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DENITROHYDROGENATION OF ALIPHATIC NITRO COMPOUNDS AND A NEW USE OF ALIPHATIC NITRO COMPOUNDS AS RADICAL PRECURSORS

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Abstract - Aliphatic nitro groups are replaced by hydrogen on treatment with tributyltin hydride which proceeds via free radical chain processes. As the nitro group is selectively denitrated and other reducible groups are not affected with tributyltin hydride, this reaction can be used as a method for removing the nitro group from polyfunctional compounds. The radical intermediates generated via denitration can be also used for the carbon-carbon bond forming reactions.

Reduction of the nitro compounds has been used for a long time as a routine method for the preparation of various nitrogen derivatives such as amines, hydroxylamines, or oximes.[1] However, very recently, the reduction of the nitro compounds which results in the replacement of the nitro group by hydrogen has been found.[2-7]

$$R\text{-}NO_2 \rightarrow \begin{cases} R\text{-}NH_2,\ R\text{-}NO,\ R\text{-}NHOH,\ \text{etc.} \\ R\text{-}H \end{cases} \qquad (1)$$

The nitro groups of secondary or tertiary nitro compounds are replaced by hydrogen very effectively on treatment with tributyltin hydride. Although several methods are known for this conversion, the method using tributyltin hydride is the method of choice for denitrohydrogenation of aliphatic nitro compounds.[4] This reaction is now becoming a useful synthetic tool.[8] In this paper we wish to report the details of this denitration and its application to the carbon-carbon bond forming reactions via free radicals.

Denitrohydrogenation. The nitro group of tertiary nitro compounds (1) is cleanly replaced by hydrogen with tributyltin hydride (Bu_3SnH). Simply heating a mixture of 1, Bu_3SnH (1.2-1.3 equiv) and azobisisobutyronitrilr (AIBN, 0.2-0.3 equiv) in benzene at 80 °C for 1-2 h gave the denitrated products (2) in 80-95% yield. The results are summarized in Table 1.

$$-\overset{|}{\underset{|}{C}}\text{-}NO_2 \quad + \quad Bu_3SnH \xrightarrow[80\ ^\circ C]{AIBN} -\overset{|}{\underset{|}{C}}\text{-}H \quad + \quad Bu_3SnONO \qquad (2)$$

1 2

Table 1. Denitrohydrogenation of Tertiary Nitroalkanes (1)

1	R-H (2) yield, %	1	R-H (2) yield, %
$Me_3CCH_2-C(Me)(Me)-NO_2$ (1a)	2a, 75	$Me-C(Me)(NO_2)-CH_2CHSPh$ (1f)	2f, 77
			Ph
$Ph-C(Me)(Me)-NO_2$ (1b)	2b, 92	$Me-C(Me)(NO_2)-CH_2CH_2COOCH_2CH_2Cl$ (1g)	2g, 63
$p\text{-}CN\text{-}C_6H_4-C(Me)(Me)-NO_2$ (1c)	2c, 94	$Me-C(Me)(NO_2)-CH_2CH_2COOCH_2CH_2Br$ (1h)	2h, 26
$p\text{-}MeO\text{-}C_6H_4-C(Me)(Me)-NO_2$ (1d)	2d, 90	$Me_2CHCH_2-C(Me)(NO_2)-CH_2CH_2CN$ (1i)	2i, 90
$p\text{-}NO_2\text{-}C_6H_4-C(Me)(Me)-NO_2$ (1e)	2e, 0		

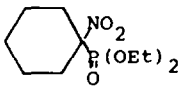
As shown in this table, various kinds of nitro compounds are cleanly denitrated by this procedure except for α,p-dinitrocumene (1e). The failure of this compound may be attributed to the strong electron accepting power of aromatic nitro groups. Denitration of 4,6-dimethyl-4-nitro-1-heptanenitrile (1i) was carried out under various conditions. The reaction was strongly accelerated by the addition of catalytic amount of AIBN and was retarded by the addition of m-dinitrobenzene. These results strongly suggest that the reaction proceeds via free radical chain mechanism as in eq 3-4.

$$R\text{-}NO_2 + Bu_3Sn\cdot \longrightarrow R + Bu_3SnONO \quad (3)$$

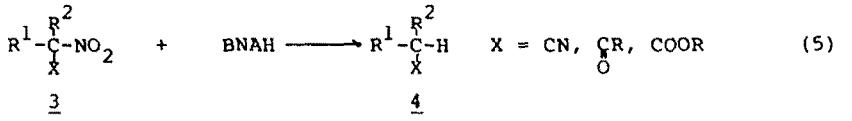
$$R\cdot + Bu_3SnH \longrightarrow R\text{-}H + Bu_3Sn\cdot \quad (4)$$

Inhibition by m-dinitrobenzene or the failure of denitration of 1e indicates that these aromatic nitro compounds are good acceptors of tin radicals. Denitration of the nitro compounds (3) substituted with X, X = CN, $-\overset{O}{\overset{\|}{C}}-$, COOR, $\overset{O}{\overset{\|}{P}}(OR)_2$, or SO_2Ar was undertaken to study the effects of these groups on denitration. The reaction was carried out in the same way as denitration of 1. The results are summarized in Table 2.

Table 2. Denitration of $R^1R^2C(X)NO_2$ (3)

3	R-H (4) yield, %		R-H (4) yield, %
$Et-C(CN)(NO_2)-CH_2CH_2\overset{O}{\overset{\|}{C}}Me$ (3a)	4a, 76	$Me-C(H)(NO_2)-\overset{O}{\overset{\|}{C}}-C_6H_4\text{-}Cl\text{-}p$ (3e)	4e, 78
$Me-C(COOMe)(NO_2)-CH_2CH_2CN$ (3b)	4b, 82	$Me-C(MeO)(NO_2)-\overset{O}{\overset{\|}{P}}(OEt)_2$ (3f)	4f, 80
$H-C(COOMe)(NO_2)-CH_2CH_2COOMe$ (3c)	4c, 75	 (3g)	4g, 90
$Me-C(MeO)-\overset{O}{\overset{\|}{C}}-Ph$ (3d)	4d, 80	$Me-C(Me)(NO_2)-SO_2C_6H_4\text{-}Me\text{-}p$ (3h)	4h, 0
NO_2		NO_2	
		$\overset{O}{\overset{\|}{P}}(OEt)_2$	

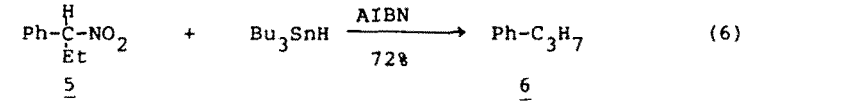
When X was CN, C(=O)R, COOR, or $P(=O)(OR)_2$, the nitro group was selectively replaced by hydrogen. The secondary nitro compounds are generally very difficult to be denitrated via radical reactions.[2] When the secondary nitro groups are activated by CN, C(=O)R, or COOR, they are readily denitrated with Bu_3SnH as shown in in Table 2. Such activated nitro compounds can be denitrohydrogenated with the very mild reducing agent, 1-benzyl-1,4-dihydronicotinamide (BNAH).[3]



$$R^1\text{-}\underset{X}{\overset{R^2}{C}}\text{-}NO_2 \quad + \quad BNAH \longrightarrow R^1\text{-}\underset{X}{\overset{R^2}{C}}\text{-}H \qquad X = CN,\ \underset{O}{CR},\ COOR \qquad (5)$$

3 4

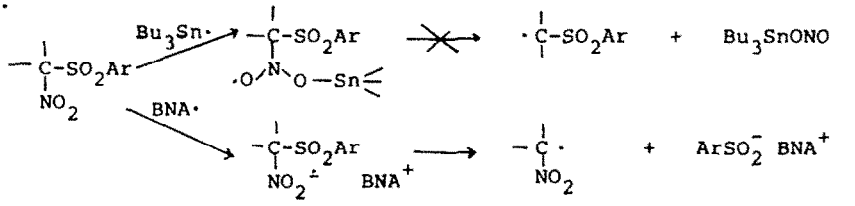
However, denitration with BNAH is only limited to the activated nitro compounds and it cannot be extended to general cases. The nitro groups at the benzylic or allylic positions are also activated, so they are readily denitrated with Bu_3SnH.[4] One example is shown in eq 6.



$$Ph\text{-}\underset{Et}{\overset{H}{C}}\text{-}NO_2 \quad + \quad Bu_3SnH \xrightarrow[72\%]{AIBN} Ph\text{-}C_3H_7 \qquad (6)$$

5 6

Denitration of α-nitro sulfones is very interesting. Although α-nitro sulfones are inert to Bu_3SnH, the sulfonyl group is replaced by hydrogen on treatment of α-nitro sulfones with BNAH.[9] These results suggest that the reaction of nitro compounds with Bu_3SnH and that with BNAH proceed in different pathway as shown in eq 7.

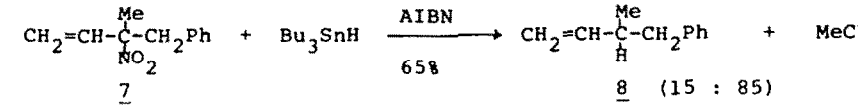


$$-\underset{NO_2}{\overset{}{C}}\text{-}SO_2Ar \xrightarrow{Bu_3Sn\cdot} -\underset{\cdot O}{\overset{}{C}}\text{-}SO_2Ar \overset{N}{\underset{O-Sn}{}} \not\longrightarrow \cdot\underset{}{\overset{}{C}}\text{-}SO_2Ar + Bu_3SnONO$$

$$-\underset{NO_2}{\overset{}{C}}\text{-}SO_2Ar \xrightarrow{BNA\cdot} -\underset{NO_2^{\pm}}{\overset{}{C}}\text{-}SO_2Ar \quad BNA^+ \longrightarrow -\underset{NO_2}{\overset{}{C}}\cdot + ArSO_2^- \ BNA^+ \qquad (7)$$

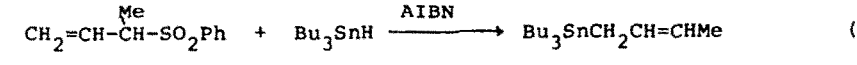
Further study is now under invesitigation on the detailed mechanism of denitration with Bu_3SnH and some ambiguous points still remain, but the solvent separated radical pair is not involved in denitration with Bu_3SnH. Tin and oxygen bond is covalent bond or tight ion pair.[10] On the other hand, free anion radicals are involved as intermediates in denitration with MeSNa,[2] BNAH,[3] or KOH in ethylene glycol.[6] From the above results we can estimate the approximate order of stabilization offered by X ($\cdot\underset{}{\overset{}{C}}\text{-}X$) is CN, C(=O)R, COOR> Aryl, C=C> Alkyl> H> SO_2Ar. ESR study also suggests that radicals are destabilized by the sulfonyl groups.[11]

Denitration of allylic nitro compounds was carried out to determine which group between the nitro and the double bond is attacked by tin radicals. The results shown in eq 8 strongly suggest that denitration of allylic nitro compounds proceed via the direct attack of tin radicals to the nitro group. On the other hand, desulfonylation of allylic sulfones with Bu_3SnH proceeds via S_H' pathway.[12]



$$CH_2{=}CH\text{-}\underset{NO_2}{\overset{Me}{C}}\text{-}CH_2Ph \quad + \quad Bu_3SnH \xrightarrow[65\%]{AIBN} CH_2{=}CH\text{-}\underset{H}{\overset{Me}{C}}\text{-}CH_2Ph \quad + \quad MeCH{=}C\overset{Me}{\underset{CH_2Ph}{}} \qquad (8)$$

7 8 (15 : 85) 9



$$CH_2{=}CH\text{-}\underset{SO_2Ph}{\overset{Me}{C}}\text{-}H \quad + \quad Bu_3SnH \xrightarrow{AIBN} Bu_3SnCH_2CH{=}CHMe \qquad (9)$$

All these results indicate that the very strong affinity of tin radicals to the nitro group. Consequently, Bu_3SnH can replace the nitro group by hydrogen without affecting other common functional groups such as CN, CHO,[8] C(=O)R, COOR, SR, SOR,[8] -C=C-, Cl.

When radical leaving groups are substituted at the β-position to the nitro group, elimination is faster than denitrohydrogenation.

$$\mathrm{Ph\text{-}\underset{NO_2}{\overset{X}{C}H\text{-}CH\text{-}Ph} + Bu_3SnH \longrightarrow Ph\text{-}CH_2\text{-}\overset{X}{C}H\text{-}Ph + Ph\text{-}CH{=}CH\text{-}Ph} \qquad (10)$$

X =		
OAc	87%	0%
NO_2	0	95
SPh	0	90
SO_2Ph	0	95

Several methods have existed so far for replacing the nitro group by hydrogen, Method A: the use of MeSNa in dipolar aprotic solvents,[2] method B: the use of BNAH,[3] method C: KOH in ethylene glycol at 120-130 °C,[6] method D: the use of Bu_3SnH.[4,5] Lithium aluminium hydride can also be used for denitration of tosylhydrazones of α-nitro ketones.[7] However, it cannot be used for denitration of general nitro compounds, for $LiAlH_4$ reduces the nitro group to the amino group generally. Method C is not suitable for denitration of base-sensitive compounds. Treatment of tertiary nitro compounds with sodium metal results in denitration in some cases, but it gives the complex mixtures of the products.[13] These methods are compared in denitration of tert-nitrooctane (1a), α-nitrocumene (1b), and α-nitroisobutyrophenone (3d). The results are summarized here.

1a ⟶ $Me_3CCH_2\text{-}\overset{Me}{\overset{|}{C}}\text{-}H$ + $Me_3CCH_2\text{-}\overset{Me}{\overset{|}{C}}{=}CH_2$ + Dimer

Na	30%	37%	18%[13]
Method A	54	0	0[2]
Method B	0	0	0
Method D	75	0	0

1b ⟶ $Ph\text{-}\overset{Me}{\overset{|}{C}}\text{-}H$ + $Ph\text{-}\overset{Me}{\overset{|}{C}}{=}CH_2$ + Dimer

Na	0%	0%	61%[13]
Method A	29	30	31[2]
Method B	0	0	0
Method C	0	complex mixtures	
Method D	92	0	0

3d ⟶ $Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{Me}{\overset{|}{C}}\text{-}H$ (Me) Method A 16%[3], Method B 60%(90% by GLC), Method D 80%, $NaBH_4$ 0% ($PhCH_2OH$ was obtained in 70% yield)

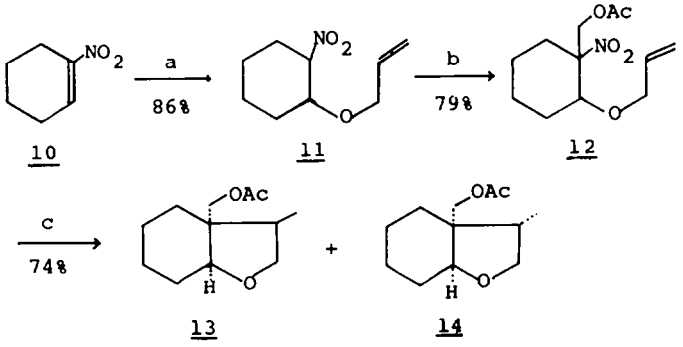
All yields refer to pure and isolated products.

Evidently, method D using Bu_3SnH is far superior to any other methods for replacing the nitro group by hydrogen. Method A can be applied to denitrohydrogenation of various kinds of tert-nitroalkanes.[2] However, denitrohydrogenation with MeSNa may give the complex mixtures of the products when stable radicals are involved as in the case of 1b. This is due to the lack of the reactivity of MeSNa as a hydrogen donor. Denitration of α-nitro ketones accompanies with some difficulties, for they are generally labile to basic conditions to cause the cleavage of the carbon-carbon bonds.[3] As the reagents of method B and D are almost neutral, they can be used for denitration of such base-sensitive compounds as α-nitro ketones. Further merits of method D lie in the simple procedure and work-up of the reaction. As the reaction can be carried out in benzene or without solvents, the isolation of the products is very easy.

Thus, a new method for generation of alkyl radicals which start from nitroalkanes is now in our hands. This promises a potent utility in organic synthesis, for aliphatic nitro compounds are available from various sources and they can be used directly for carbon-carbon bond forming reactions. Our attention is turned to the application of the radical intermediates generated by denitration.

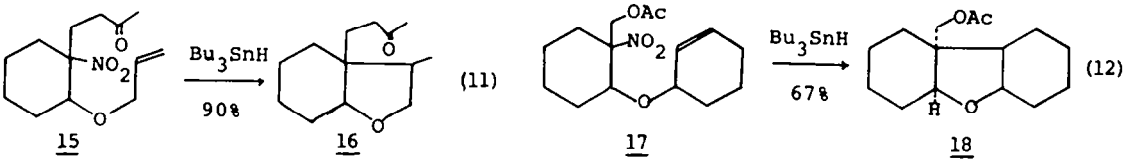
Radical Cyclization. Radical cyclization is becoming an important method for the preparation of various kinds of hetero- or carbo-cyclic compounds such as alkyl bromides or other derivatives of alcohols.[14] Radical cyclization of nitroalkanes would be a convenient one because the requisite starting materials for radical cyclization would be often more easily prepared than those required for other methods. Namely, nucleophiles and electrophiles can be introduced at the β-and α-positions of the nitro compounds by using nitroolefins, respectively. Additionally, the reaction proceeds with very high functional selectivity as is observed in denitrohydrogenation. We illustrate the preparation of tetrahydrofurans such as 13 and 14 starting with 1-nitrocyclohexene (10) in Scheme 1 in which some features of the present cyclization are summarized. Allyloxy and hydroxymethyl groups were readily introduced at the α- and β-positions, respectively, by the Michael addition of allyl alcohol to 10 followed by hydroxymethylation with formaldehyde. After acetylation, cyclization was performed simply by heating a benzene solution of 12 (ca 0.5 M), Bu_3SnH (1.3 equiv), and AIBN (0.3 equiv) at 80 °C for 2 h to yield exo-cyclized products 13 and 14 (85 : 15 ratio by GLC and ^{1}H-NMR) in 74% yield. Thus, the reaction is relatively insensitive to steric hindrance and forms a quaternary center with ease as in other cases of radical cyclization.[14]

Scheme 1



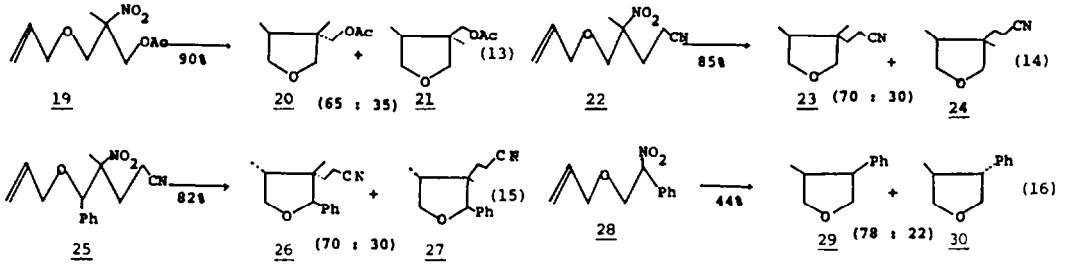
(a) CH_2=CH-CH_2OH, NaH, THF (b) 37%-HCHO, NaOH, i-PrOH; Ac_2O, pyridine (c) Bu_3SnH, AIBN, 80 °C, 2 h.

When methyl vinyl ketone was used as an electrophile, compound 16 was obtained as shown in eq 11 and if 2-cyclohexen-1-ol was used as a nucleophile, tricyclic compounds 18 and 19 were obtained as shown in eq 13.



15 16 17 18

As various nitroolefins and allylic alcohols are readily available, and the α-position of the nitro group can be alkylated with various electrophiles, substituted tetrahydrofurans are readily prepared by the present transformations. Some typical examples are presented here.

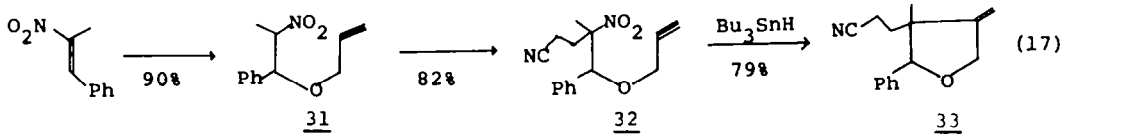


19 20 (65 : 35) 21 22 23 (70 : 30) 24

25 26 (70 : 30) 27 28 29 (78 : 22) 30

The present ring closures are also stereoselective: cyclic compounds such as 12 and 17 afford mainly cis-fused bicyclic or tricyclic compounds, respectively, which is in good agreement with previous observations.[15] Cyclizations of acyclic substituted hex-5-enyl radicals follow the general guideline: 1 or 3-substituted systems give mainly cis-disubstituted cyclic compounds whereas 2 or 4-substituted systems give mainly trans-compounds.[16] However, it is very difficult to predict the stereochemistry of ring closure in highly substituted cases such as 19, 22, or 25. Even in such cases, the reaction proceeded with a certain degree of stereoselectivity and cyclization of 19 or 22 afforded 3,3,4-trisubstituted tetrahydrofurans 20, 21 (65 : 35 ratio) or 23, 24 (70 : 30 ratio). Cyclization of 25 yielded 2,3,3,4-tetrasubstituted furans mainly 26 and 27 (70 : 30 ratio). Cyclization of 28 gave cis-3-phenyl-4-methyltetrahydrofuran (29) mainly. This is rather suprising, because cyclization of 6-bromo-6-phenyl-1-hexene is reported to give trans-1-methyl-2-phenylcyclopentane stereoselectively.[17] However, the preferential formation of the cis product from 1-substituted hexenyl radicals would be more likely according to the general guideline.[16]

Similar sequences consisted of the Michael addition of proparoyl alcohol to nitroolefins, alkylation with electrophiles (E), and cyclization with Bu_3SnH gave the exo-cyclized products, 3-alkylideneoxolanes (33) in good yield.



31 32 33

Intermolecular Addition of Radicals to Alkenes. Intermolecular addition of alkyl radicals to alkenes is currently becoming a useful method for carbon-carbon bond formation.[18] The free radical intermediates generated via denitration are also expected to undergo the carbon-carbon bond forming reactions via radical chain processes as shown in eq 18-20.

$$R\text{-}NO_2 + Bu_3Sn\cdot \longrightarrow R\cdot \quad (18) \qquad R\cdot + CH_2{=}CH\text{-}Y \longrightarrow R\text{-}CH_2\dot{C}HY \quad (19)$$

$$R\text{-}CH_2\dot{C}HY + Bu_3SnH \longrightarrow R\text{-}CH_2CH_2Y + Bu_3Sn\cdot \quad (20) \quad Y = CN, COOR$$

However, it is very difficult to control the reactivity of this radical chain reaction to get the desired product. After examining the results carried out under various conditions, we have found that the desired compound (35) is obtained in fairly good yield by heating a mixture of tertiary nitroalkanes (34, 4 mmol) electron deficient olefins (4-6 mL), Bu_3SnH (10 mmol), and AIBN (4 mmol) in benzene (1-3 mL) at 100 °C (bath temperature of the oil bath) for 5-10 min.

$$R^1\text{-}\overset{R^3}{\underset{R^2}{C}}\text{-}NO_2 \quad (34) \quad + \quad CH_2{=}C\overset{R^4}{\underset{Y}{<}} \quad + \quad Bu_3SnH \xrightarrow{AIBN} R^1\text{-}\overset{R^3}{\underset{R^2}{C}}\text{-}CH_2\overset{R^4}{C}H\text{-}Y \quad (35) \qquad (21)$$

The results are summarized in Table 3. As tertiary nitro compounds are available via various routes such as the Michael addition of nitroalkanes, single electron transfer reactions of the nitro compounds, or the Diels-Alder reaction of nitro olefins, the reaction of eq 21 provides a useful method for the conjugate addition of tertiary alkyl groups to electron deficient olefins.

Table 3. Conjugate Addition of Tertiary Alkyl Groups to Electron Deficient Olefins

R^1	R^2	R^3	R^4	Y	35, yield %
Me	Me	CH_2CH_2COOEt	H	COOMe	35a 60
Me	$PhCH_2$	CH_2CH_2CN	H	COOMe	35b, 54
Me	$PhCH_2$	CH_2CH_2OAc	H	COOMe	35c, 40
Me	$PhCH_2$	CH_2CH_2CN	H	CN	35d, 44
Me	$PhCH_2$	CH_2CH_2CN	Me	COOMe	35e, 46
Me	Me	Me_3CCH_2	Me	COOMe	35f, 42
Me	Me	$CH_2CH_2\overset{O}{C}Me$	Me	COOMe	35g, 62
Me	n-Pr	CH_2CH_2COOEt	Me	CN	35h, 58

Thus, denitration of aliphatic nitro compounds with Bu_3SnH opens a new area in organic synthesis. As functional selectivity of this reaction is extremely high, it may find its utility especially for the preparation of highly functionalized compounds.

Experimental. Infrared spectra were measured on a Hitachi 215 spectrometer. Proton NMR spectra were obtained with a JEOL PS-100 spectrometer. Mass spectra were recorded on a JEOL JMS-DX-300 spectrometer. GLC analyses were performed with a Shimadzu GC-8A with a 2 m column packed with Silicon DC-500. Elemental analyses were performed by the Kyoto University Microanalytical Laboratory.

Preparation of Nitro Compounds. Tertiary nitro compounds, 1a, 1b, 1c, 1d, and 1e were prepared according to the method of the literature.[2] Other nitro compounds of 1 and 34 were prepared by the Michael addition of nitroalkanes or hydroxymethylation of nitroalkanes.[19] Additional transformation is sometimes required to get some of them. For example, 1f was prepared by deoxygenation of the corresponding sulfoxide.[20] Compound 1g and 1h were prepared by the ester

exchange of the ethyl ester with 2-chloroethanol or 2-bromoethanol, respectively. The nitro compounds 3a-3e,[3] 3f,[21] 3g,[21] and 3h[22] were prepared by the methods of the literature. Allylic nitro compound (7) was prepared by the Michael addition of 1-phenyl-2-nitropropane to phenyl vinyl sulfoxide and the subsequent thermolysis.[23] As most nitro compounds were prepared by well known procedures, the assignment of their structure was done mainly by IR and NMR. Some of them are shown here. The spectra of other compounds are in good agreement with those of reported ones. 1f: IR (neat) 1350, 1450 cm^{-1}, NMR ($CDCl_3$) δ 1.40 (d, 6), 2.53(d, 2, J = 7 Hz), 3.90-4.38 (m, 1), 7.06-7.26 (m, 10). 1g: IR (neat) 1350, 1450 cm^{-1}, NMR ($CDCl_3$) δ 1.56 (s, 3), 2.12-2.36 (m, 4), 3.54 (t, 2, J = 8 Hz), 4.12 (t, 2, J = 8 Hz). 1h: IR(neat) 1350, 1540 cm^{-1}, NMR ($CDCl_3$) δ 1.58 (s, 6), 2.16-2.42 (m, 4), 3.45 (t, 2, J = 8 Hz), 4.28 (t, 2, J = 8 Hz). 1i: IR (neat) 1370, 1535, 2250 cm^{-1}, NMR ($CDCl_3$) δ 0.83 (d, 3), 0.96 (d, 3), 1.58 (s, 3), 1.66-2.22 (m, 4), 2.24-2.56 (m, 3). 7: IR (neat) 1350, 1540 cm^{-1}, NMR ($CDCl_3$) δ 2.04 (s, 3), 5.26 (d, 1, J = 17 Hz), 5.48 (d, 1, J = 10 Hz), 6.60 (d,d, 1, J = 17,10 Hz), 7.4 (m, 5).

Denitrohydrogenation of tert-Nitrooctane (1a). A mixture of 1a (1.59 g, 10 mmol), Bu_3SnH (3.50 g, 12 mmol), and AIBN (0.5 g, 3 mmol) in cumene (1.5 mL) was heated at 80 °C for 1 h. Then direct distillation of the reaction mixture gave pure isooctane (2a), 0.85 g (75%). NMR ($CDCl_3$) δ 0.88 (s, 9), 1.12 (d, 9), 1.46-1.82 (m, 1). The product was further confirmed by comparison with commercially available isooctane by NMR and GLC,

Denitrohydrogenation of α-Nitrocumene (1b). A mixture of 1b (0.98 g, 4.7 mmol), Bu_3SnH (1.65 g, 5.7 mmol), and AIBN (0.16 g, 0.9 mmol)in benzene was heated at 80 °C for 90 min. Distillation gave pure cumene (2b), bp 72=78 °C/80-90 mmHg, 0.52 g (92%). NMR ($CDCl_3$) δ 1.22 (d, 6), 2.6-3.1 (m, 1), 6.94-7.30 (m, 5), which were in good agreement with those of authentic cumene.

Denitration of other nitro compounds was carried out by the same procedure and following compounds were obtained. The method of purification and the spectral data of the product was summarized. p-Cyanocumene (2c): Column chromatography (silica gel/benzene-hexane) followed by distillation with Kugelrohr, 60-67 °C/18 mmHg. IR (neat) 2225 cm^{-1}, NMR ($CDCl_3$) δ 1.24 (d, 6), 2.76-3.08 (m, 1), 7.18-7.56 (m, 4), MS, m/e (M^+) 145; Anal. ($C_{10}H_{11}N$) C, H, N. p-Methoxycumene (2d): NMR ($CDCl_3$) δ 1.20 (d, 6), 2.6-3.0 (m, 1), 3.68 (s, 3), 6.8-7.2 (m, 4), MS m/e (M^+) 150. 1-Phenyl-1-phenylthio-3-methylbutane (2f): Column chromatography and distillation, 55-60 °C/0.6 mmHg. NMR ($CDCl_3$) δ 0.87 (d, 6), 1.36-1.38 (m, 3), 4.08 (t, 1), 6.92-7.20 (m, 10), MS, m/e (M^+) 256; Anal. ($C_{17}H_{20}S$) C, H. 2-Chloroethyl 4-Methylpentanoate (2g): Column chromatography and distillation, 68-70 °C/18 mmHg. IR (neat) 1720 cm^{-1}, NMR ($CDCl_3$) δ 0.90 (d, 6), 1.32-1.66 (m, 3), 2.05 (t, 2), 4.05 (t, 2), MS, m/e (M^+) 192. 2-Bromoethyl-4-methylpentanoate (2h): Column chromatography and distillation, 55-60 °C/18 mmHg, in this case debrominated product was also produced in 25% yield. IR (neat) 1738 cm^{-1}, NMR ($CDCl_3$) δ 0.90 (d, 6), 1.33-1.75 (m, 3), 2.27 (t, 2), 3.42 (t, 2), 4.26 (t, 2), MS, m/e (M^+) 233.

Denitration of 6-Cyano-2,4-dimethyl-4-nitrohexane (1i). A mixture of 1i (1.10 g, 6.0 mmol), Bu_3SnH (2.10 g, 7.2 mmol), and AIBN (0.30 g, 1.8 mmol) in 5 mL of benzene was heated at 80 °C for 90 min. Distillation with Kugelrohr gave 1-cyano-3,5-dimethylhexane (2i), bp 66-69 °C/18 mmHg, 0.75 g (90%). IR (neat) 2250 cm^{-1}, NMR ($CDCl_3$) δ 0.86 (d, 3), 0.88 (d, 3), 0.90 (d, 3), 0.96-1.18 (m, 2), 1.24-1.82 (m, 4), 2.28 (t, 2), MS, m/e (M^+) 139. The same reaction was carried out in the absence of AIBN or in the presence of m-dinitrobenzene (0.3 g, 1.8 mmol).

Denitrohydrogenation of 5-Cyano-5-nitro-2-heptanone (3a). A mixture of 3a (1.84 g, 10 mmol), Bu_3SnH (3.50 g, 12 mmol), and AIBN (0.5 g, 3 mmol) in 5 mL of benzene was heated at 80 °C for 90 min. Then the reaction mixture was subjected to column chromatography (silica gel/benzene-hexane) and the subsequent distillation gave 5-cyano-2-heptanone (4a),[3] 98-100 °C/3 mmHg, 1.04 g (76%).

4-Carbomethoxypentanenitrile (4b),[3] dimethyl glutarate (4c), isobutyrophenone (4d),[3] p-chloropropiophenone (4e),[3] diethyl 2-propylphosphonate (4f), and diethyl 1-cyclohexylphosphonate (4g) were prepared by this procedure. 4f: IR(neat) 1280 cm^{-1}, NMR ($CDCl_3$) δ 1.18 (d,d, 6, J = 15,8 Hz), 1.32 (t, 6, J = 7 Hz), 2.0 (m, 1), 4.12 (q, 4, J = 7 Hz), MS, m/e (M^+) 180.0927 ($C_7H_{17}O_3P$ requires 180.0938). 4g: IR(neat) 1050, 1280 cm^{-1}, NMR ($CDCl_3$) δ 1.36 (t, 6), 1.4-2.2 (m, 11), 4.18 (m, 4), MS, m/e (M^+) 220.1213 ($C_{10}H_{21}O_3P$ requires 220.1199).

Denitrohydrogenation of 1e and 3h was carried out under the same conditions but no reaction occurred and the starting material was recovered.

Denitrohydrogenation of 1-Phenyl-1-nitropropane (5). A mixture of 5 (1.65 g, 10 mmol), Bu_3SnH (3.50 g, 12 mmol), and AIBN (0.5 g) in 2 mL of benzene was heated at 80 °C for 2 h. Distillation gave n-propylbenzene (6), 0.86 g (72%).

Denitrohydrogenation of 3-Methyl-3-nitro-4-phenyl-1-butene (7). A mixture of 7 (1.91 g, 10 mmol), Bu_3SnH (3.50 g, 12 mmol), and AIBN (0.5 g) in 5 mL of benzene was heated at 80 °C for 90 min. Distillation of the crude product gave the mixture of 3-methyl-4-phenyl-1-butene (8) and 2-methyl-1-phenyl-2-butene (9), 0.95 g (65%), whose ratio was determined by GLC and NMR to be 15 : 85. NMR ($CDCl_3$) of 8 δ 0.95 (d, 3), 2.2-2.7 (m, 3), 4.8-5.0 (m, 2), 5.6-5.9 (m, 1), 7.1 (m, 5). NMR ($CDCl_3$) of 9 δ 1.5-1.8 (m, 6), 3.34 (d, 2), 5.2-5.4 (m, 1), 7.2 (m, 5).

Denitration of 1-Acetoxy-1,2-diphenyl-2-nitroethane. A mixture of 1-acetoxy-1,2-diphenyl-2-nitroethane[19] (2.85 g, 10 mmol), Bu_3SnH (3.50 g, 12 mmol), and AIBN (0.5 g) in 5 mL of benzene was refluxed for 2 h and the mixture was subjected to column chromatography to yield 1-acetoxy-1,2-diphenylethane, 2.10 g (87%). NMR ($CDCl_3$) δ 1.98 (s, 3), 3.08 (d,d, 2), 5.82 (t, 1), 6.9-7.3 (m, 10). MS, m/e (M^+) 239.1062 ($C_{16}H_{16}O_2$ requires 239.1071).

Denitration of vic-Dinitro compounds, β-Nitro Sulfides, or β-Nitro Sulfones. A mixture of 1,2-diphenyl-1,2-dinitroethane[19] (2.72 g, 10 mmol), Bu_3SnH (4.4 g, 15 mmol), and AIBN (0.7 g) in 8 mL of benzene was heated at 80 °C for 1 h. The reaction mixture was subjected to column chromatography (silica gel/benzene-hexane) to give E-stilbene, mp 122-123 °C, 1.66 g (95%). E-Stilbene was also prepared from 1,2-diphenyl-1-phenylthio-2-nitroethane or the corresponding sulfone by the same procedure.

Radical Cyclization. Preparation of 1-Allyloxy-2-acetoxymethyl-2-nitrocyclohexane (12). To a stirred mixture of NaH (50% dispersion, 1.06 g, 22 mmol) in 10 mL of THF was added allyl alcohol (1.23 g, 22 mmol) at 0-5 °C and stirring was continued till evolution of gas was ceased. Then 1-nitrocyclohexene (2.54 g, 20 mmol) was added to the reaction mixture at 0-5 °C and the resulting mixture was stirred at this temperature for 15 min. The reaction mixture was poured into ice-water and acidified by acetic acid. The usual work-up followed by distillation gave 11, bp 88-90 °C/1 mmHg, 3.20 g (86%). A mixture of 11 (1.85 g, 10 mmol), 37%-HCHO (0.97 g, 12 mmol), and NaOH (0.05 g) in 10 mL of i-PrOH was stirred at room temperature for 24 h, and worked up in the usual way. The crude product was acetylated by stirring a solution of this crude product and Ac_2O (1.23 g, 12 mmol) in 10 mL of pyridine at room temperature for 20 h. Column chromatography after the usual work-up gave 12, 2.03 g (79%). IR (neat) 1360, 1540, 1730 cm^{-1},

NMR ($CDCl_3$) δ 1.2-2.4 (m, 8), 2.01 (s, 3), 3.7-4.3 (m, 3), 4.4-4.8 (m, 2), 5.0-5.4 (m, 2), 5.6-6.0 (m, 1). Anal. ($C_{12}H_{19}NO_5$) C, H, N.

Denitration of 12. A mixture of 12 (0.80 g, 3.11 mmol), Bu_3SnH (1.18 g, 4.05 mmol) and AIBN (0.15 g, 0.93 mmol) in 10 mL of benzene was heated at 80 °C for 2 h. The reaction mixture was subjected to column chromatography (silica gel/benzene-hexane) to give the mixture of 13 and 14, 0.49 g (74%). IR (neat) 1730 cm^{-1} NMR ($CDCl_3$) δ 0.95 (d, Me of 14), 1.0 (d, Me of 13), 1.2-2.2 (m, 9), 2.10 (s, 3), 3.54 (m, 1), 3.8-4.4 (m, 4), The ratio of 13/14 was determined by NMR and GLC. MS, m/e (M^+) 212.1432 ($C_{12}H_{20}O_3$ requires 212.1411). Following compounds were prepared by this procedure. Compounds 15, 22, and 25 were prepared by the Michael addition to methyl vinyl ketone or acrylonitrile using catalytic amount of tetramethylguanidine as a base.[24] Physical properties of them are summarized.

15: IR (neat) 1360, 1545, 1710 cm^{-1}, NMR ($CDCl_3$) δ 1.3-2.8 (m, 12), 2.18 (s, 3), 3.95-4.3 (m, 3), 5.1-5.5 (m, 2), 5.7-6.2 (m, 1). 16: IR (neat) 1710 cm^{-1}, NMR ($CDCl_3$) 0.98 (d, 3), 1.2-2.1 (m, 11), 2.22 (s, 3), 2.3-2.7 (m, 2), 3.6-3.8 (m, 2), 4.24 (t, 1), MS, m/e (M^+) 210.1605 ($C_{13}H_{22}O_2$ requires 210.1619).

17: IR (neat) 1360, 1545, 1730 cm^{-1}, NMR ($CDCl_3$) δ 1.1-2.4 (m, 13), 2.05 (s, 3), 3.4-3.8 (m, 2), 4.28 (m, 2), 5.6-5.9 (m, 2). 18: The major isomer NMR ($CDCl_3$) δ 1.2-2.0 (m, 17), 2.04 (s, 3), 3.58 (m, 1), 3.98 (m, 1), 4.02 (d, 2). The minor isomer NMR ($CDCl_3$) δ 1.2-2.0 (m, 17), 2.04 (s, 3), 4.0 (m, 1), 4.26 (d, 1), 4.40 (m, 1), MS, m/e (M^+) 252.1712 ($C_{15}H_{24}O_3$ requires 252.1724).

19: IR (neat) 1370, 1535, 1735 cm^{-1}, NMR ($CDCl_3$) δ 1.62 (s, 3), 2.06 (s, 3), 3.80 (s, 2), 3.96-4.08 (m, 2), 4.34-4.66 (m, 2), 5.10-5.36 (m, 2), 5.62-6.04 (m, 1). Anal. ($C_9H_{15}NO_5$) C, H, N. 20 + 21: IR (neat) 1720 cm^{-1}, NMR ($CDCl_3$) δ 0.95-1.0 (m, 3), 1.0 (s, Me of 20), 1.12 (s, Me of 21), 1.3-1.7 (m, 1), 2.05 (s, 3), 3.4-4.2 (m, 6). Anal. ($C_9H_{16}O_3$) C, H.

22: IR (neat) 1360, 1540, 2225 cm^{-1}, NMR ($CDCl_3$) δ 1.60 (s, 3), 2.2-2.7 (m, 4), 3.80 (s, 2), 3.8-4.1 (m, 2), 5.1-5.3 (m, 2), 5.6-6.0 (m, 1). Anal. ($C_9H_{14}N_2O$) C, H, N. 23 + 24: IR (neat) 2220 cm^{-1}, NMR ($CDCl_3$) δ 0.9-1.05 (m, 3), 0.98 (s, Me of 24), 1.06 (s, Me of 25), 1.6-2.2 (m, 3), 2.3-2.5 (m, 2), 3.4-4.2 (m, 4), MS, m/e (M^+) 153.1138 ($C_9H_{15}NO$ requires 153.1153).

25: IR (neat) 1350, 1530, 2225 cm^{-1}, NMR ($CDCl_3$) δ 1.42, 1.60 (s, 3), 2.10-2.84 (m, 2), 5.56-6.00 (m, 1), 7.2-7.5 (m, 5). Anal. ($C_{15}H_{18}N_2O_3$) C, H, N. 26 + 27: IR (neat) 2225 cm^{-1}, NMR ($CDCl_3$) δ 1.98 (s, 3), 2.02 (d, 3), 1.4-2.4 (m, 5), 3.50 (m, 1), 4.30 (m, 1), 4.54 (s, 1); 1.61 (s, 3), 2.04 (d, 3), 1.7-2.4 (m, 5), 3.60 (m, 1), 4.32 (d, 1), 4.64 (s, 1). MS, m/s (M^+) 229.1467 ($C_{15}H_{19}NO$ requires 229.1466).

28: IR (neat) 1360, 1535 cm^{-1}, NMR ($CDCl_3$) δ 3.7-4.1 (m, 3), 4.40 (t, 1), 5.0-5.4 (m, 2), 5.6-6.0 (m, 2), 7.3-7.6 (m, 5), Anal. ($C_{11}H_{13}NO_3$) C, H, N. 29 + 30: NMR ($CDCl_3$) δ 0.68 (d, Me of 30), 1.02 (d, Me of 29), 2.2-3.0 (m, 2), 3.4-4.3 (m, 4), 7.2-7.5 (m, 5). MS, m/e (M^+) 166.1345 ($C_{11}H_{14}O$ requires 166.1357).

32: IR (neat) 1360, 1540, 2230 cm^{-1}, NMR ($CDCl_3$) δ 1.46, 1.62 (s, 3), 2.1-2.8 (m, 4), 3.7-4.3 (m, 2), 5.16, 5.17 (s, 1), 7.2-7.5 (m, 5). 33: IR (neat) 2220 cm^{-1}, NMR ($CDCl_3$) δ 1.16 (s, 3), 1.4-2.3 (m, 3), 4.3-4.8 (m, 3), 4.88 (m,1), 5.06 (m, 1), 7.2-7.4 (m, 5), MS, m/e (M^+) 227.0957 ($C_{15}H_{17}NO$ requires 227.0949).

Conjugate Addition of Tertiary Alkyl Groups. Preparation of Ethyl Methyl 4,4-Dimethylheptanedioate (35a). A mixture of ethyl 4-methyl-4-nitropentanoate (34a, 0.567 g, 3 mmol), Bu_3SnH (2.62 g, 9 mmol), AIBN (0.5 g, 3 mmol), methyl acrylate (3 mL), and benzene (2 mL) was heated by the oil bath at 100 °C and stirred for 10 min at this temperature. The reaction mixture was cooled at ca 20 °C and was subjected to column chromatography (silica gel/benzene-hexane) to give 35a, 0.41 g (60%). IR (neat) 1730 cm^{-1}, NMR ($CDCl_3$) δ 0.92

(s, 6), 1.30 (t, 3), 1.5-1.8 (m, 4), 2.2-2.4 (m, 2), 3.76 (s, 3), 4.18 (q, 2), MS, m/e (M^+) 230.1512 ($C_{12}H_{22}O_4$ requires 230.1516).

Following compounds were prepared by this procedure.

35b: IR (neat) 1730, 2240 cm^{-1}, NMR ($CDCl_3$) δ 0.86 (s, 3), 1.5-1.8 (m, 4), 2.2-2.5 (m, 4), 2.58 (s, 2), 3.78 (s, 3), 7.1-7.5 (m, 5), MS, m/e (M^+) 259.1556 ($C_{16}H_{21}NO_2$ requires 259.1571).

35c: IR (neat) 1730 cm^{-1}, NMR ($CDCl_3$) δ 0.90 (s, 3), 1.6-1.9 (m, 2), 2.16 (s, 3), 2.3-2.5 (m, 2), 2.65 (s, 2), 3.75 (s, 3), 3.80 (s, 2), 7.1-7.5 (m, 5), MS, m/e (M^+) 276.1602 ($C_{16}H_{22}O_4$ requires 278.1516).

35d: IR (neat) 2250 cm^{-1}, NMR ($CDCl_3$) δ 0.92 (s, 3), 1.64 (t, 4), 2.32 (t, 4) 2.58 (s, 2), 7.1-7.4 (m, 5), MS, m/e (M^+) 224.1458 ($C_{15}H_{18}N_2$ requires 226.1470).

35e: IR (neat) 1735, 2250 cm^{-1}, NMR ($CDCl_3$) δ 0.86 (s, 3), 1.20 (d, 3), 1.5-2.4 (m, 7), 2.6 (s, 2), 3.78 (s, 3), 7.0-7.4 (m, 5), MS, m/e (M^+) 273.1741 ($C_{17}H_{23}NO_2$ requires 273.1728).

35f: IR (neat) 1740 cm^{-1}, NMR ($CDCl_3$) δ 0.98 (s, 6), 1.0 (s, 9), 1.18 (d, 2), 1.22 (s, 2), 1.9 (d,d. 2), 2.4-2.7 (m, 1), 3.75 (s, 3), MS, m/e (M^+) 214.1918 ($C_{13}H_{26}O_2$ requires 214.1941).

35g: IR (neat) 1720, 1730 cm^{-1}, NMR ($CDCl_3$) δ 0.94 (s, 6), 1.08 (d, 3), 1.4 -1.6 (m, 2), 1.8-2.0 (m, 2), 2.18 (s, 3), 2.3-2.8 (m, 3), 3.75 (s, 3), MS, m/e (M^+) 225.1248 ($C_{13}H_{23}NO_2$ requires 225.1269).

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