Oxidative Ring Cleavage of 2-Nitrocycloalkanones: Synthesis and Radical-Induced Transformations of Methyl ω,ω-Dihalo-ω-nitroalkanoates

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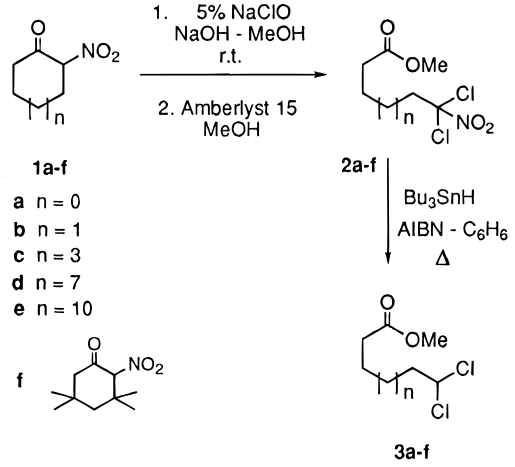
Received March 11, 1996

Ring cleavage often represents a particularly effective route to α,ω-difunctionalized frameworks. In this context 2-nitrocycloalkanones[1] are able to produce a consistent array of functionalized molecules through an easy nucleophilic retro-Claisen condensation.[2] Since 2-nitrocycloalkanones are readily available from the corresponding ketones or olefins by several nitrating processes,[3] these substrates are profitable precursors in many synthetic procedures. The utilization of a nucleophile-oxidizing agent couple allows the tandem ring cleavage−oxidation of the nitro function, thus affording dicarboxylic acids.[4] Basic solutions of hypohalite salts induce the oxidative demolition of α,α′-keto dinitronates to give α,ω-dinitro-α,α,ω,ω-tetrahaloalkanes.[5] The widespread interest in halogenated nitro compounds mainly stems from their recognized antimicrobial and insecticide activities.[6] Recently a direct synthesis of dichloronitro ketones starting from trichloronitromethane has been devised.[7]

In this context 2-nitrocycloalkanones **1** can be efficiently cleaved at room temperature by employing basic solutions of sodium hypochlorite, leading to the corresponding ω,ω-dichloro-ω-nitroalkanoic acids. These acids can be directly converted into their methyl esters with the use of methanol in the presence of Amberlyst 15 ion exchange resin (Scheme 1).[8] The double halogenation process can be rationalized by taking into account the ease of addition of hypohalite ion to nitronates.[9] Chloronitrocycloalkanone **5** is readily cleaved because of the enhanced ability of the α-chloronitro moiety to act as a leaving group. Chlorination of the resulting α-chloronitronate anion **6** leads to the dichloronitro compound **2b** after an acid catalyzed methyl esterification (Scheme 2).[10] A variety of 2-nitrocycloalkanones are cleaved in respectable yield regardless the ring size (Table 1). The so-called two-step transformation can be avoided by using an alternative procedure that uses NCS as chlorinating agent. In this case sodium methoxide is used as a base, directly affording the corresponding open chain esters **2**. This process is particularly effective for the ring opening of 2-nitrotetralone and derivatives since the Amberlyst 15 method to carry out the methyl esterification is scantly efficient with benzoic acids (Scheme 3).[8]

Compounds **2** generated by this methodology may represent an attractive class of substrates since the presence of three functional groups on the same carbon atom foretells potentially useful synthetic applications. Chlorine atoms as well as nitro groups are usually

Scheme 1



Scheme 2

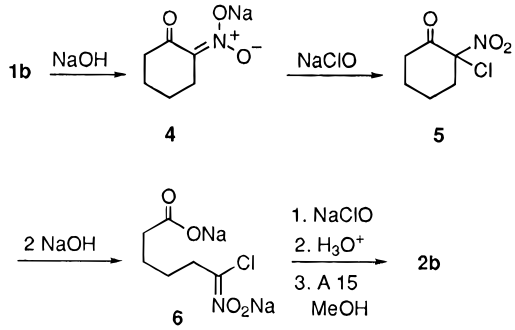


Table 1. Ring Cleavage and Denitration of 2-Nitrocycloalkanones (1)

entry	substrate **1**	cleavage product **2** yield %[a]	denitration product **3** yield %[a]
1	a	75 (70)	78
2	b	85 (75)	82
3	c	65 (68)	70
4	d	71 (65)	75
5	e	70 (70)	77
6	f	78 (71)	70
7	g	(80)	85
8	h	(72)	65

[a] Yields of pure, isolated products. Yields in parentheses refer to method B (see Experimental Section).

(1) Reviews: (a) Rosini, G.; Ballini, R.; Petrini, M.; Marotta, E.; Righi, P. *Org. Prep. Proc. Int.* **1990**, *22*, 707. (b) Fischer, R. H.; Weitz, H. M. *Synthesis* **1980**, 261.

(2) For some recent examples see: (a) Ballini, R.; Bartoli, G.; Giovannini, R.; Marcantoni, E.; Petrini, M. *Tetrahedron Lett.* **1993**, *34*, 3301. (b) Ballini, R.; Petrini, M.; Polzonetti, V. *Synthesis* **1992**, 355. (c) Ballini, R.; Petrini, M.; Rosini, G. *Tetrahedron* **1990**, *46*, 7531.

(3) (a) Rathore, R.; Lin, Z.; Kochi, J. K. *Tetrahedron Lett.* **1993**, *34*, 1859. For a complete mechanistic study of this procedure see: Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1996**, *61*, 627. (b) Venkat Ram Reddy, M.; Kumareswaran, R.; Vankar, Y. D. *Tetrahedron Lett.* **1995**, *36*, 7149. (c) Dampawan, P.; Zajac, W. W. *Synthesis* **1983**, 545. (d) Ballini, R.; Sorrenti, P. *Org. Prep. Proc. Int.* **1984**, *16*, 289.

(4) Ballini, R.; Marcantoni, E.; Petrini, M.; Rosini, G. *Synthesis* **1988**, 915.

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(6) Metcalf, R. L. *Organic Insecticides: Their Chemistry and Mode of Action*; Interscience: New York, 1955; p 134.

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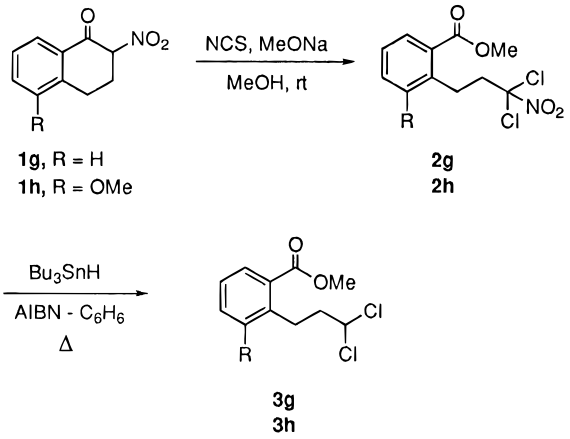
(8) Petrini, M.; Ballini, R.; Marcantoni, E.; Rosini, G. *Synth. Commun.* **1988**, *18*, 847.

(9) Nielsen, A. T. *The Chemistry of the Nitro and Nitroso Groups;* Feuer, H., Ed.; John Wiley and Sons, Inc.: New York, 1969; p 393.

(10) Similar results can be obtained with 2-(phenylsulfonyl)cycloalkanones but monochlorinated phenylsulfonyl derivatives are obtained in this instance since the open chain α-chlorophenyl sulfone is less prone to chlorination: Sholtz, D. *Liebigs Ann. Chem.* **1984**, 264.

S0022-3263(96)00488-4 CCC: $12.00

Scheme 3

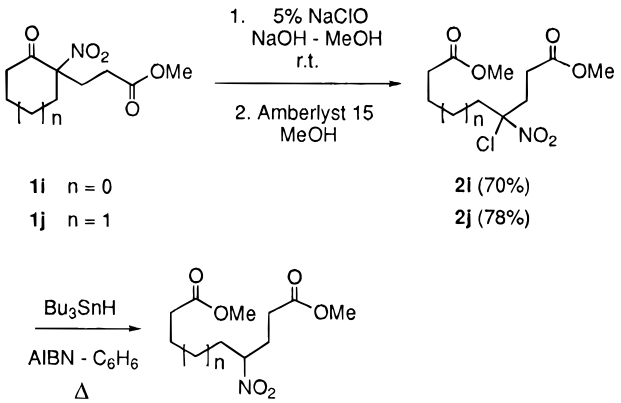


1g, R = H
1h, R = OMe

2g
2h

3g
3h

Scheme 4



1i n = 0
1j n = 1

2l (70%)
2j (78%)

3i (66%)
3j (71%)

sensitive toward radical processes.[11] Tributyltin hydride is known to produce a radical-induced denitration of tertiary, secondary, or activated nitro compounds.[12] We found that the chlorine atoms make possible the removal of the nitro group from methyl ω,ω-dichloro-ω-nitroalkanoates **2** using Bu_3SnH in benzene at reflux in the presence of AIBN as initiator. Chlorine atoms are unaffected by these conditions and hence methyl ω,ω-dichloroalkanoates are the final products of this procedure.[13] A substantial weakening of the carbon−nitrogen bond is expected in compounds **2**, and this effect, coupled with the low mobility of chlorine atoms in radical processes, could be responsible for the success of this selective denitration. Indeed a different behavior is displayed by compounds **2i,j**, obtained by the usual oxidative ring cleavage from precursors **1i,j**. These chloronitro esters, upon treatment with Bu_3SnH, suffer the removal of the chlorine atom while the nitro group is retained in the molecule (Scheme 4).

At this point it is clearly evident that *gem*-dichlorocarbon radicals are stable enough to possibly undergo other radical processes. These radicals possess an electrophilic nature, and therefore their reactivity would be enhanced using electron-rich alkenes.[11] However, attempts to add chloronitro ester **2b** to butyl vinyl ether by standard conditions (Bu_3SnH, AIBN, benzene at reflux), gave a rather unclean mixture of products in which the denitrated compound **3b** predominated. This clearly means that the reductive process is faster than the addition of the dichloro radical to the olefin. Fragmentation processes, which avoid the use of hydride donors in radical reactions, could be of some benefit for our purposes.[14] Allylation can be successfully performed with the use of allyltin derivatives that have been proved to be about 10-fold more reactive than ordinary alkenes.[15] α-Chloro-α-nitro compounds have been converted by Ono *et al.* into the corresponding allyl derivatives through a selective removal of the halogen atom by using allyltributyltin and AIBN as radical initiator.[16] The same process conducted on compounds **2** shows a completely different pattern since in this case the nitro group is substituted by the allyl framework, giving the products **7**. Allylation is best conducted in toluene at reflux with the use of 2 equiv of tin derivative and AIBN as initiator (Table 2). The yields of this reaction are modest, and therefore we attempted to improve them by using different allyltin derivatives as shown in Scheme 5. Triphenylallyltin gives comparable results to that obtained with the tributyl derivative but only after prolonged reaction times. Trimethylallyltin is able to slightly improve the yield of the allylated product but this reagent is much more expensive than the butyl one and furthermore its preparation is more difficult to carry out.

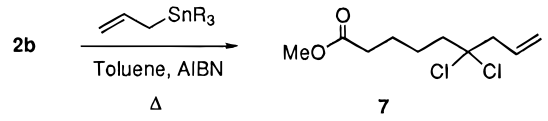
A similar procedure used for the preparation of nitro derivatives **2** (Br_2, NaOH, H_2O) can be adopted for the oxidative bromination of compounds **1** although it is less effective in terms of yield. The direct ring cleavage−bromination (NBS, MeONa, MeOH) is more efficient, but the yields are always comparably lower to that obtained

Table 2. Allylation of ω,ω-Dichloro-ω-nitro Esters (2) with Allyltributyltin

entry	nitro ester **2**	product **7** yield %[a]
1	b	68
2	d	62
3	g	70
4	h	68

[a] Yields of pure, isolated products.

Scheme 5

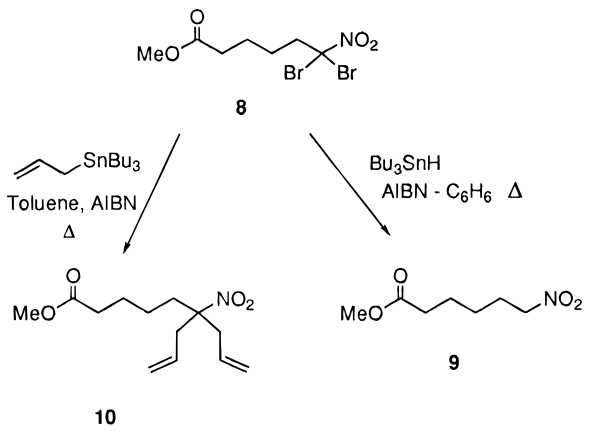


7

R	Reaction Time (h)	Yield (%)
*n*Bu	8	68
Ph	18	64
Me	6	70

(11) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986.
(12) Ono, N. *Nitro Compounds: Recent Advances in Synthesis and Reactivity*; Feuer, H., Nielsen, A. T., Eds.; VCH; Weinheim, 1990; p 1.
(13) Dichlorides are usually reduced using the tributyltin hydride−triethylborane couple: (a) Miura, K.; Ichinose, Y.; Nozaki, K.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1989**, *63*, 143. (b) Hamada, T.; Fukuda, T.; Imanishi, H.; Katsuki, T. *Tetrahedron* **1996**, *52*, 515.
(14) Curran, D. P. *Synthesis* **1988**, 489.
(15) Curran, D. P.; van Elburg, P. A.; Giese, B.; Gilges, S. *Tetrahedron Lett.* **1990**, *31*, 2861.
(16) Ono, N.; Zinsmeister, K.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1069.

Scheme 6



with the corresponding chlorination procedure.These ω,ω-dibromo-ω-nitro esters also behave in a completely different fashion when treated with the above cited tin reagents. Methyl 6,6-dibromo-6-nitrohexanoate (**8**) is reduced by tributyltin hydride and loses two bromine atoms giving the corresponding nitro ester **9** (Scheme 6). Further evidence for the enhanced mobility of the bromine atoms is given by the allylation process that experiences the double substitution of the halogen atoms with the allyl framework as displayed in Scheme 5. The latter procedure requires a large excess (6 equiv) of the allyltin reagent to go to completion. Indeed, upon lowering the amount of the tin reagent, a mixture of mono- and bisallylated products are obtained.

In conclusion, the oxidative ring cleavage of 2-nitrocycloalkanones provides an efficient entry to a new class of functionalized compounds, namely methyl ω,ω-dichloronitro-ω-alkanoates. These compounds can be denitrated to afford the corresponding methyl ω,ω-dichloroalkanoates or allylated, giving a selective substitution of the nitrogroup by the allyl framework. The corresponding ω,ω-dibromo-ω-nitro esters behave differently with tin reagents, suffering the removal of the halogen atoms. It is therefore evident that significant structural changes can be performed with this class of cleavage products, and many other changes are to be expected from further studies.

Experimental Section

^{1}H NMR spectra were performed at 300 MHz. Mass spectra were performed with the EI technique. All chemicals used are commercially available. 2-Nitrocycloalkanones **1a**−**h** were prepared by nitration of the enol derivatives of the corresponding cycloalkanones.[3] Compounds **1i,j** were prepared by conjugate addition of **1a,b** with methyl acrylate.[17]

Oxidative Ring Cleavage of 2-Nitrocycloalkanones. Methyl 6,6-Dichloro-6-nitrohexanoate (2b). Method A. 2-Nitrocyclohexanone (1.43 g, 10 mmol) was dissolved in 10% KOH methanolic solution (30 mL), and then 5% NaClO (25 mL) was added at 0 °C. After 10 min the cooling bath was removed, and strirring was continued for 1 h. The mixture was acidified with 2 N HCl, and then most of the methanol was removed at reduced pressure. The aqueous solution was exctracted with dichloromethane and dried over $MgSO_4$. Removal of the solvent afforded the crude acid that was dissolved in methanol (30 mL) and stirred 15 h in the presence of Amberlyst 15 ion exchange resin (0.8 g). The resin was removed by filtration, and after evaporation of the solvent, the crude ester was purified by flash chromatography (hexane−ethyl acetate (8:2)), affording 2.07 g (85%) of chloronitro ester **2b** as an oil: IR (cm^{-1}, neat) 1735 (C=O), 1560, 1325 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.53−1.81 (m, 4H), 2.35 (t, 2H, J = 7.3 Hz), 2.67−2.76 (m, 2H), 3.68 (s, 3H); ^{13}C NMR δ ppm 24.13, 25.12, 33.82, 46.53, 52.15, 111.05, 173.71; MS m/z 214 (M^+ − 31), 197, 165, 101, 85, 74, 59. Anal. Calcd for $C_7H_{11}Cl_2NO_4$ (244.07) C, 34.45; H, 4.54; N, 5.74. Found C, 34.50; H, 4.52; N, 5.78.

Method B. 2-Nitrocyclohexanone (1.43 g, 10 mmol) was dissolved in methanol (60 mL), and then sodium methoxide (1,-35 g, 25 mmol) and NCS (3.33 g, 25 mmol) were added at 0 °C. After 10 min the cooling bath was removed, and strirring was continued for 2 h. Most of the methanol was then removed at reduced pressure, and the solid residue was dissolved in dichloromethane (50 mL). The organic solution was washed with water and dried over $MgSO_4$. After evaporation of the solvent the crude ester was purified as for method A, giving 1.83 g (75%) of **2b**.

Methyl 5,5-dichloro-5-nitropentanoate (2a): yield 75% (method A); oil; IR (cm^{-1}, neat) 1735 (C=O), 1560, 1325 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.85−2.03 (m, 2H), 2.45 (t, 2H, J = 7.5 Hz), 2.72−2.83 (m, 2H), 3.81 (s, 3H). Anal. Calcd for $C_6H_9Cl_2NO_4$ (230.04) C, 31.33; H, 3.94; N, 6.09. Found C, 31.29; H, 3.96; N, 6.04.

Methyl 8,8-dichloro-8-nitrooctanoae (2c): yield 65% (method A); oil; IR (cm^{-1}, neat) 1735 (C=O), 1555, 1330 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.28−1.44 (m, 4H), 1.46−1.69 (m, 4H), 2.27 (t, 2H, J = 7.3 Hz), 2.63−2.75 (m, 2H), 3.66 (s, 3H). Anal. Calcd for $C_9H_{15}Cl_2NO_4$ (272.13) C, 39.72; H, 5.56; N, 5.15. Found C, 39.76; H, 5.53; N, 5.19.

Methyl 12,12-dichloro-12-nitrododecanoate (2d): yield 71% (method A); oil; IR (cm^{-1}, neat) 1735 (C=O), 1565, 1330 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.15−1.42 (m, 10H), 1.46−1.70 (m, 6H), 2.29 (t, 2H, J = 7.3 Hz), 2.66−2.71 (m, 2H), 3.65 (s, 3H). Anal. Calcd for $C_{13}H_{23}Cl_2NO_4$ (328.23) C, 47.57; H, 7.06; N, 4.27. Found C, 47.61; H, 7.02; N, 4.30.

Methyl 15,15-dichloro-15-nitropentadecanoate (2e): yield 70% (method A); oil; IR (cm^{-1}, neat) 1735 (C=O), 1560, 1325 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.20−1.48 (m, 18H), 1.50−1.70 (m, 4H), 2.30 (t, 2H, J = 7.3 Hz), 2.64−2.72 (m, 2H), 3.67 (s, 3H). Anal. Calcd for $C_{16}H_{29}Cl_2NO_4$ (370.31) C, 51.90; H, 7.89; N, 3.78. Found C, 51.86; H, 7.92; N, 3.75.

Methyl 3,3,5,5-tetramethyl-6,6-dichloro-6-nitrohexanoate (2f): yield 78% (method A); oil; IR (cm^{-1}, neat) 1735 (C=O), 1560, 1325 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.16 (s, 6H) 1.42 (s, 6H), 1.72 (s, 2H), 2.33 (s, 2H), 3.67 (s, 3H). Anal. Calcd for $C_{11}H_{19}Cl_2NO_4$ (300.18) C, 44.01; H, 6.38; N, 4.67. Found C, 44.06; H, 6.35; N, 4.67.

Methyl 2-(3,3-dichloro-3-nitropropyl)benzoate (2g): yield 80% (method B); oil; IR (cm^{-1}, neat) 1735 (C=O), 1560, 1325 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.95−3.10 (m, 2H), 3.18−3.28 (m, 2H), 3.91 (s, 3H), 7.25−7.50 (m, 3H), 7.92 (m, 1H). Anal. Calcd for $C_{11}H_{11}Cl_2NO_4$ (292.12) C, 45.23; H, 3.80; N, 4.79. Found C, 45.19; H, 3.84; N, 4.74.

Methyl 2-(3,3-dichloro-3-nitropropyl)-3-methoxybenzoate (2h): yield 72% (method B); oil; IR (cm^{-1}, neat) 1735 (C=O), 1560, 1325 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 2.93−3.05 (m, 2H), 3.12−3.26 (m, 2H), 3.88 (s, 3H), 3.91 (s, 3H), 7.01 (dd, 1H, J = 8.1,1.0 Hz), 7.22−7.31 (m, 1H), 7.46 (dd, 1H, J = 7.8, 1.2 Hz). Anal. Calcd for $C_{12}H_{13}Cl_2NO_5$ (322.14) C, 44.74; H, 4.07; N, 4.35. Found C, 44.79; H, 4.02; N, 4.4.38.

Dimethyl 4-chloro-4-nitrooctandioate (2i): yield 70% (method A); oil; IR (cm^{-1}, neat) 1735 (C=O), 1560, 1335 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.60−1.80 (m, 2H), 2.20−2.80 (m, 8H), 3.67 (s, 3H), 3.69 (s, 3H). Anal. Calcd for $C_{10}H_{16}ClNO_6$ (281.69) C, 42.64; H, 5.73; N, 4.97. Found C, 42.68; H, 5.77; N, 4.94.

Dimethyl 4-chloro-4-nitrononanedioate (2j): yield 78% (method A); oil; IR (cm^{-1}, neat) 1735 (C=O), 1560, 1335 (NO_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 1.50−1.85 (m, 4H), 2.15−2.90 (m, 8H), 3.68 (s, 3H), 3.70 (s, 3H). Anal. Calcd for $C_{11}H_{18}ClNO_6$ (295.72) C, 44.68; H, 6.14; N, 4.74. Found C, 44.73; H, 6.18; N, 4.72.

Radical Denitration of Methyl ω,ω-dichloronitroalkanoates. Methyl 6,6-Dichlorohexanoate (3b). Nitro ester **2b** (1.22 g, 5 mmol) was dissolved in dry benzene (20 mL), and then Bu_3SnH (2.91 g, 10 mmol) and AIBN (0.12 g, 0.75 mmol) were added. The mixture was refluxed for 1 h, and then the solvent was removed at reduced pressure. The crude product was purified by flash chromatography [hexane−ethyl acetate (95:

(17) Nakashita, Y.; Hesse, M. *Helv. Chim. Acta* **1983**, *66*, 845.

5)], affording 0.82 g (82%) of dichloro ester **3b** as an oil: IR (cm^{-1}, neat) 1720 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.50−1.80 (m, 4H), 2.15−2.28 (m, 2H), 2.35 (t, 2H, J = 7.1 Hz), 3.70 (s, 3H), 5.75 (t, 1H, J = 6.0 Hz); MS m/z 167 ($M^+ - 31$), 131, 101, 74, 59. Anal. Calcd for $C_7H_{12}Cl_2O_2$ (199.07) C, 43.23; H, 6.08. Found C, 43.29; H, 6.02.

Methyl 5,5-dichloropentanoate (3a): yield 78%; oil; IR (cm^{-1}, neat) 1735 (C=O), ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.77−1.98 (m, 2H), 2.15−2.26 (m, 2H), 2.48 (t, 2H, J = 7.3 Hz), 3.78 (s, 3H), 5.76 (t, 1H, J = 6.0 Hz). Anal. Calcd for $C_6H_{10}Cl_2O_2$ (185.05) C, 38.94; H, 5.45. Found C, 39.00; H, 5.41.

Methyl 8,8-dichlorooctanoate (3c): yield 70%; oil; IR (cm^{-1}, neat) 1735 (C=O), ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.20−1.75 (m, 8H), 2.12−2.25 (m, 2H), 2.34 (t, 2H, J = 7.3 Hz), 3.68 (s, 3H), 5.75 (t, 1H, J = 6.0 Hz). Anal. Calcd for $C_9H_{16}Cl_2O_2$ (227.13) C, 47.59; H, 7.10. Found C, 47.56; H, 7.12.

Methyl 12,12-dichlorododecanoate (3d): yield 75%; oil; IR (cm^{-1}, neat) 1735 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.15−1.70 (m, 16H), 2.12−2.21 (m, 2H), 2.29 (t, 2H, J = 7.3 Hz), 3.68 (s, 3H), 5.74 (t, 1H, J = 6.0 Hz). Anal. Calcd for $C_{13}H_{24}Cl_2O_2$ (283.24) C, 55.13; H, 8.54. Found C, 55.15; H, 8.52.

Methyl 15,15-dichloropentadecanoate (3e): yield 77%; oil; IR (cm^{-1}, neat) 1735 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.15−1.45 (m, 18H), 1.50−1.75 (m, 4H), 2.12−2.21 (m, 2H), 2.31 (t, 2H, J = 7.3 Hz), , 3.66 (s, 3H), 5.74 (t, 1H, J = 6.0 Hz). Anal. Calcd for $C_{16}H_{30}Cl_2O_2$ (325.32) C, 59.07; H, 9.29. Found C, 59.11; H, 9.25.

Methyl 3,3,5,5-tetramethyl-6,6-dichlorohexanoate (3f): yield 70%; oil; IR (cm^{-1}, neat) 1735 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.14 (s, 6H) 1.21 (s, 6H), 1.72 (s, 2H), 2.30 (s, 2H), 3.64 (s, 3H), 5.63 (s, 1H). Anal. Calcd for $C_{11}H_{20}Cl_2O_2$ (255.18) C, 51.77; H, 7.90. Found C, 51.72; H, 7.94.

Methyl 2-(3,3-dichloropropyl)benzoate (3g): yield 85%; oil, IR (cm^{-1}, neat) 1715 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 2.45−2.60 (m, 2H), 3.20 (t, 2H, J = 7.3 Hz), 3.91 (s, 3H), 5.76 (t, 1H, J = 6.0 Hz), 7.25−7.50 (m, 3H), 7.92 (m, 1H). Anal. Calcd for $C_{11}H_{12}Cl_2O_2$ (247.12) C, 53.46; H, 4.89. Found C, 53.50; H,4.95.

Methyl 2-(3,3-dichloropropyl)-3-methoxybenzoate (3h): yield 65%; oil; IR (cm^{-1}, neat) 1715 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 2.40−2.52 (m, 2H), 3.15−3.28 (m, 2H), 3.88 (s, 3H), 3.91 (s, 3H), 7.01 (dd, 1H, J = 8.0,1.0 Hz), 7.22−7.31 (m, 1H), 7.41 (dd, 1H, J = 7.6, 1.2 Hz). Anal. Calcd for $C_{12}H_{14}Cl_2O_3$ (277.14) C, 52.01; H, 5.09. Found C, 52.06; H, 5.14.

Methyl 4-nitrooctandioate (3i): yield 66%; oil; IR (cm^{-1}, neat) 1735 (C=O), 1535, 1365 (NO_2); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.50−1.65 (m, 2H), 1.80−2.37 (m, 8H), 3.67 (s, 3H), 3.69 (s, 3H), 4.45−4.60 (m, 1H). Anal. Calcd for $C_{10}H_{17}NO_6$ (247.25) C, 48.58; H, 6.93. Found C, 48.54; H, 6.98.

Methyl 4-nitrononanedioate (3j): yield 71%; oil; IR (cm^{-1}, neat) 1720 (C=O), 1540, 1365 (NO_2); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.55−1.70 (m, 4H), 1.90−2.45 (m, 8H), 3.64 (s, 3H), 3.68 (s, 3H), 4.45−4.60 (m, 1H); MS m/z 215 ($M^+ - 46$), 183, 151, 123, 81, 55, 41. Anal. Calcd for $C_{11}H_{19}NO_6$ (261.27) C, 50.57; H, 7.33. Found C, 50.63; H, 7.36.

Reaction of ω,ω-Dichloro-ω-nitroesters with Allyltributyltin. Methyl 6,6-Dichloro-8-nonenoate (7b). Nitro ester **2b** (1.95 g, 8 mmol) was dissolved in dry toluene (25 mL), and then allyltributiltin (6.62 g, 20 mmol) and AIBN (0.36 g, 2 mmol) were added. The mixture was refluxed for 8 h, and during this time AIBN (0.72 g, 4 mmol) dissolved in toluene (5 mL) was added in two portions. The solvent was removed at reduced pressure, and the crude product was purified by flash chromatography [hexane−ethyl acetate (95:5)], affording 0.82 g (68%) of allylchloro ester **7b** as an oil: IR (cm^{-1}, neat) 1720 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.60−1.85 (m, 4H), 2.10−2.21 (m, 2H), 2.32−2.45 (m, 2H), 2.97 (t, 1H, J = 1.2 Hz), 3.02 (t, 1H, J = 1.2 Hz), 3.68 (s, 3H), 5.16−5.32 (m, 2H), 5.84−6.06 (m, 1H); MS m/z 208 ($M^+ - 31$), 171, 135 128, 93, 74, 59. Anal. Calcd for $C_{10}H_{16}Cl_2O_2$ (239.14) C, 50.23; H, 6.74. Found C, 50.29; H, 7.02.

Methyl 12,12-dichloro-14-pentadecenoate (7d): yield 62%; oil; IR (cm^{-1}, neat) 1720 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.15−1.80 (m, 16H), 2.10−2.19 (m, 2H), 2.22−2.40 (m, 2H), 2.92 (d, 1H, J = 1.2 Hz), 2.98 (d, 1H, J = 1.2 Hz), 3.65 (s, 3H), 5.14−5.30 (m, 2H), 5.80−6.05 (m, 1H). Anal. Calcd for $C_{16}H_{28}Cl_2O_2$ (323.30) C, 59.44; H, 8.73. Found C, 59.39; H, 8.67.

Methyl 2-(3,3-dichloro-5-hexenyl)benzoate (7g): yield 70%; oil; IR (cm^{-1}, neat) 1720 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 2.40−2.60 (m, 2H), 3.03 (d, 1H, J = 1.0 Hz), 3.07 (d, 1H, J = 1.0 Hz), 3.28−3.40 (m, 2H), 3.91 (s, 3H), 5.15−5.36 (m, 3H), 5.92−6.12 (m, 1H). Anal. Calcd for $C_{14}H_{16}Cl_2O_2$ (287.18) C, 58.55; H, 5.62. Found C, 58.60; H, 5.65.

Methyl 2-(3,3-dichloro-5-hexenyl)-3-methoxybenzoate (7h): yield 68%; oil; IR (cm^{-1}, neat) 1720 (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 2.35−2.50 (m, 2H), 3.00 (d, 1H, J = 1.0 Hz), 3.04 (d, 1H, J = 1.0 Hz), 3.32−3.48 (m, 2H), 3.85 (s, 3H), 3.92 (s, 3H), 5.15−5.36 (m, 2H), 5.92−6.12 (m, 1H). Anal. Calcd for $C_{15}H_{18}Cl_2O_3$ (317.21) C, 56.80; H, 5.72. Found C, 56.85; H, 5.74.

Methyl 6,6-dibromo-6-nitrohexanoate (8). This product was prepared with the use of NBS according to method B used for the synthesis of compounds **2**: yield 72%; oil; IR (cm^{-1}, neat) 1735 (C=O), 1560, 1330 (NO_2); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.53−1.88 (m, 4H), 2.38 (t, 2H, J = 7.0 Hz), 2.82−2.91 (m, 2H), 3.68 (s, 3H). Anal. Calcd for $C_7H_{11}Br_2NO_4$ (332.97) C,-25.25; H, 3.33; N, 4.21. Found C, 25.21; H, 3.35; N, 4.25.

Reaction of Methyl 6,6-Dibromo-6-nitrohexanoate (8) with Tributyltin Hydride. Methyl 6-Nitrohexanoate (9). Product **8** (1.0 g, 3 mmol) was treated as for denitration of compounds **2** and gave 0.34 (75%) of pure **9** whose spectroscopic data were in full agreement with those reported.[2b]

Reaction of Methyl 6,6-Dibromo-6-nitrohexanoate (8) with Allyltributyltin. Methyl 6-Nitro-6-allyl-8-nonenoate (10). Nitro ester **8** (1.30 g, 4 mmol) was dissolved in dry toluene (30 mL), and then allyltributiltin (7.95 g, 24 mmol) and AIBN (0.54 g, 3 mmol) were added. The mixture was refluxed for 8h, and during this time AIBN (0.90 g, 5 mmol) dissolved in toluene (5 mL) was added in two portions. The solvent was removed at reduced pressure, and the crude product was purified by flash chromatography [hexane−ethyl acetate (95:5)], affording 0.71 g (70%) of nitrodiallyl ester **10** as an oil: IR (cm^{-1}, neat) 1720 (C=O) 1545, 1360 (NO_2); ^1H NMR (300 MHz, $CDCl_3$) δ ppm 1.50−1.75 (m, 4H), 1.85−1.95 (m, 2H), 2.25−2.40 (m, 2H), 2.63 (d, 2H, J = 0.9 Hz), 2.67 (d, 2H, J = 0.9 Hz), 3.65 (s, 3H), 5.09−5.31 (m, 4H), 5.53−5.85 (m, 1H); MS m/z 224 ($M^+ - 31$), 177, 149 135, 93, 107, 93, 79, 41. Anal. Calcd for $C_{13}H_{21}NO_4$ (255.31) C, 61.16; H, 8.29; N, 5.49. Found C, 61.21; H, 8.26; N, 5.53.

Acknowledgment. The authors thank University of Camerino for the financial assistance.

JO960488F