Group Transfer Carbonylations: Photoinduced Alkylative Carbonylation of Alkenes Accompanied by Phenylselenenyl Transfer

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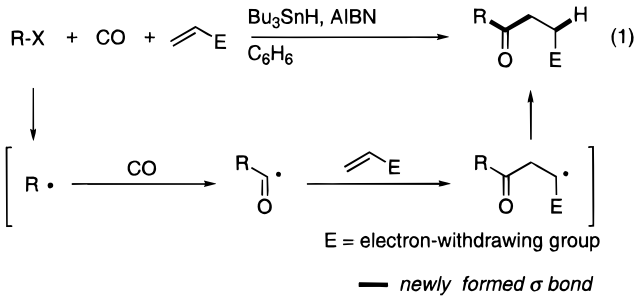
The photolysis of methyl α-(phenylseleno)acetate (**1b**) and related compounds in the presence of an alkene and CO leads to acyl selenides **2** via group transfer carbonylation. The mechanism of this three-component coupling reaction involves the addition of a (methoxycarbonyl)methyl radical to an alkene, the trapping of the produced alkyl free radical by CO, and termination of the reaction by a phenylselenenyl group transfer from the starting material.

Introduction

Free-radical carbonylations have been recently recognized as useful and practical methods for the synthesis of carbonyl compounds.[1] In a particularly useful sequence, the consecutive addition of carbon radicals to CO and alkenes provides a powerful pathway for the preparation of a variety of unsymmetrical ketones (eq 1).[2] Acyl



radicals have a nucleophilic nature and alkenes, having an electron-withdrawing substituent, are ideal reagents for such a three-component coupling reaction. A slightly different three-component coupling reaction involving the reaction of carbon radical, alkene, and CO also represents an experimental possibility. The prototype of such a three-component coupling reaction, involving carbon tetrachloride, ethylene, and CO, was reported in 1956,[3a] in which trichloromethyl radical adds to ethylene to generate the key radical for the subsequent CO trapping. A modified method, which was reported in 1970, used several dinuclear transition metal carbonyl complexes as the initiator rather than di-*tert*-butyl peroxide.[3b] The reaction, as reported, gave rather low yields (up to 20%) of carbonylation products and, in addition, required high CO pressures (<200 atm). Two key features of free radicals are important in such carbonylation reactions. The acyl radical must be capable of undergoing a smooth S_H2 reaction with the polyhalocarbons[4] or related reagents, and the resulting carbon radicals must possess sufficient electrophilicity to allow them to add to ordinary alkenes.[5]

The recent notable development in free-radical group transfer chemistry[6−8] has prompted us to reconsider this type of olefin-carbonylation chemistry on the basis of *group transfer carbonylation*. Byers and co-workers found that the group transfer addition of some α-seleno-substituted compounds, such as ethyl α-(phenylseleno)-acetate and α-(phenylseleno)acetone, to ordinary alkenes are very efficient under photolysis conditions.[6] Curran and co-workers also have shown the versatility of group transfer additions of methyl α-(phenylseleno)malononitrile to alkenes.[7] More recently, Curran, Newcomb, and co-workers provided a kinetic basis that is useful for formulating applications of group transfer reactions.[9] In these transformations, an alkyl radical cleaves a carbon−chalcogen bond in an S_H2 manner to generate another carbon radical and thus allowing the chain propagation to be ensured. In order for a group transfer carbonylation to be successful, the acyl radical must cleave a carbon−chalcogen bond with liberation of a carbon radical at a synthetically meaningful rate.[10]

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(1) For recent reviews, see: (a) Ryu, I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1050. (b) Ryu, I.; Sonoda, N.; Curran, D. P. *Chem. Rev.* **1996**, *96*, 177.

(2) (a) Ryu, I.; Kusano, K.; Yamazaki, H.; Sonoda, N. *J. Org. Chem.* **1991**, *56*, 5003. (b) Ryu, I.; Hasegawa, M.; Kurihara, A.; Ogawa, A.; Tsunoi, S.; Sonoda, N. *Synlett* **1993**, 143.

(3) (a) Foster, R. E.; Larchar, A. W.; Lipscomb, R. D.; McKusick, B. C. *J. Am. Chem. Soc.* **1956**, *78*, 5606. (b) Susuki, T.; Tsuji, J. *J. Org. Chem.* **1970**, *35*, 2982.

(4) (a) Walling, C.; Savas, E. S. *J. Am. Chem. Soc.* **1960**, *82*, 1738. (b) Thaler, A. *J. Am. Chem. Soc.* **1967**, *89*, 1902. For kinetics, see: (c) Brown, C. E.; Neville, A. G.; Rayner, D. M.; Ingold, K. U.; Lusztyk, J. *Aust. J. Chem.* **1995**, *48*, 363.

(5) Examples of recent applications to intramolecular alkene addition: (a) Lee, G. M.; Weinreb, S. M. *J. Org. Chem.* **1990**, *55*, 1281. (b) Pirrung, F. O. H.; Steeman, W. J. M.; Hiemstra, H.; Speckamp, W. N.; Kaptein, B; Boesten, W. H. J.; Schoemaker, H. E.; Kamphuis, J. *Tetrahedron Lett.* **1992**, *33*, 5141. (c) Seijas, J. A.; Vázquez-Tato, M. P.; Castedo, L.; Estévez, R.; Ónega, M. G.; Ruíz, M. *Tetrahedron* **1992**, *48*, 1637. (d) Nagashima, H.; Ozaki, N.; Ishii, M.; Seki, K.; Washiyama, M.; Itoh, K. *J. Org. Chem.* **1993**, *58*, 464. (e) Ishibashi, H.; Uemura, N.; Nakatani, H.; Okazaki, M.; Tatsunori, S.; Nakamura, N.; Ikeda, M. *J. Org. Chem.* **1993**, *58*, 2360.

(6) Phenylselenenyl group transfer to alkenes: (a) Byers, J. H.; Lane, G. C. *Tetrahedron Lett.* **1990**, *31*, 5697. (b) Byers, J. H.; Gleason. T. G.; Knight, K. S. *J. Chem. Soc., Chem. Commun.* **1991**, 354. (c) Byers, J. H.; Harper, B. C. *Tetrahedron Lett.* **1992**, *33*, 6953. (d) Byers, J. H.; Lane, G. C. *J. Org. Chem.* **1993**, *58*, 3355. (e) Byers, J. H.; Thissell, J. G.; Thomas, M. A. *Tetrahedron Lett.* **1995**, *36*, 6403.

(7) (a) Curran, D. P.; Thoma, G. *J. Am. Chem. Soc.* **1992**, *114*, 4436. (b) Curran, D. P.; Eichenberger, E.; Collis, M.; Roepel, M. G.; Thoma, G. *J. Am. Chem. Soc.* **1994**, *116*, 4279.

(8) (a) Han, L. B.; Ishihara, K.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 7591. (b) Vionnet, J. P.; Renaud, P. *Helv. Chim. Acta* **1994**, *77*, 1781. (c) Pandey, G.; Rao, K. S. S. P.; Sekhar, B. B. V. S. *J. Chem. Soc., Chem. Commun.* **1993**, 1636. (d) Back, T. G.; Gladstone, P. L. *Synlett* **1993**, 699. (e) Renaud, P.; Abazi, S. *Synthesis* **1996**, 253.

(9) For rate constants for chalcogen group transfer, see: Curran, D. P.; Martin-Esker, A. A.; Ko, S.-B; Newcomb, M. *J. Org. Chem.* **1993**, *58*, 4691.

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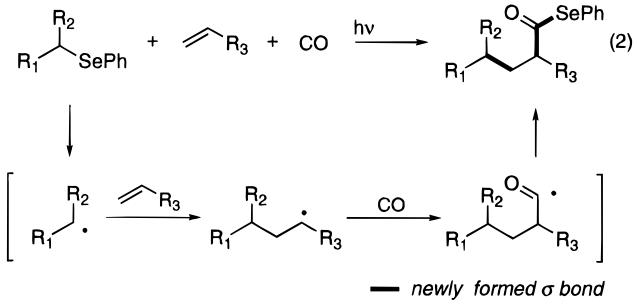
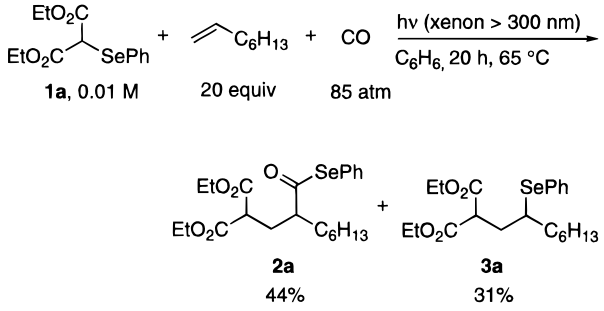
In this study, we wish to report a new type of three-component coupling reaction, based on group transfer carbonylation, that involves α-(phenylseleno)carbonyl compounds (and related derivatives), terminal alkenes, and CO (eq 2). The transformation involves the consecu-



tive trapping of carbon radicals by an alkene and CO followed by a group transfer of the phenylselenenyl group to give acyl selenides. Unlike free-radical carbonylations reported thus far, the carbonylation reactions were conducted under *photolysis conditions under CO pressure*. A new type of autoclave, equipped with quartz windows, was developed for this work. The detailed design is presented in the supporting information.

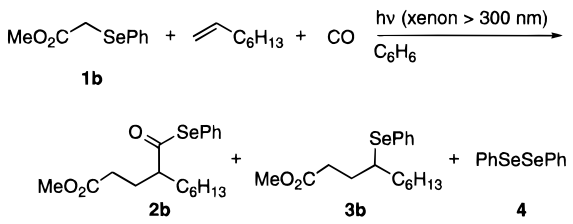
Results and Discussion

In initial experiments, we examined the photoinduced reaction of 1-octene with diethyl α-(phenylseleno)malonate (**1a**) in the presence of carbon monoxide. In a Pyrex glass lined autoclave that was equipped with quartz windows, a mixture of **1a** and 1-octene in benzene was introduced and then charged with 80 atm of CO. Irradiation of this mixture (500-W xenon lamp at 65 °C for 20 h) yielded the predicted three-component coupling product **2a**, suggesting that the S_H2 reaction of an acyl radical with **1a** takes place. The present transformation achieved the formal insertion of an olefin and CO into C−Se bond of the starting selenide **1a**. The formation of the acyl selenide **2a** most likely occurs via the addition of the malonyl radical, which arises from the photoinduced homolysis of **1a**, to 1-octene, the addition of the resulting alkyl radical to CO to form an acyl radical, and the S_H2 reaction of the acyl radical at the selenium of **1a** to yield an acyl selenide **2a**, along with the regeneration of the malonyl radical. Attempts to improve the yield of the carbonylated product were, however, not fruitful, since the direct S_H2 reaction of the alkyl radical, which arises from the addition of malonyl radical to 1-octene, with **1a** was largely competitive. For example, the use of high dilution ([substrate] = 0.01 M) with high CO pressures (up to 85 atm) still yielded, at best, carbonylated and uncarbonylated products **2a** and **3a**, respectively, in a ratio of 4:3 (eq 3). These results suggest that group transfer addition of the α-selenomalonate to alkenes is too efficient to hinder the efficient CO trapping process, at least for conditions involving CO pressures of less than 100 atm.



We next examined methyl α-(phenylseleno)acetate (**1b**), a slower group transfer reagent,[9] and found that the desired reaction proceeds with reasonable efficiency and favors group transfer carbonylation. Table 1 lists the results of experiments involving the group transfer carbonylation of 1-octene with **1b** under a variety of reaction conditions. For example, when a benzene solution of methyl α-(phenylseleno)acetate (**1b**, 0.01 M) and 1-octene (50 equiv) was irradiated using a 500-W xenon lamp (>300 nm) for 20 h at 60 °C under 80 atm of CO pressure, acyl selenide **2b**, the three-component coupling product, was formed in 58% yield (Table 1, run 3), where the ratio of carbonylated/uncarbonylated products was 7. As a comparison, the reaction with α-(phenylseleno)-malonate (**1a**) was examined using the same conditions and gave carbonylation/uncarbonylation products in a ratio of 1. For the carbonylation reaction to predominate, a high dilution appeared effective as has been used in other radical carbonylation systems: such a system involves high concentrations of CO relative to that of the starting selenide, the group transfer reagent. The overall reaction is, however, slow, under these conditions. Consequently, the experiments used a large quantity of alkene, so as to keep its concentration high, while the seleno substrate concentration was maintained at low levels. To obtain satisfactory results, a reaction time of 20 h appeared necessary but the longer reaction

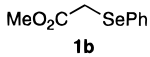
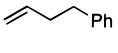
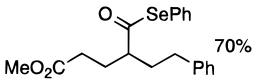
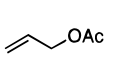
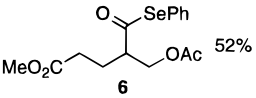
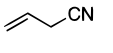
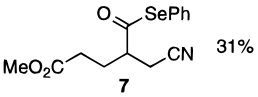
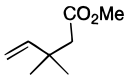
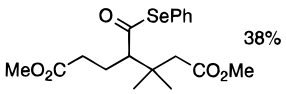
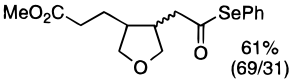
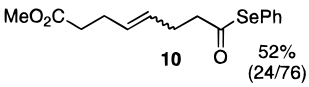
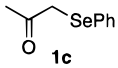
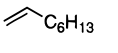
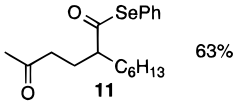
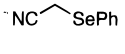
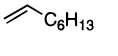
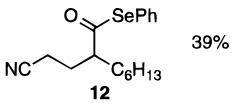
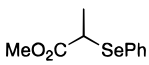
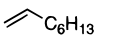
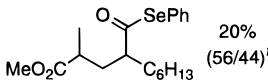
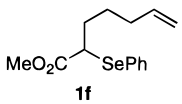
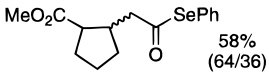
Table 1. Control Experiments for Group Transfer Carbonylation with 1b



run	[1b] (M)	alkene (equiv)	CO (atm)	reaction time (h)	GC yields (%) 1b	2b	3b	4
1	0.01	10	80	48	24	40	7	15
2	0.01	20	80	20	15	47	8	15
3	0.01	50	80	20	7	58	8	13
4	0.01	50	80	12	15	54	9	11
5	0.01	50	80	8	23	54	8	7
6	0.01	50	80	40	7	54	7	16
7	0.01	50	30	20	6	44	21	15
8	0.01 (hexane)	50	80	20	5	47	8	20
9	0.01 (chloroform)	50	80	24	6	44	4	23

(10) Very recently, Crich and co-workers have demonstrated that acyl radicals can be trapped by diphenyl diselenide and disulfide to give acyl selenides and sulfides, respectively. In this reaction, the S_H2 process appeared to be significantly rapid because of the liberation of stable phenylchalcogen radicals. S_H2 reaction of an acyl radical that occurs with C-hetero atom bond cleavage is not common. Photoinduced disproportionation reaction of acyl tellurides may involve such a rare S_H2 process, see: (a) Chen, C.; Crich, D.; Papadatos, A. *J. Am. Chem. Soc.* **1992**, *114*, 8313. (b) Chen, C.; Crich, D. *Tetrahedron Lett.* **1993**, *34*, 1545. (c) Crich, D.; Chen, C.; Hwang, J.-T.; Yuan, H.; Papadatos, A.; Walter, R. I. *J. Am. Chem. Soc.* **1994**, *116*, 8937.

Table 2. Group Transfer Carbonylation of Terminal Alkenes[a]

run	starting selenides	alkenes[b]	products	yields[c] (cis/trans)[d]
1	 **1b**		 **5**	70%
2	**1b**		 **6**	52%
3	**1b**		 **7**	31%
4	**1b**		 **8**	38%
5	**1b**		 **9**	61% (69/31)
6	**1b**		 **10**	52% (24/76)
7	 **1c**		 **11**	63%
8	 **1d**		 **12**	39%
9[e]	 **1e**		 **13**	20% (56/44)[f]
10	 **1f**		 **14**	58% (64/36)

[a] Except for run 9, reactions were conducted on a 0.3 mmol scale in benzene ([**1**] = 0.01 M) with irradiation using a 500-W xenon lamp (>300 nm) for 20 h at 60 °C under 80−85 atm of CO pressure. [b] Except for 1-octene (20 equiv), 50 equiv of alkenes was used. [c] All products were isolated by flash chromatography on silica gel. [d] Stereoisomers were determined by NMR. [e] A benzene solution of **1e** (0.01 M) was irradiated by 500-W xenon lamp (>420 nm) with 20 equiv of 1-octene for 160 h at 60 °C under 80 atm of CO pressure. [f] Diastereomers (major/minor = 56/44) could not be determined.

time did not necessarily improve the yield of **2b**. The reaction can be conducted equally well with hexane and chloroform (Table 1, runs 8 and 9), but no reaction took place under thermal conditions initiated by AIBN.

Additional data are summarized in Table 2. In all cases where a terminal alkene is used, the photoinduced group transfer carbonylation of alkenes leading to acyl selenides proceeds efficiently. All products were isolated by flash chromatography on silica gel. With allyl cyanide, the yields of the product were somewhat low. This may be due to the stabilizing effect of the cyano group to the β-radical, which might reduce the reactivity of the key radical with CO.[11] In cases where diallyl ether and vinylcyclopropane were used as a substrate, carbonylation was accompanied by 5-*exo-trig* cyclization of the 5-hexenyl radical and ring opening of a cyclopropylmethyl radical, respectively (Table 2, runs 5 and 6).[12] The failure of carbonylation of cyclohexene with **1b** suggests that the present group transfer carbonylations are suited only for terminal alkenes as substrates.[13] The carbonylation of alkenes with α-(phenylseleno)acetone (**1c**) and α-(phenylseleno)acetonitrile (**1d**) also took place. Regarding the carbonylation/direct addition efficiency, the former proceeds in a manner analogous to **1b**, whereas the latter gave more direct addition product. This may be a reflection of the relative ease of side reactions; Curran, Newcomb, and co-workers[9] recently reported that the rate constant for phenylseleno group transfer of α-(phenylseleno)acetonitrile (**1d**) to *n*-octyl radical is 2.3×10^5 M^{-1} s^{-1}, whereas that of ethyl α-(phenylseleno)acetate is 1.0×10^5 M^{-1} s^{-1} (50 °C in C_6H_6).

Unlike acetate **1b**, the reaction of methyl α-(phenylseleno)propionate (**1e**) was problematic. When **1e** was irradiated with wavelengths longer than 300 nm (Pyrex tube), it was consumed within 2 h, but the desired carbonylated product **13** was formed only in trace amounts. In this experiment, a large amount of diphenyl diselenide was obtained as a detectable product by GC. In order to examine the fate of the propionate ester, we carried out an irradiation experiment using the corresponding butyl ester **1g**. This experiment suggested that butyl propionate and butyl acrylate were formed in the ratio of 27:73 as the major products.[14,15] These data suggest that **1e** and **1g** are exceedingly sensitive to xenon light so that they cannot provide the low concentration of α-(methoxycarbonyl)ethyl radical, which is required for the addition to an alkene. As a result, disproportionation reactions predominate and overwhelm the desirable alkene addition. Diart and Roberts reported that the addition of α-methylmalonyl radical ($^{\bullet}CMe(CO_2Et)_2$) to an alkene is three to four times slower than that of malonyl radical ($^{\bullet}CH(CO_2Et)_2$).[16] In light of this, the alkene addition of **1e** may be inhibited by the steric effect of the α-methyl substituent.

When the longer wavelength light was tested (wavelength in excess of 420 nm), the reaction became very sluggish but gave the desired product **13**, after 160 h reaction, in 20% yield with a larger amount of direct group transfer product (40%) (Table 2, run 9). On the other hand, in the case of the substrate having an α-pentenyl substituent (**1f**), the cyclization/carbonyla-

(11) For radical polar effect of β-cyano substituent, see: Giese, B.; Engelbrecht, R. *Polym. Bull.* **1984**, *12*, 55.

(12) Related work, see: (a) Ryu, I.; Kurihara, A.; Muraoka, H.; Tsunoi, S.; Kambe, N.; Sonoda, N. *J. Org. Chem.* **1994**, *59*, 7570. (b) Tsunoi, S.; Ryu, I.; Muraoka, H.; Tanaka, M.; Komatsu, M.; Sonoda, N. *Tetrahedron Lett.*, in press.

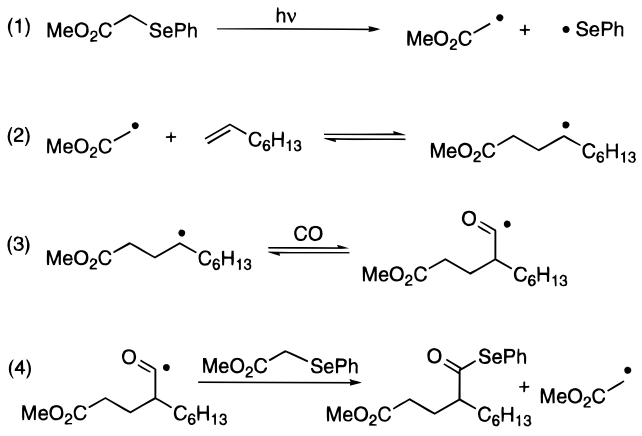
(13) Cf. ref 6d. For steric effects associated with radical additions, see: Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753.

(14) The precise mechanism for the disproportionation is not clear yet, but we are now inclined to a possibility of elimination of PhSeH to give butyl acrylate and reduction of **1g** by the resulting PhSeH to give butyl propionate. Cf.: Kropp, P. J.; Fryxell, G. E.; Tubergen, M. W.; Hager, M. W.; Harris, G. D., Jr.; McDermott, T. P., Jr.; Tornero-Verez, R. *J. Am. Chem. Soc.* **1991**, *113*, 7300.

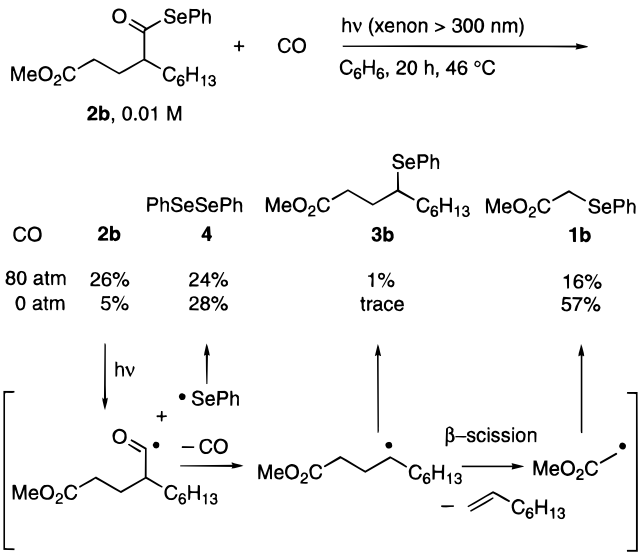
(15) The similar irradiation of 2-(phenylseleno)cyclohexanone resulted in the formation of cyclohexanone (35%) and 2-cyclohexenone (45%), but no alkene−addition products were detected with this substrate.

(16) Diart, V.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1761.

Scheme 1



Scheme 2

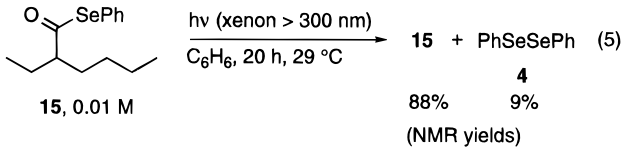


tion proved successful under standard conditions (Table 2, run 10).[17]

The reaction mechanism shown in Scheme 1 may account for the formation of the acyl selenides **2**. (1) The photoinduced homolysis of methyl α-(phenylseleno)acetate takes place, (2) thus generated, the (methoxycarbonyl)methyl radical adds to 1-octene, (3) the addition of the resulting alkyl radical to CO leads to an acyl radical, and (4) an S_H2 reaction of the acyl radical with the α-seleno ester at selenium yields an acyl selenide and regenerates a (methoxycarbonyl)methyl radical. Apart from alkylphenyl selenide **3**, another major byproduct of this reaction was diphenyl diselenide (**4**) (Table 1). Diphenyl diselenide most likely arises from the decomposition of the starting material and/or the product under irradiation conditions.

In order to examine the pathway involved in diselenide production, a benzene solution of **2b** was irradiated under CO pressure as shown in Scheme 2 ([**2b**] = 0.01 M, 20 h, 46 °C, 80 atm, 500-W xenon lamp (>300 nm)). Under these conditions, a photolysis reaction occurred with the production of not only diphenyl diselenide (**4**; 24%) but also the starting selenide **1b** (16%). Similarly, when acyl selenide **2b** was irradiated under a nitrogen atmosphere, it was consumed and **1b** was formed in 57% yield. These experiments clearly demonstrate that the photoinduced reverse reaction of the product **2b** can also take place in this reaction system to generate an acyl radical, which undergoes decarbonylation and β-scission leading to **1b**.[18] This may account for the experimental fact that prolongation of reaction time did not necessarily lead to an improvement in yield. It should be noted that the UV absorption spectra of the starting selenide **1b** and a carbonylated product **2b** were similar in terms of C−Se absorption (λ_{max} < 400 nm, hexane). For reactions of this type, the use of a large excess of alkenes and CO may have merit in that they cause a shift in equilibrium in the direction of the acyl selenide product **2b**.

Unlike acyl telluride[10] and sulfide[19] chemistry, the generation of an acyl radical by the photoinduced homolysis of a carbonylcarbon−selenium bond has not clearly been demonstrated. As a result, we examined the possibility that the photolysis of typical acyl selenide **15** is capable of generating an acyl radical. When a solution of **15** in benzene (0.01 M) was irradiated with a 500-W xenon lamp for 20 h at 29 °C, the starting acyl selenide **15** was largely recovered (88%) along with a small amount of diphenyl diselenide (**4**; 9%) (eq 5). Thus, the acyl selenide **2b** is more prone to undergo photolytic decomposition than acyl selenide **15**.



Acyl selenides are useful synthetic intermediates in organic synthesis.[20] The followng examples represent the palladium-catalyzed reductions of products **2b** and **12** with tri-n-butyltin hydride to give methyl 4-formyldecanoate (**16**) and 4-formyldecanenitrile (**17**), respectively (Scheme 3).[20i] Thus, the overall two-step process represents the formal *carboformylation* of alkenes,[21] which is difficult to achieve by transition metal mediated carbonylation reactions.

In summary, we have shown that photoinduced free-radical carbonylation can effect a three-component coupling accompanied via a phenylselenenyl group transfer, providing a first useful method for carbonylation of 1-alkenes by a free-radical method. The use of a relatively slow group transfer reagent is desirable for this carbonylation reaction. The acyl selenide products are photosensitive, and the reverse reaction can also take

(17) For kinetic effects on the cyclization of the radicals substituted by α-electron-withdrawing group, see: (a) Newcomb, M.; Filipkowski, M. A.; Johnson, C. C. *Tetrahedron Lett.* **1995**, *36*, 3643. (b) Newcomb, M.; Horner, J. H.; Filipkowski, M. A.; Ha, C.; Park, S.-U. *J. Am. Chem. Soc.* **1995**, *117*, 3674.

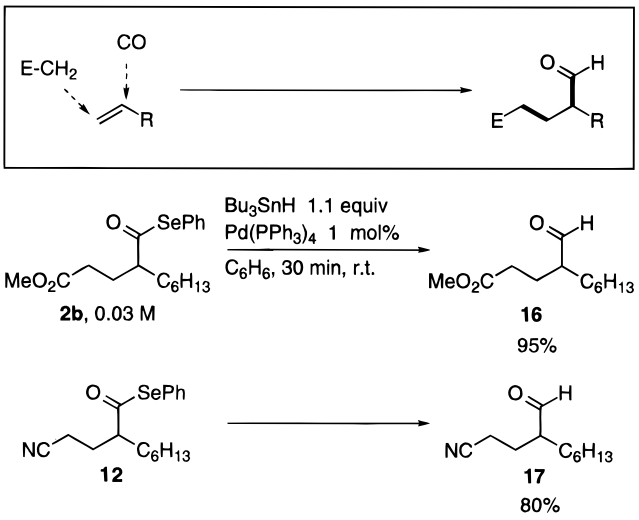
(18) Under the photolytic conditions described in Scheme 2, **3b** would not survive, if formed. In a separate experiment, photolysis of **3b** took place to give **1b** and diphenyl diselenide (**4**) as the main products ([**3b**] = 0.01 M, benzene, CO 80 atm, 44 °C, 20 h).

(19) Penn, J. H.; Liu, F. *J. Org. Chem.* **1994**, *59*, 2608.

(20) Examples: (a) Pfenninger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2328. (b) Sviridov, A. F.; Ermolenko, M. S.; Yashunsky, D. V.; Kochetkov, N. K. *Tetrahedron Lett.* **1983**, *24*, 4355, 4359. (c) Ireland, R. E.; Norbeck, D. W.; Mandel, G. S.; Mandel, N. S. *J. Am. Chem. Soc.* **1985**, *107*, 3285. (d) Back, T. G.; Kerr, R. G. *Tetrahedron* **1985**, *41*, 4759. (e) Kozikowski, A. P.; Ames, A. *Tetrahedron* **1985**, *41*, 4821. (f) Schwartz, C. E.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 9272. (g) Batty, D.; Crich, D.; Fortt, S. M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2875. (h) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1992**, *57*, 1429. (i) Kuniyasu, H.; Ogawa, A.; Higaki, K.; Sonoda, N. *Organometallics* **1992**, *11*, 3937. (j) Kuniyasu, H.; Ogawa, A.; Sonoda, N. *Tetrahedron Lett.* **1993**, *34*, 2491. (k) Hayes, C. J.; Pattenden, G. *Tetrahedron Lett.* **1996**, *37*, 271.

(21) Cf. For carbocarboxylations of alkenes, see: Ryu, I.; Alper, H. *J. Am. Chem. Soc.* **1993**, *115*, 7543.

Scheme 3



place in the same reaction system. The product acyl selenides are useful compounds for use in organic synthesis.

Experimental Section

General. ^{1}H NMR spectra were recorded with a JEOL JNM-GX67S (270 MHz) spectrometer and a Bruker AM600 (600 MHz) spectrometer. Chemical shifts are reported in parts per million (δ) relative to internal TMS. ^{13}C NMR spectra were recorded with a JEOL JNM-GX67S (68 MHz) spectrometer and a Bruker AM600 (150 MHz) spectrometer. Infrared spectra were recorded with a Perkin-Elmer FT-IR (Model 1600). UV−vis spectra were recorded on a Hitachi U-3500 spectrophotometer. Both conventional and high-resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC yields were assayed with a Shimadzu GC-14A gas chromatograph equipped with Supelco fused silica capillary column SPB-5. The products were purified by flash chromatography on silica gel (Fuji Silysia BW-820MH, 70−200 mesh) and, if necessary, were further purified by a recycling preparative HPLC (JAI LC-908) equipped with GPC columns using $CHCl_3$ as an eluant. Photolyses were carried out using a stainless autoclave with quartz glass windows lined with a standard Pyrex glass liner (Taiatsu Scientific Co., LTD. T-93179) and using a 500-W xenon lamp (Ushio Co., LTD., lamp house, UI-502Q; starter, XS-50102AA-A; power supply, XB-50101AA-A; xenon lamp, UXL-500D-O). The schematic figures of an autoclave and an irradiation instrument are given in the supporting information. The starting organoselenium compound **1a** was synthesized using the procedure described in ref 6d.

Preparation of Selenides 1b−e and 15. Synthesis of methyl α-(phenylseleno)acetate (**1b**) represents a typical example. Selenium powder (4.0 g, 50 mmol) was suspended in 100 mL of anhydrous THF under N_2 and cooled to 0 °C. When PhLi (1.00 M, cyclohexane−diethyl ether solution; 50 mL, 50 mmol) was added to the suspension via a syringe, the color of the mixture changed from black to pale yellow. After being stirred for 30 min at 0 °C, the mixture was cooled to −78 °C. Methyl α-bromoacetate (50 mmol, 4.7 mL) was added dropwise over a 5 min period, and the solution was stirred until the temperature became ambient. The resulting mixture was quenched by NH_4Cl (aq), and the organic portion was extracted into diethyl ether (50 mL × 3). The organic phase was dried over anhydrous $MgSO_4$ and filtered, and the solvent was evaporated. The resulting crude oil was purified by flash chromatography on silica gel (5% ether/hexane eluant) to give 8.6 g of methyl α-(phenylseleno)acetate (**1b**; 75%). Other selenides **1c** (68%), **1d** (72%), **1e** (75%), and **15** (93%) were prepared from the corresponding halides by similar methods. **1b**: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 3.52 (s, 2 H), 3.67 (s, 3 H), 7.28−7.30 (m, 3 H), 7.56−7.60 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 27.23 (t), 52.31 (q), 127.76 (s), 127.82 (d), 129.14 (d), 133.32 (d), 171.22 (s); IR (neat) 1731.9 cm^{-1} ($\nu_{C=O}$); MS (EI) *m*/*z* 230 (M$^+$, 100), 171 (55), 157 (32), 117 (4), 91 (46), 77 (21), 65 (6), 51 (11), 39 (4); HRMS (EI) *m*/*z* 229.9859 ($C_9H_{10}O_2Se$ requires 229.9846). **1c**:[22a] ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 2.27 (s, 3 H), 3.59 (s, 2 H), 7.27−7.30 (m, 3 H), 7.51−7.54 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 28.01 (t), 36.83 (q), 127.94 (d), 129.33 (d), 133.28 (d), 203.49 (s). The peak of the ipso position in the phenyl group could not be found. **1d**:[22b] ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 3.35 (s, 2 H), 7.35−7.37 (m, 3 H), 7.65−7.69 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 7.94 (t), 117.32 (s), 127.06 (s), 129.23 (d), 129.61 (d), 134.73 (d). **1e**: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 1.55 (d, J = 7.12 Hz, 3 H), 3.64 (s, 3 H), 3.78 (q, J = 7.12 Hz, 1 H), 7.26−7.34 (m, 3 H), 7.58−7.61 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 17.75 (q), 37.21 (d), 52.05 (q), 127.76 (s), 128.55 (d), 128.98 (d), 135.77 (d), 173.83 (s); IR (neat) 1731.8 cm^{-1} ($\nu_{C=O}$); MS (EI) *m*/*z* 244 (M$^+$, 100), 185 (64), 157 (37), 105 (36), 87 (6), 77 (20), 59 (7); HRMS (EI) *m*/*z* 244.0022 ($C_{10}H_{12}O_2Se$ requires 244.0003). **15**: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.90 (t, J = 6.84 Hz, 3 H), 0.98 (t, J = 7.45 Hz, 3 H), 1.21−1.41 (m, 4 H), 1.44−1.65 (8-line m, J = ca. 7.13 Hz, 2 H), 1.65−1.81 (6-line m, J = ca. 7.37 Hz, 2 H), 2.63 (tt, J = 5.37, 8.18 Hz, 1 H), 7.33−7.42 (m, 3 H), 7.44−7.56 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 11.66 (q), 13.88 (q), 22.71 (t), 25.64 (t), 29.34 (t), 31.85 (t), 59.21 (d), 126.60 (s), 128.66 (d), 129.23 (d), 135.78 (d), 204.65 (s); IR (neat) 1715.8 cm^{-1} ($\nu_{C=O}$); MS (EI) *m*/*z* 284 (M$^+$, 3), 157 (11), 127 (M$^+$ − SePh, 75), 99 (M$^+$ − COSePh, 28), 77 (7), 57 (100), 43 (17); HRMS (EI) *m*/*z* 284.0689 ($C_{14}H_{20}OSe$ requires 284.0679).

Butyl α-(Phenylseleno)propionate (1g). To a solution of *i*-Pr_2NH (3.1 mL, 22 mmol) in 60 mL of THF at −78 °C was added n-BuLi (1.6 M hexane solution; 13.8 mL, 22 mmol) via a syringe. After the mixture was stirred for 30 min, butyl propionate (2.6 g, 20 mmol) was added dropwise. Diphenyl diselenide (6.2 g, 20 mmol) was then added, and the reaction mixture was stirred for 30 min at −78 °C. The resulting mixture was poured into aqueous HCl (2 N), and the organic portion was extracted into diethyl ether (50 mL × 3). The organic phase was dried over anhydrous $MgSO_4$ and filtered, and the solvents were evaporated. The resulting crude oil was purified by flash chromatography on silica gel (5% ether/hexane eluant) to give 4.2 g of **1g** (74%): ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.90 (t, J = 7.32 Hz, 3 H), 1.31 (sext, J = 7.32 Hz, 2 H), 1.48−1.56 (m, 5 H), 3.78 (q, J = 7.08 Hz, 1 H), 4.04 (t, J = 6.59 Hz, 2 H), 7.26−7.31 (m, 3 H), 7.58−7.61 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 13.68 (q), 17.71 (q), 19.04 (t), 30.52 (t), 37.47 (d), 64.88 (t), 127.99 (s), 128.40 (d), 128.97 (d), 135.58 (d), 173.57 (s); IR (neat) 1724.4 cm^{-1} ($\nu_{C=O}$); MS (EI) *m*/*z* 286 (M$^+$, 100), 230 (30), 185 (72), 157 (28), 136 (4), 105 (36), 94 (6), 77 (14), 57 (10), 41 (6); HRMS (EI) *m*/*z* 286.0478 ($C_{13}H_{18}O_2Se$ requires 286.0472). Anal. Calcd for $C_{13}H_{18}O_2Se$: C, 54.74; H, 6.36. Found: C, 54.46; H, 6.27.

Methyl 2-(Phenylseleno)-6-heptenoate (1f). To a solution of *i*-Pr_2NH (1.5 mL, 11 mmol) in 30 mL of THF at −78 °C was added *n*-BuLi (1.6 M hexane solution; 6.9 mL, 11 mmol) via a syringe. After the mixture was stirred for 30 min, methyl α-(phenylseleno)acetate (**1b**; 2.3 g, 10 mmol) was added dropwise to the mixture. 4-Pentenyl iodide (2.2 g, 11 mmol) and DMSO (20 mL) were then added after cooling at −78 °C, and the reaction mixture was stirred for 30 min at −78 °C. The resulting mixture was poured into aqueous HCl (2 N), and the organic portion was extracted into diethyl ether (50 mL × 3). The organic phase was dried over anhydrous $MgSO_4$ and filtered, and the solvents were evaporated. The resulting crude oil was purified by flash chromatography on silica gel (5% ether/hexane eluant) to give 2.0 g of **1f** (88%): ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 1.49 (m, 2 H), 1.78 (m, 1 H), 1.91 (m, 1 H), 2.04 (q-like, J = 7.08 Hz, 2 H), 3.58 (m, 1 H), 3.62 (s, 3 H), 4.94 (d, J = 7.81 Hz, 1 H), 4.98 (d, J = 15.14 Hz, 1 H), 5.74 (m, 1 H), 7.31 (m, 3 H), 7.58 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68

(22) These compounds are already known, and the obtained spectroscopic data are in good agreement with those described in the following literature. (a) Toshimitsu, A.; Aoai, T.; Owada, H.; Uemura, S.; Okano, M. *J. Chem. Soc., Chem. Commun.* **1980**, 412. (b) Detty, M. R.; Wood, G. P. *J. Org. Chem.* **1980**, *45*, 80.

MHz) δ 27.25 (t), 31.27 (t), 33.06 (t), 43.34 (d), 51.90 (q), 114.94 (t), 127.87 (s), 128.40 (d), 128.92 (d), 135.54 (d), 137.89 (d), 173.26 (s); IR (neat) 1731.7 cm^{-1} ($\nu_{C=O}$), 1640.1 ($\nu_{C=C}$); MS (EI) *m/z* 298 (M^+, 60), 184 (9), 158 (38), 141 (M^+ − SePh, 100), 109 (51), 99 (6), 87 (8), 81 (77), 67 (17), 55 (14), 41 (8), 27 (4); HRMS (EI) *m/z* 298.0460 ($C_{14}H_{18}O_2Se$ requires 298.0472).

General Procedure for Phenylselenenyl Group Transfer Carbonylations. Benzene (30 mL), methyl α-(phenylseleno)acetate (**1b**; 70 mg, 0.30 mmol), and 1-octene (673 mg, 6.00 mmol) were placed in a 50-mL stainless steel autoclave for irradiation use (for details of the autoclave, see the supporting information) lined with a Pyrex glass tube. The autoclave was closed, purged twice with carbon monoxide, and then charged with 80 atm of CO and was irradiated with stirring for 20 h using a 500-W xenon lamp (>300 nm) placed 30 cm from the solution. During the reaction, the temperature increased to ca. 60 °C. After excess CO was discharged at room temperature, the benzene was evaporated to give an yellow oil. The residue was purified by flash chromatography on silica gel (hexane, 10% Et_2O−hexane eluant). The major fraction (10% Et_2O−hexane eluant) eluted from the column contained 64 mg of phenyl 2-hexyl-4-(methoxycarbonyl)selenobutanoate (**2b**; 58%). The spectroscopic data of the photocarbonylated products are listed below.

***Se*-Phenyl 2-hexyl-4,4-bis(ethoxycarbonyl)selenobutanoate (2a):** ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 0.89 (t, J = 6.93 Hz, 3 H), 1.24−1.33 (m, 12 H), 1.38 (qui, J = 7.30 Hz, 2 H), 1.51−1.60 (m, 1 H), 1.71−1.79 (m, 1 H), 2.12 (ddd, J = 14.30, 9.66, 4.74 Hz, 1 H), 2.25 (ddd, J = 14.30, 9.24, 5.29 Hz, 1 H), 2.79−2.84 (m, 1 H), 3.48 (dd, J = 9.93, 5.29 Hz, 1 H), 4.16−4.21 (10-line m, J = ca. 3.70 Hz, 2 H), 4.24 (q, J = 7.15 Hz, 2 H), 7.36−7.40 (m, 3 H), 7.48−7.51 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 14.02 (q, 2 peaks), 14.09 (q), 22.53 (t), 26.76 (t), 29.14 (t), 30.72 (t), 31.51 (t), 32.86 (t), 49.62 (d), 54.88 (d), 61.58 (t), 61.61 (t), 126.32 (s), 128.88 (d), 129.30 (d), 135.72 (d), 168.85 (s), 168.92 (s), 203.73 (s); IR (neat) 1732.1 cm^{-1} ($\nu_{C=O}$); MS (FAB, +KI, $CDCl_3$ as a solvent, 3-nitrobenzyl alcohol as a matrix) *m/z* (relative intensity) 495 (M^+ + K, 90), 393 (25), 355 (30), 299 (M^+ − SePh, 100), 271 (M^+ − COSePh, 20), 253 (90), 192 (30), 39 (100); HRMS (CI, methane) *m/z* 457.1483 ($C_{22}H_{32}O_5Se$ + H requires 457.1493).

***Se*-Phenyl 2-hexyl-4-(methoxycarbonyl)selenobutanoate (2b):** ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 0.89 (t, J = 6.94 Hz, 3 H), 1.23−1.34 (m, 6 H), 1.38 (qui, J = 7.33 Hz, 2 H), 1.48−1.55 (6-line m, J = ca. 7.81 Hz, 1 H), 1.70−1.77 (6-line m, J = ca. 7.81 Hz, 1 H), 1.85−1.91 (m, 1 H), 1.96−2.02 (m, 1 H), 2.39 (ddd, J = 16.11, 8.73, 7.21 Hz, 1 H), 2.44 (ddd, J = 16.11, 9.79, 5.88 Hz, 1 H), 2.78 (tt-like, J = 8.43, 5.39 Hz, 1 H), 3.68 (s, 3 H), 7.36−7.39 (m, 3 H), 7.48−7.51 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 14.02 (q), 22.54 (t), 26.96 (t), 27.20 (t), 29.21 (t), 31.39 (t), 31.54 (t), 32.51 (t), 51.64 (q), 56.57 (d), 126.40 (s), 128.81 (d), 129.29 (d), 135.74 (d), 173.23 (s), 204.07 (s); IR (neat) 1738.5, 1715.8 cm^{-1} ($\nu_{C=O}$); MS (CI, isobutane) *m/z* 371 (M^+ + 1, 1), 231 (4), 213 (M^+ − SePh, 100), 199 (3), 187 (10); HRMS (CI, methane) *m/z* 371.1139 ($C_{18}H_{26}O_3Se$ + H requires 371.1126). Anal. Calcd for $C_{18}H_{26}O_3Se$: C, 58.53; H, 7.10. Found: C, 58.66; H, 7.07.

***Se*-Phenyl 2-[(methoxycarbonyl)ethyl]-4-phenylselenobutanoate (5):** ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.79−1.86 (m, 1 H), 1.89−1.97 (m, 1 H), 2.01−2.13 (m, 2 H), 2.34−2.47 (14-line m, 2 H), 2.64−2.76 (14-line m, 2 H), 2.83 (tt, J = 5.27, 8.47 Hz, 1 H), 3.67 (s, 3 H), 7.17−7.22 (m, 3 H), 7.29 (t, J = 7.28 Hz, 2 H), 7.36−7.42 (m, 3 H), 7.487.52 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ 27.24 (t), 31.28 (t), 33.18 (t), 34.12 (t), 51.70 (q), 55.93 (d), 126.14 (d), 126.21 (s), 128.40 (d), 128.49 (d), 128.94 (d), 129.36 (d), 135.77 (d), 141.09 (s), 173.15 (s), 203.90 (s); IR (neat) 1713.4, 1738.0 cm^{-1} ($\nu_{C=O}$); MS (CI, isobutane) *m/z* 233 (M^+ − SePh, 100), 201 (26), 191 (2), 173 (3), 115 (5). Anal. Calcd for $C_{20}H_{22}O_3Se$: C, 61.70; H, 5.70. Found: C, 61.89; H, 5.83.

***Se*-Phenyl 2-(acetoxymethyl)-4-(methoxycarbonyl)selenobutanoate (6):** ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.89−1.96 (m, 1 H), 2.03−2.10 (m, 1 H), 2.08 (s, 3 H), 2.41−2.51 (m, 2 H), 3.18 (tt, J = 5.65, 7.89 Hz, 1 H), 3.69 (s, 1 H), 4.24 (dd, J = 5.42, 11.29 Hz 1 H), 4.28 (dd, J = 7.48, 11.29 Hz, 1 H), 7.37−7.42 (m, 3 H), 7.48−7.51 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 20.72 (q), 24.09 (t), 30.89 (t), 51.74 (q), 55.03 (d), 63.81 (t), 125.85 (s), 129.07 (d), 129.38 (d), 135.63 (d), 170.51 (s), 172.74 (s), 201.30 (s); IR (neat) 1738.2, 1715.0 cm^{-1} ($\nu_{C=O}$); MS (CI, methane) *m/z* 359 (M^+ + 1, 1), 267 (4), 201 (M^+ − SePh, 50), 159 (100), 141 (95), 113 (10), 61 (5); HRMS (CI, methane) *m/z* 359.0372 ($C_{15}H_{18}O_5Se$ + H requires 359.0398). Anal. Calcd for $C_{15}H_{18}O_5Se$: C, 50.43; H, 5.08. Found: C, 50.53; H, 5.14.

***Se*-Phenyl 2-(cyanomethyl)-4-(methoxycarbonyl)selenobutanoate (7):** ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 2.07 (dt-like, J = 5.93, 21.36 Hz, 1 H), 2.17 (dt-like, J = 7.34, 21.36 Hz, 1 H), 2.49 (t, J = 7.41 Hz, 2 H), 2.58 (dd, J = 6.89, 17.05 Hz, 1 H), 2.70 (dd, J = 6.76, 17.05 Hz, 1 H), 3.22 (qui, J = 6.80 Hz, 1 H), 3.72 (s, 3 H), 7.38−7.45 (m, 3 H), 7.49−7.52 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 19.43 (t), 26.64 (t), 30.53 (t), 51.41 (d), 51.91 (q), 116.68 (s), 125.27 (s), 129.46 (d), 129.58 (d), 135.69 (d), 172.32 (s), 200.89 (s); IR (neat) 1734.9 cm^{-1} ($\nu_{C=O}$), 2249.7 cm^{-1} (ν_{CN}); MS (CI, methane) *m/z* 326 (M^+ + 1, 3), 294 (M^+ − OMe, 5), 197 (3), 168 (M^+ − SePh, 100), 140 (M^+ − COSePh, 10); HRMS (CI, methane) *m/z* 326.0284 ($C_{14}H_{15}NO_3Se$ + H requires 326.0295).

***Se*-Phenyl 2-[(methoxycarbonyl)ethyl]-3,3-dimethyl-4-(methoxycarbonyl)selenobutanoate (8):** ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.15 (s, 3 H), 1.17 (s, 3 H), 1.96 (dd, J = 8.06, 14.57 Hz, 2 H), 2.40 (dd, J = 14.45, 40.92 Hz, 2 H), 2.44 (dt, J = 8.14, 16.47 Hz, 1 H), 2.54 (dt, J = 7.04, 16.47 Hz, 1 H), 3.00 (dd, J = 6.55, 7.81 Hz, 1 H), 3.68 (s, 3 H), 3.70 (s, 3 H), 7.37−7.41 (m, 3 H), 7.46−7.49 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ 23.39 (t), 25.19 (q), 25.63 (q), 32.24 (t), 36.22 (s), 44.00 (t), 51.40 (q), 51.73 (q), 64.23 (d), 127.08 (s), 129.02 (d), 129.40 (d), 135.43 (d), 172.00 (s), 173.14 (s), 203.74 (s); IR (neat) 1737.6 cm^{-1} ($\nu_{C=O}$); MS (CI, isobutane) *m/z* 401 (M^+ + 1, 7), 373 (3), 243 (M^+ − SePh, 100), 217 (10); HRMS (CI, methane) *m/z* 401.0867 ($C_{18}H_{25}O_5Se$ + H requires 401.0867).

***Se*-Phenyl 2-[2-[(methoxycarbonyl)ethyl]-4-oxacyclopentyl]selenoethanoate (9):** ^{1}H-NMR ($CDCl_3$, 600 MHz) a cis/trans mixture (cis) δ 1.54−1.62 (m, 1 H, MeO_2CCH_2CH), 1.71−1.78 (m, 1 H, MeO_2CCH_2CH), 2.23−2.32 (m, 1 H, CH), 2.25−2.36 (m, 2 H, MeO_2CCH_2), 2.72 (dd, J = 7.88, 20.42 Hz, 1 H, PhSeCOCH), 2.73−2.78 (m, 1 H, CH), 2.86 (dd, J = 9.74, 20.42 Hz, 1 H, PhSeCOCH), 3.46 (dd, J = 7.22, 8.40 Hz, 1 H, OCH), 3.61 (dd, J = 4.65, 8.75 Hz, 1 H, OCH), 3.68 (s, 3 H, OCH_3), 3.91 (dd, J = 7.13, 8.40 Hz, 1 H, OCH), 3.93 (dd, J = 5.98, 8.75 Hz, 1 H, OCH), 7.37−7.42 (m, 3 H), 7.48−7.52 (m, 2 H); (trans) δ 1.62−1.66 (m, 1 H, MeO_2CCH_2CH), 1.83−1.89 (m, 1 H, MeO_2CCH_2CH), 1.85−1.92 (m, 1 H, CH), 2.23−2.32 (m, 1 H, CH), 2.25−2.36 (m, 2 H, MeO_2CCH_2), 2.70−2.78 (m, 1 H, PhSeCOCH), 2.94 (dd, J = 5.76, 14.91 Hz, 1 H, PhSeCOCH), 3.40 (dd, J = 6.56, 8.61 Hz, 1 H, OCH), 3.50 (dd, J = 6.05, 8.90 Hz, 1 H, OCH), 3.65 (s, 3 H, OCH_3), 3.97 (dd, J = 7.25, 8.61 Hz, 1 H, OCH), 4.00 (dd, J = 7.24, 8.90 Hz, 1 H, OCH), 7.37−7.42 (m, 3 H), 7.48−7.52 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 150 MHz) a cis/trans mixture (cis) δ 22.94 (t), 32.74 (t), 38.32 (d), 41.12 (d), 45.69 (t), 51.72 (q), 71.53 (t), 72.37 (t), 126.17 (s), 129.06 (d), 129.42 (d), 135.77 (d), 173.33 (s), 199.41 (s); (trans) δ 27.94 (t), 32.51 (t), 41.68 (d), 44.23 (d), 50.68 (t), 51.68 (q), 72.81 (t, 2 peaks), 126.14 (s), 129.06 (d), 129.43 (d), 135.74 (d), 173.40 (s), 199.14 (s); IR (neat) 1735.5 cm^{-1} ($\nu_{C=O}$); MS (CI, methane) *m/z* 357 (M^+ + 1, 3), 325 (M^+ − OMe, 2), 235 (2), 213 (1), 199 (M^+ − SePh, 100), 181 (4), 155 (10), 139 (4); HRMS (CI, methane) *m/z* (cis) 357.0604 (trans) 357.0594 ($C_{16}H_{21}O_4Se$ + H requires 357.0605).

***Se*-Phenyl 7-(methoxycarbonyl)seleno-4-heptenoate (10):** ^{1}H-NMR ($CDCl_3$, 600 MHz) a *E*/*Z* mixture (*E* isomer) δ 2.31 (q-like, J = 6.58 Hz, 1 H, C=CCH), 2.34−2.39 (m, 3 H, MeO_2CCH_2, C=CCH), 2.75 (t, J = 7.43 Hz, 2 H, $PhSeCOCH_2$), 3.66 (s, 3 H, OCH_3), 5.46 (dt, J = 5.47, 15.23 Hz, 1 H, C=CH), 5.50 (dt, J = 5.47, 15.32 Hz, 1 H, C=CH), 7.35−7.40 (m, 3 H), 7.48−7.52 (m, 2 H); (*Z* isomer) δ 2.34−2.39 (m, 3 H, MeO_2CCH_2, C=CCH), 2.44 (q-like, J = 6.91 Hz, 1 H, C=CCH), 2.75 (t, J = 7.49 Hz, 2 H, $PhSeCOCH_2$), 3.67 (s, 3 H, OCH_3), 5.39−5.42 (m, 2 H, C=CH, C=CH), 7.35−7.40 (m, 3 H), 7.48−7.52 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 150 MHz) a *E*/*Z* mixture (*E* isomer) δ 27.74 (t, C=CC), 28.08 (t, C=C-C), 33.86 (t, MeO_2CCH_2), 47.19 (t, $CH_2COSePh$), 51.54 (q, OCH_3), 126.41 (s), 128.59 (d, C=C), 128.88 (d), 129.34 (d), 130.11 (d, C=C), 135.78 (d), 173.48 (s, MeO_2C), 199.60(s, COSePh); (*Z* isomer) δ 22.74 (t,

C═C*C*), 23.08 (t, C═C*C*), 33.88 (t, MeO_2CCH_2), 47.13 (t, CH_2-COSePh), 51.58 (q, OCH_3), 126.40 (s), 128.16 (d, *C*═C), 128.89 (d), 129.34 (d), 129.53 (d, *C*═C), 125.78 (d), 173.44 (s, MeO_2C), 199.63 (s, *C*OSePh); IR (neat) 1718.3, 1734.9 cm^{-1} ($\nu_{C=O}$); MS (CI, methane) *m*/*z* 327 ($M^+ + 1$, 5), 169 ($M^+ -$ SePh, 32), 157 (3), 137 (100), 109 (5), 81 (3); HRMS (CI, methane) *m*/*z* 327.0506 ($C_{15}H_{18}O_3Se$ + H requires 327.0500).

***Se*-Phenyl 2-hexyl-5-oxoselenohexanoate (11):** ^{1}H-NMR ($CDCl_3$, 270 MHz) δ 0.89 (t, J = 6.83 Hz, 3 H), 1.18−1.43 (m, 8 H), 1.39−1.58 (m, 1 H), 1.62−1.82 (m, 1 H), 1.88 (q, J = 7.32 Hz, 2 H), 2.14 (s, 3 H), 2.52 (t, J = 7.45 Hz, 2 H), 2.74 (qui, J = 6.30 Hz, 1 H), 7.43−7.44 (m, 3 H), 7.44−7.60 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 14.02 (q), 22.52 (t), 25.95 (t), 27.00 (t), 29.20 (t), 30.01 (q), 31.53 (t), 32.66 (t), 56.54 (d), 126.38 (s), 128.80 (d), 129.28 (d), 135.68 (d), 204.38 (s), 207.59 (s); IR (neat) 1715.8 cm^{-1} ($\nu_{C=O}$); MS (CI, methane) *m*/*z* 225 (2), 197 ($M^+ -$ SePh, 100), 169 ($M^+ -$ COSePh, 30), 151 (5); HRMS (CI, methane) *m*/*z* 355.1171 ($C_{18}H_{26}O_2Se$ + H requires 355.1176). Anal. Calcd for $C_{18}H_{26}O_2Se$: C, 61.18; H, 7.42. Found: C, 61.37; H, 7.52.

***Se*-Phenyl 2-hexyl-4-cyanoselenobutanoate (12):** ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 0.89 (t, J = 6.78 Hz, 3 H), 1.22−1.35 (m, 6 H), 1.39 (qui, J = 7.53 Hz, 2 H), 1.54 (dt-like, J = 6.85, 21.19 Hz, 1 H), 1.77 (dt-like, J = 7.68, 21.62 Hz, 1 H), 1.85 (ddd-like, J = 4.79, 7.99, 21.62 Hz, 1 H), 2.06 (dt-like, J = 7.01, 21.19 Hz, 1 H), 2.39 (dd-like, J = 7.81, 17.0 Hz, 1 H), 2.45 (dd-like, J = 7.60, 17.0 Hz, 1 H), 2.87−2.93 (m, 1 H), 7.42−7.47 (m, 3 H), 7.47−7.52 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 13.97 (q), 15.09 (t), 22.48 (t), 26.73 (t), 27.52 (t), 29.10 (t), 31.47 (t), 32.28 (t), 55.78 (d), 118.84 (s), 125.96 (s), 129.06 (d), 129.40 (d), 135.68 (d), 203.52 (s); IR (neat) 1711.3 ($\nu_{C=O}$), 2246.5 cm^{-1} (ν_{CN}); MS (CI, methane) *m*/*z* 338 ($M^+ + 1$, 54), 180 ($M^+ -$ SePh, 100), 152 ($M^+ -$ COSePh, 78), 139 (3), 110 (3); HRMS (CI, methane) *m*/*z* 338.1014 ($C_{17}H_{23}NOSe$ + H requires 338.1023).

***Se*-Phenyl 2-Hexyl-4-(methoxycarbonyl)selenopentanoate (13).** Benzene (30 mL), methyl α-(phenylseleno)-propionate (**1e**; 75.5 mg, 0.31 mmol), and 1-octene (681.5 mg, 6.07 mmol) were placed in a 50-mL stainless steel autoclave for irradiation use (for details of the autoclave, see the supporting information) lined with a Pyrex glass tube. The autoclave was closed, purged twice with carbon monoxide, and then charged with 70 atm of CO and was irradiated with stirring for 160 h using a 500-W xenon lamp placed 30 cm from the solution and a glass filter (Toshiba L42, it cuts shorter wavelength than 420 nm). During the reaction, the temperature increased to ca. 45 °C. After excess CO was discharged at room temperature, the benzene was evaporated to give an yellow oil. The residue was purified by flash chromatography on silica gel (hexane, 10% Et_2O−hexane eluant). The major fraction (10% Et_2O−hexane eluant) eluted from the column contained 22.8 mg of *Se*-phenyl 2-hexyl-4-(methoxycarbonyl)-4-methylselenobutanoate (**13**; 20%). The spectroscopic data of the photocarbonylated products are listed below: ^{1}H-NMR ($CDCl_3$, 600 MHz) a mixture of diastereomers (major) δ 0.89 (t, J = 6.88 Hz, 3 H), 1.21 (d, J = 6.98 Hz, 3 H), 1.23−1.33 (m, 6 H), 1.33−1.40 (m, 2 H), 1.50 (dt, J = 5.72, 13.56 Hz, 1 H), 1.57 (dd-like, J = 5.89, 14.20 Hz, 1 H), 1.70 (dt, J = 8.05, 13.56 Hz, 1 H), 2.16 (ddd, J = 6.67, 7.94, 14.20 Hz, 1 H) 2.57 (sex-like, J = 7.03 Hz, 1 H), 2.74−2.81 (m, 1 H), 3.68 (s, 3 H), 7.35−7.40 (m, 3 H), 7.47−7.52 (m, 2 H); (minor) δ 0.89 (t, J = 6.88 Hz, 3 H), 1.17 (d, J = 7.01 Hz, 3 H), 1.23−1.33 (m, 6 H), 1.33−1.40 (m, 2 H), 1.45−1.55 (m, 1 H), 1.72 (dt-like, J = 5.34, 13.01 Hz, 1 H), 1.77 (ddd, J = 4.68, 9.62, 14.10 Hz, 1 H), 1.85 (ddd, J = 4.42, 9.76, 14.10 Hz, 1 H) 2.58 (sex-like, J = 7.18 Hz, 1 H), 2.74−2.81 (m, 1 H), 3.74 (s, 3 H), 7.35−7.40 (m, 3 H), 7.47−7.52 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) a mixture of diastereomers (major) δ 14.06 (q), 17.06 (q), 22.57 (t), 26.96 (t), 29.24 (t), 31.57 (t), 32.75 (t), 35.75 (t), 37.05 (d), 51.74 (q), 55.00 (d), 126.40 (s), 128.82 (d), 129.30 (d), 135.77 (d), 176.34 (s), 203.91 (s); (minor) δ 14.06 (q), 18.33 (q), 22.57 (t), 26.87 (t), 29.22 (t), 31.57 (t), 33.30 (t), 36.15 (t), 37.51 (d), 51.70 (q), 55.68 (d), 126.50 (s), 128.82 (d), 129.30 (d), 135.76 (d), 176.54 (s), 204.49 (s); IR (neat) 1736.6 cm^{-1} ($\nu_{C=O}$); MS (EI) a mixture of diastereomers (major) *m*/*z* 353 ($M^+ - OCH_3$, 4), 227 ($M^+ -$ SePh, 100), 199 (46), 167 (52), 149 (18), 139 (10), 111 (12), 97 (12), 83 (38), 69 (30), 55 (20), 41 (10); (minor) *m*/*z* 353 ($M^+ - OCH_3$, 4), 227 ($M^+ -$ SePh, 100), 199 (48), 167 (58), 149 (18), 111 (12), 97 (10), 83 (38), 69 (30), 55 (20), 41 (10); HRMS (EI) a mixture of diastereomers (major) *m*/*z* 353.1015; (major) *m*/*z* 353.1015 ($C_{19}H_{28}O_3Se - OCH_3$ requires 353.1019).

***cis*- and *trans*-*Se*-Phenyl 2-[2-(Methoxycarbonyl)cyclopentyl]selenoethanoates (14).** Benzene (30 mL) and methyl 2-(phenylseleno)-6-heptenoate (**1f**; 97.0 mg, 0.30 mmol, 0.01 M) were placed in a 50-mL stainless steel autoclave lined with Pyrex glass. The autoclave was closed, purged twice with carbon monoxide, and then charged with 85 atm of CO and was irradiated with stirring for 20 h using a 500-W xenon lamp (>300 nm) placed 30 cm from the solution. After excess CO was discharged at room temperature, benzene was evaporated. The residue was purified by flash chromatography on silica gel (hexane, 10% Et_2O−hexane eluant). The major fraction (10% Et_2O−hexane eluant) eluted from the column contained 56.7 mg of *Se*-phenyl 2-[2-(methoxycarbonyl)cyclopentyl]-selenoethanoate (**14**; 58%) as a 64:36 mixture of cis and trans isomers. These stereoisomers were separated by HPLC (38 cycles in the recycle mode for separation, GPC columns using $CHCl_3$ as an eluant). Cis: ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.50−1.55 (m, 1 H), 1.56−1.63 (m, 1 H), 1.81−1.91 (m, 3 H), 1.91−1.98 (m, 1 H), 2.62 (sex.-like, J = 7.70 Hz, 1 H), 2.71 (dd, J = 8.30, 15.99 Hz, 1 H), 2.85 (dd, J = 6.52, 15.99 Hz, 1 H), 2.94 (dd-like, J = 7.48, 13.42 Hz, 1 H), 3.66 (s, 3 H), 7.35−7.41 (m, 3 H), 7.48−7.54 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ 23.61 (t), 28.51 (t), 31.13 (t), 39.55 (d), 46.55 (d), 49.06 (t), 51.47 (q), 126.47 (s), 128.88 (d), 129.35 (d), 135.76 (d), 175.30 (s), 199.34 (s); IR (neat) 1728.8 cm^{-1} ($\nu_{C=O}$); MS (CI, isobutane) *m*/*z* 327 ($M^+ + 1$, 2), 295 (2), 215 (1), 187 (1), 169 ($M^+ -$ SePh, 100), 155 (3), 143 (8); HRMS (CI, methane) *m*/*z* 327.0503 ($C_{15}H_{18}O_3$-Se + H requires 327.0500). Trans: ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 1.35 (dt-like, J = 8.49, 20.26 Hz, 1 H), 1.69 (dt-like, J = 7.40, 21.18 Hz, 2 H), 1.86 (dt-like, J = 7.78, 20.88 Hz, 1 H), 1.96 (dt-like, J = 7.01, 20.88 Hz, 1 H), 2.03 (dt-like, J = 6.35, 20.26 Hz, 1 H), 2.45 (dd-like, J = 8.57, 17.16 Hz, 1 H), 2.59 (dt-like, J = 8.40, 22.39 Hz, 1 H), 2.72 (dd, J = 8.56, 15.28 Hz, 1 H), 2.97 (dd, J = 5.38, 15.28 Hz, 1 H), 3.67 (s, 3 H), 7.35−7.41 (m, 3 H), 7.48−7.52 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ 24.38 (t), 29.72 (t), 32.28 (t), 40.63 (d), 49.45 (d), 51.78 (q), 52.11 (t), 126.48 (s), 128.88 (d), 129.33 (d), 135.73 (d), 175.78 (s), 199.07 (s); IR (neat) 1730.8 cm^{-1} ($\nu_{C=O}$); MS (CI, isobutane) *m*/*z* 327 ($M^+ + 1$, 4), 295 (2), 169 ($M^+ -$ SePh, 100), 143 (8); HRMS (CI, methane) *m*/*z* 327.0490 ($C_{15}H_{18}O_3Se$ + H requires 327.0500).

Photoirradiation of an Acyl Selenide 2b. Benzene (11 mL), *Se*-phenyl 2-hexyl-4-(methoxycarbonyl)selenobutanoate (**2b**; 41.2 mg, 0.11 mmol), and nonane (internal standard; 6.7 mg) were placed in a 50-mL autoclave lined with Pyrex glass. The autoclave was then charged with 80 atm of CO and was irradiated with stirring for 20 h using a 500-W xenon lamp (>300 nm) placed 30 cm from the solution. After excess CO was discharged at room temperature, the product mixture was analyzed by GC, which showed that **1b**, **2b**, **3b**, and **4** were formed in 16%, 26%, 1%, and 24% yields, respectively. When a similar irradiation experiment was carried out under 1 atm of N_2, **1b**, **2b**, **3b**, and **4** were formed in 57%, 5%, trace, and 28% yields, respectively.

Photoirradiation of an Acyl Selenide 15. Benzene (30 mL) and *Se*-phenyl 2-ethylselenohexanoate (**15**; 86.0 mg, 0.30 mmol) were placed in a 50-mL volumetric flask containing a small stir bar. The flask was sealed with a septum and flushed with N_2 and was then irradiated for 20 h using a 500-W xenon lamp (>300 nm) placed 30 cm from the solution. The resulting mixture was evaporated and analyzed by NMR using *sym*-trioxane as an internal standard (12.3 mg, 0.14 mmol), indicating that diselenide **4** was formed in 9% yield with major recovery of **15** (88%).

Palladium-Catalyzed Reductions of Acyl Selenides 2b and 12 with *n*-Bu_3SnH. Synthesis of methyl 4-formyldecanoate (**16**) represents a typical example. To a benzene (10 mL) solution of *Se*-phenyl 2-hexyl-4-(methoxycarbonyl)selenobutanoate (**2b**; 99.4 mg, 0.27 mmol) and $Pd(PPh_3)_4$ (3.3 mg, 0.0029 mmol) was added *n*-Bu_3SnH (0.1 M of benzene solution, 10 mL) dropwise over a period of 5 min at room temperature. The reaction mixture was then instantly evaporated and

separated by flash chromatography on silica gel (hexane, 10% Et_2O−hexane eluant). The major fraction (10% Et_2O−hexane eluant) eluted from the column contained 55.2 mg of methyl 4-formyldecanoate (**16**; 95%). 4-Formyldecanenitrile (**17**; 80%) was prepared from **12** in a similar manner. The spectroscopic data are listed below.

Methyl 4-formyldecanoate (16): ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 0.86 (t, J = 6.66 Hz, 3 H), 1.19−1.35 (m, 8 H), 1.39−1.48 (m, 1 H), 1.60−1.69 (m, 1 H), 1.76 (dt-like, J = 6.89, 13.93 Hz, 1 H), 1.94 (dt-like, J = 8.02, 14.80 Hz, 1 H), 2.25−2.38 (m, 3 H), 3.65 (s, 3 H), 9.57 (d, J = 0.99 Hz, 1 H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ 13.97 (q), 22.50 (t), 23.54 (t), 26.78 (t), 28.76 (t), 29.24 (t), 31.34 (t), 31.53 (t), 51.02 (d or q), 51.59 (d or q), 173.39 (s), 204.36 (d); IR (neat) 1740.0 cm^{-1} ($\nu_{C=O}$); MS (CI, methane) m/z 215 ($M^+ + 1$, 44), 197 (12), 183 (100), 165 (42), 155 (6), 147 (16), 123 (9), 74 (13); HRMS (CI, methane) m/z 215.1649 ($C_{12}H_{22}O_3$ + H requires 215.1647).

4-Formyldecanenitrile (17): ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 0.88 (t, J = 6.95 Hz, 3 H), 1.23−1.39 (m, 8 H), 1.51 (ddd, J = 6.51, 8.14, 14.99 Hz, 1 H), 1.68−1.78 (m, 2 H), 2.02 (dddd, J = 6.46, 7.53, 7.62, 13.85 Hz, 1 H), 2.38 (dd, J = 7.75, 17.07 Hz, 1 H), 2.44 (ddd, J = 6.37, 7.53, 17.07 Hz, 1 H), 2.49 (ddt-like, J = 2.03, 6.63, 13.43 Hz, 1 H), 9.65 (d, J = 1.09 Hz, 1 H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ 14.02 (q), 15.17 (t), 22.53 (t), 23.86 (t), 26.66 (t), 28.61 (t), 29.25 (t), 31.53 (t), 50.20 (d), 119.17 (s), 203.15 (d); IR (neat) 1724.6 cm^{-1} ($\nu_{C=O}$), 2247.2 cm^{-1} (ν_{CN}); MS (EI) m/z 181 (M^+, 0.5), 152 (5), 138 (2), 125 (4), 110 (11), 97 (74), 84 (26), 69 (32), 57 (100), 41 (54), 29 (14); HRMS (EI) m/z 181.1452 ($C_{11}H_{19}NO$ requires 181.1467).

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Supporting Information Available: Schematic photoirradiation apparatus and copies of the ^{1}H and ^{13}C NMR spectra for products (49 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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