 79.4 (*C*HOH), 126.2, 127.3, 128.4, 128.6, 128.7, 128.9, 129.6, 130.4, 131.2, 133.9, 137.8, 179.6 (*C*O). EI-MS *m*/*z*:244 (M^+ – PhCH=CH), 210, 190, 130, 117, 105, 91, 77. HR-EI-MS *m*/*z* calcd. for $C_{16}H_{22}O_2$: 244.1456; found: 244.1454.

Oxidation of 13b

Pyridinium chlorochromate (0.35 g, 1.6 mmol) and **13b** (0.32 g, 1 mmol) in dry CH_2Cl_2 (5 mL) were heated at reflux for 1.5 h. The black mixture was filtered through Celite, washed with ether, and the filtrate was concentrated. Chromatography (hexane–EtOAc, 7:3) gave 1,12-diphenyldodeca-1,11-diene-6,7-dione (**14b**) as a yellow oil (0.18 g, 52%), 81:19 *E*/*Z* double bonds. IR ($CDCl_3$) (cm^{-1}): 1711. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.81–1.94 (m, 4, $CH_2CH_2CH_2$), 2.37–2.41 (m, 4, $CHCH_2CH_2$), 2.43 (t, 4, CH_2CH_2CO), J = 7.6 Hz), 5.61–5.72 (m, *Z*-PhC*H*=CH), 6.18–6.28 (m, *E*-PhC*H*=CH), 6.40–6.58 (m, 2, PhCH=C*H*), 7.17–7.45 (m, 10, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.5, 29.9, 32.5, 126.2, 127.4, 128.2, 128.4, 128.7, 129.6, 130.5, 131.2, 197.0 (*C*O). EI-MS *m*/*z*: 243 (M^+ – Ph-CH=CH), 215 ($M^+ - C_{10}H_{11}$), 202 ($M^+ - C_{11}H_{13}$), 190 ($M^+ - C_{12}H_{13}$), 174 ($M^+ - C_{12}H_{13}O$), 146 ($M^+ - C_{13}H_{13}O_2$), 130, 117, 105, 91, 77. HR-EI-MS *m*/*z* calcd. for $C_{16}H_{19}O_2$: 243.1177; found: 243.1192.[2]

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[2] Supplementary data (^1H NMR spectra) may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically).

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