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On the Mechanism of Reductive Cleavage of the Carbon–Nitrogen Bond of Aliphatic Nitro Compounds with Tributyltin Hydride[1)]

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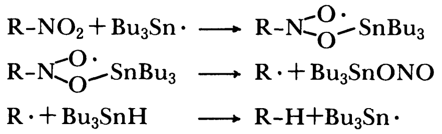
Denitrohydrogenation reaction of aliphatic nitro compounds with tributyltin hydride (Bu_3SnH) is accelerated in the presence of radical initiators. ESR and electrochemical measurements reveal that the reductive cleavage of the carbon-nitrogen bond proceeds not via anion radicals of nitro compounds such as $S_{RN}1$ reaction but via β-scission of (tributylstannyloxy)nitroxyl radicals. The relative reactivities of tin radicals toward substituted α-nitrocumenes, α-nitroethylbenzenes, and α-nitropropiophenones exhibits excellent Hammett correlations with positive ρ values. This tendency has also been found in the reaction of benzyl halides with tin radical. These results suggest that the carbon-nitrogen bond breaking from nitroxyl radical intermediates should take place in rate-determining step for the reaction.

Recently we and Tanner have reported that aliphatic nitro groups are readily replaced by hydrogen in good yield on treatment with tributyltin hydride (Bu_3SnH) in the presence of radical initiators.[2,3)] As Bu_3SnH can replace the nitro group by hydrogen without affecting other reducible groups such as carbonyl, alkoxycarbonyl, formyl, cyano, sulfinyl, or sulfonyl groups, this reaction has been widely used in organic synthesis.[4)] Mechanism of the reductive cleavage of the carbon–nitrogen bond with tin radicals has been of interest for recent years because of high chemoselectivity of the reaction. An electron-transfer mechanism is postulated from the analogy to $S_{RN}1$ reaction of nitro compounds.[2,3)] Namely, Tanner and co-workers have proposed that the reaction proceeds via mechanism A (see below) without concrete evidences, where anion radicals of nitro compounds are assumed as intermediates of the reaction.[5)] We have proposed two possible mechanism, mechanism A and B as shown in Scheme 1.[2)] The difference between mechanism A and B is that alkyl radicals are formed from anion radicals of nitro compounds in mechanism A, whereas alkyl radicals are formed from (tributylstannyloxy)nitroxyl radicals in mechanism B.

Mechanism A

$$\begin{aligned} &R\text{-}NO_2 + Bu_3Sn\cdot \longrightarrow R\text{-}NO_2^{\cdot-} + Bu_3Sn^+ \\ &R\text{-}NO_2^{\cdot-} \longrightarrow R\cdot + NO_2^- \\ &R\cdot + Bu_3SnH \longrightarrow R\text{-}H + Bu_3Sn\cdot \end{aligned}$$

Mechanism B



$$\begin{aligned} &R\text{-}NO_2 + Bu_3Sn\cdot \longrightarrow R\text{-}N\overset{O\cdot}{\underset{O}{\lessdot}}SnBu_3 \\ &R\text{-}N\overset{O\cdot}{\underset{O}{\lessdot}}SnBu_3 \longrightarrow R\cdot + Bu_3SnONO \\ &R\cdot + Bu_3SnH \longrightarrow R\text{-}H + Bu_3Sn\cdot \end{aligned}$$

Scheme 1.

The mechanism A is proposed based on following two facts.[3)] The reaction is catalyzed by radical initiators such as azobisisobutyronitrile (AIBN) and inhibited by the presence of a catalytic amount of m-dinitrobenzene (m-DNB). However, these evidences cannot exclude the mechanism B, for all radical reactions induced by tin radicals are catalyzed by AIBN and inhibited by m-DNB. For example, the reduction of alkyl bromides with tributyltin hydride, the typical radical reaction induced by tin radicals is inhibited by the presence of m-DNB. This reaction proceeds via S_H process and it is not certain whether electron-transfer mechanism is operated or not in the reduction of alkyl bromides with tributyltin radicals. Thus, there have been no concrete evidences for the reaction mechanism of denitration with tributyltin hydride.

Recently, Giese and co-workers also have shown that this reaction undergoes via mechanism B through their ESR and kinetic studies.[6)] Independently, we have reached the same conclusion and found that the (tributylstannyloxy)nitroxyl radicals undergo the different reaction from that of the anion radicals of nitro compounds. In this paper, we report that this reaction proceeds via nitroxyl radical intermediates and that kinetic studies support the carbon–nitrogen bond breaking from nitroxyl radical intermediates takes place in the transition state for the reaction.

Results and Discussion

The replacement of tertiary nitro groups by hydrogen with CH_3SNa[7)] or 1-benzyl-1,4-dihydronicotinamide (BNAH)[8)] involves anion radical intermediates. This mechanism has been well-established (Scheme 2). Collapse of anion radical of nitro compounds into a alkyl radical and nitrite ion is fundamental process of $S_{RN}1$ reaction of nitro compounds.[9)]

$$\begin{aligned} &R\text{-}NO_2 + BNAH \longrightarrow R\text{-}NO_2^{\cdot-} + BNAH^{\cdot+} \\ &R\text{-}NO_2^{\cdot-} \longrightarrow R\cdot + NO_2^- \\ &R\cdot + BNAH \longrightarrow R\text{-}H + BNA\cdot \\ &BNA\cdot + R\text{-}NO_2 \longrightarrow R\text{-}NO_2^{\cdot-} + BNA^+ \end{aligned}$$

Scheme 2.

On the other hand, the reaction of α-nitro sulfone **1** with BNAH gives 2-nitropropane, where the carbon–sulfur bond was cleaved in preference to the carbon–nitrogen bond (Eq. 1).[10)]

$$\underset{\mathbf{1}}{\mathrm{Me_2C(NO_2)SO_2Ph}} + \mathrm{BNAH} \longrightarrow \mathrm{Me_2CHNO_2} \qquad (1)$$

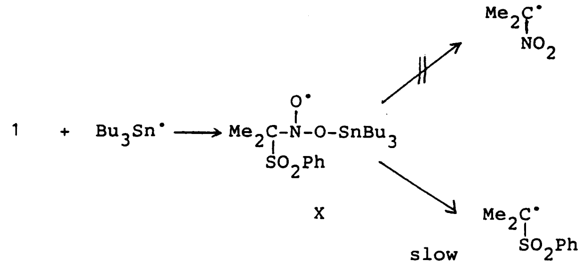
Thus, the anion radicals of α-nitro sulfones collapsed to the α-nitroalkyl radicals and sulfinate ions (Eq. 2).

$$\mathbf{1}^{\cdot-} \longrightarrow \mathrm{Me_2\dot{C}NO_2} + \mathrm{PhSO_2^-} \qquad (2)$$

However, α-nitro sulfones do not react with tributyltin hydride under the conditions that the nitro groups of other nitro compounds are replaced by hydrogen. Namely, heating a mixture of **1**, Bu_3SnH (2 equiv), and AIBN (0.3 equiv) in toluene at 110 °C for 3 h resulted in clean recovery of **1** (Eq. 3).[11]

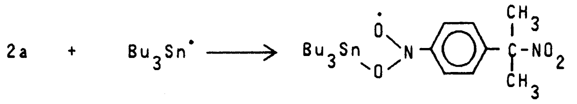
$$\mathbf{1} + \mathrm{Bu_3SnH} \longrightarrow \text{No reaction} \qquad (3)$$

In general, Bu_3SnH is much more reactive to nitro compounds for denitration than BNAH.[4] The low reactivity of **1** toward tin radicals suggest that the anion radicals are not intermediates for the reaction of nitro compounds with tin radicals. If the nitroxyl radicals **X** are intermediates, the above results are explained. The cleavage of carbon-sulfur bond is impossible from **X**, being easy from the corresponding anion radicals. And also the cleavage of carbon-sulfur bond is inhibited due to destabilization of radicals by the adjacent sulfonyl groups (Eq. 4).[12]



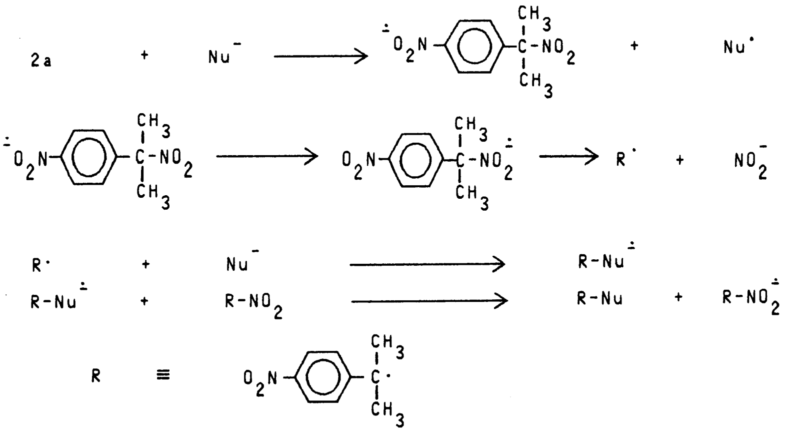
(4)

The reaction of α,*p*-dinitrocumene **2a** is also a good diagnosis for an electron-transfer process. This compounds react with various nucleophiles via electron-transfer processes and it is generally more reactive than other nitro compounds for $S_{RN}1$ reaction.[9] For example, **2a** react with various nucleophiles quite rapidly to give the substitution products in good yield, but α-nitrocumene **2b** does not undergo the $S_{RN}1$ reaction with most nucleophiles. *p*-Nitro group is essential for a smooth $S_{RN}1$ reaction.[9] However, **2a** was inert to Bu_3SnH for denitration, and the nitro group of **2b** is readily replaced by hydrogen on treatment with Bu_3SnH. Thus, these results show that the reaction of nitro compounds with Bu_3SnH proceeds via the completely different pathway from that of $S_{RN}1$ reaction. It is well-established that the $S_{RN}1$ reaction of nitro compounds proceeds via an electron-transfer process as shown in Scheme 3. Intramolecular electron transfer takes place in $S_{RN}1$ reaction.[13] The reaction of **2a** with tin radicals does not give **2a**$^{\cdot-}$, for if anion radical is formed alkyl radical should be formed in the similar pathway as in Scheme 3. Tin radicals may attack the aromatic nitro group to give the nitroxyl radical, which is stable and does not collapse to alkyl radical. In fact, ESR measurements of the reaction mixture of **2a**, Bu_3SnH, and AIBN gave the spectra of the nitroxyl radical as shown in Fig. 1. It was reported that the similar ESR spectra was obtained by photolysis of hexamethyldistannane in the presence of aromatic nitro compounds (Eq. 5).[14] As the nitroxyl radicals derived from aromatic nitro compounds are more stable than those derived from aliphatic ones, denitration does not proceeds from this intermediate. If observed spectra is from an anion radical, the α-nitro group should be eliminated very quickly. Consequently, aromatic nitro compounds act as excellent inhibitors for radical reduction with tin radicals. Although inhibition by *m*-DNB has been used as the diagnosis of an electron-transfer process from tin radicals in several cases,[3] it cannot be used as the diagnosis of an electron-transfer process as discussed here.



$$\mathbf{2a} + \mathrm{Bu_3Sn^{\bullet}} \longrightarrow \mathrm{Bu_3Sn{-}O{-}\dot{N}(O^{\bullet})\text{-}C_6H_4\text{-}C(CH_3)_2NO_2} \qquad (5)$$

ESR measurements of the reaction mixture of various nitro compounds **3**—**7** and Bu_3SnH in benzene were carried out under the same reaction conditions as in denitration of nitro compounds in preparative works. When nitro compounds were mixed with



Scheme 3.

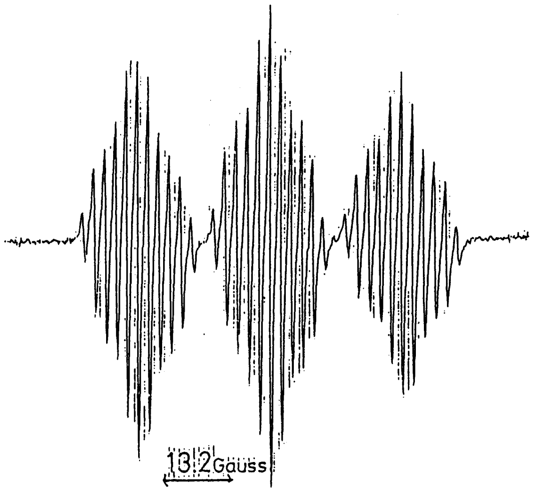


Fig. 1. ESR spectra of a solution of **2a**, Bu_3SnH, and AIBN in benzene at 65 °C.

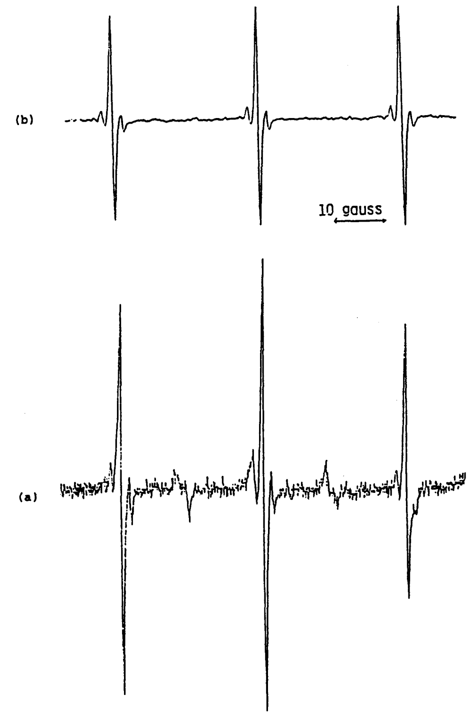


Fig. 2. ESR spectra (a): Solution of **7** and Bu_3SnH in benzene under irradiation with high pressure mercury lamp. (b): Solution of **3**, Bu_3SnH, and AIBN in benzene at 65 °C.

Bu_3SnH and AIBN in benzene and they were irradiated with UV light or heated at 65 °C, strong triplet or sextet [$a(N)=27—28$ G, $a(H)=4—5$ G ($1G=10^{-4}T$)] was detected. Typical spectra are shown in Fig. 2 and the ESR parameters are summarized in Table 1.

Me_3CNO_2 **3** Me_2CHNO_2 **4** $PhCH(Me)NO_2$ **5**

$Ph(C{=}O)CH(Me)NO_2$ **6** $Ph(C{=}O)CMe_2NO_2$ **7**

Table 1. ESR Parameters in the Reaction of Nitro Compounds with Tin Radicals

Nitro compd	Initiator	g Factor	hfs/G	
			a_N	a_H
3	AIBN	2.0050	27.9	—
4	AIBN	2.0049	27.8	5.83
5	AIBN	2.0049	27.8	4.44
6	AIBN	2.0050	27.1	5.56
7	UV	2.0049	27.5	—

The ESR spectra also can be interpreted in terms of the formation of (tributylstannyloxy)nitroxyl radical as well as nitro anion radicals. Recently, Giese and his co-workers reported the similar ESR spectra by the reaction of several nitro compounds with Bu_3SnH.[6] They concluded that they were (tributylstannyloxy)-nitroxyl radicals. A weak coupling of tin isotope (^{119}Sn and ^{117}Sn) was detected in ESR spectra as shown in Fig. 2, where a triplet was surrounded by a weak doublet. This suggests that the tin radical adds to the nitro group to form tin-oxygen covalent bond. The ESR parameters obtained here are very close to those of anion radicals of nitro compounds. Considering these facts and low reactivity of **1** and **2a** for denitration, the observed spectra should be (tributylstannyloxy)-nitroxyl radicals. The detected radicals are real intermediates for denitration of nitro compounds, for they are not detected by ESR in the absence of AIBN. Further, Giese has reported that observed radicals decay by first order process.[6] In the photolytic experiment, the ESR signal disappears immediately, if the light is switched off, but comes back on further irradiation. Thus, the observed radicals are short-lived intermediates which decompose to give alkyl radicals.

Electrochemical measurements were carried out for various kinds of nitro compounds. It is well-known that single electron reduction of aliphatic nitro compounds forms corresponding anion radicals of nitro compounds, which decompose readily to give alkyl radicals and nitrite ion.[15] As expected, cyclic voltammetry of α-nitroethylbenzene shows irreversible wave as shown in Fig. 3. The half wave reduction potentials ($E_{1/2}$) of various nitro compounds were measured by polarography. The results are summarized in Tables 2—4. Relative low reduction potentials were observed:

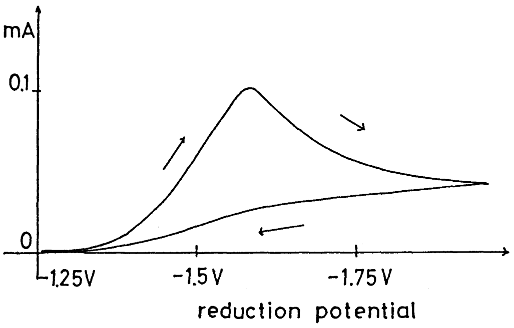


Fig. 3. Cyclic voltammetry of α-nitroethylbenzene, 0.10 M Bu_4NClO_4 in acetonitrile, at Hg.

Table 2. Relative Rate in the Reduction of Compounds **2** and $E_{1/2}$

Compound	X	σ	k_{rel}	$E_{1/2}/\text{V}^{\text{a)}}$
2c	*p*-MeO	−0.27	0.68±0.01	−1.70
2d	*m*-Me	−0.07	0.93±0.03	
2b	H	0	1	−1.70
2e	*p*-F	+0.06	1.15±0.01	
2f	*m*-MeO	+0.12	1.11±0.04	
2g	*p*-Cl	+0.23	1.52±0.01	−1.60
2h	*m*-Cl	+0.37	1.49±0.05	
2i	*m*-CF_3	+0.43	1.66±0.03	
2j	*p*-CO_2Me	+0.45	1.71±0.07	—-1.60
2k	*p*-COMe	+0.50	1.57±0.07	
21	*p*-CF_3	+0.54	1.74±0.01	
2m	*p*-CN	+0.66	1.62±0.04	−1.61
2a	*p*-NO_2	+0.78	0	

a) vs. Ag/Ag^+.

Table 3. Relative Rate in the Reaction of Compounds **9** and $E_{1/2}$

Compound	X	k_{rel}	$E_{1/2}/\text{V}^{\text{a)}}$
9a	*p*-MeO	0.87±0.04	−1.55
9b	*p*-Me	0.92±0.01	−1.56
9c	*m*-Me	0.91±0.01	−1.62
9d	H	1	−1.68
9e	*m*-MeO	1.19±0.01	−1.57
9f	*p*-Cl	1.19±0.01	−1.66
9g	*m*-Cl	1.22±0.05	−1.51
9h	*p*-CO_2Me	1.59±0.01	−1.47
9i	*p*-CN	1.44±0.01	−1.49

a) vs. Ag/Ag^+.

Table 4. Relative Rate in the Reduction of Compounds **11** and $E_{1/2}$

Compound	X	k_{rel}	$E_{1/2}/\text{V}^{\text{a)}}$
11a	*p*-MeO	0.76±0.01	−1.36
11b	*p*-Me	0.96±0.01	−1.36
11c	H	1	−1.37
11d	*p*-Cl	1.24±0.01	
11e	*p*-CO_2Me	1.36±0.14	−1.39
11f	*p*-CN	1.17±0.01	−1.32

a) vs. Ag/Ag^+.

compared to trifluoroacetophenone ($E_{1/2}$=−2.00 V) and acetophenone ($E_{1/2}$=−2.61 V):[16] α-nitropropiophenones, $E_{1/2}$=ca.−1.37 V; α-nitrocumenes $E_{1/2}$=ca. −1.58 V. These results are reasonable because the nitro group is strong electron acceptor. The positive ρ value was observed in Hammett plots of $E_{1/2}$. However, the value is very small (ρ=ca. 0.1—0.2), compared to that of the corresponding bromides (ρ=ca. 0.40).[17] This means that substituents have few effects on easiness of the electron transfer to the nitro groups.

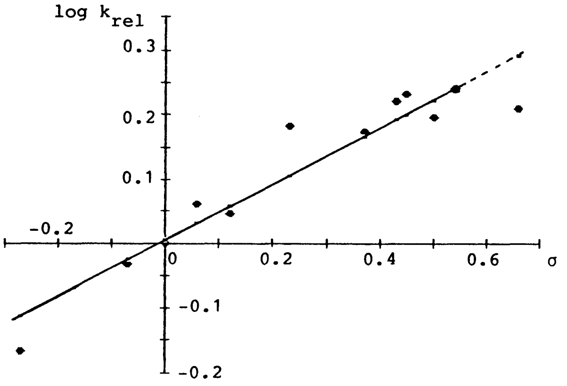
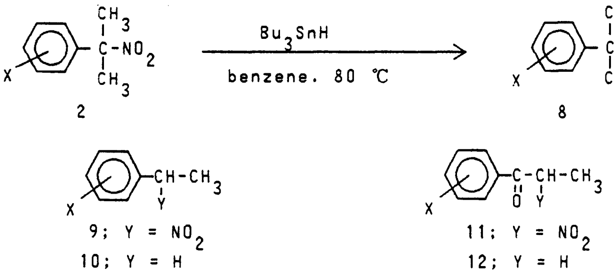


Fig. 4. Hammett plots of log k_{rel} vs. substituent constants σ for the reaction of **2** with Bu_3SnH.

Relationship between the relative reactivity of nitro compounds with Bu_3SnH and substituent constants σ was examined. The relative reactivities of substituted α-nitrocumenes **2** with Bu_3SnH in benzene at 80 °C were obtained by competitive reactions of **2** vs. **2b** on the basis of measurement of appearance of products cumenes **8** and **8b**. The results are summarized in Table 2, and their Hammett plots are shown in Fig. 4. Hammett plots of log k_{rel} vs. substituent constants σ exhibits quite good correlation except for *p*-cyano-α-nitrocumene **2m**. ρ Value of **2** can be calculated by the least squares method (ρ=0.54, *r*=0.98). Similarly, the relative reactivities of substituted α-nitroethylbenzenes **9** and α-nitropropiophenones **11** with Bu_3SnH were obtained in the same way as above mentioned. The results are summarized in Tables 3 and 4. Good Hammett correlations between log k_{rel} and σ are obtained except *p*-cyano derivatives, which are less reactive than expected from the correlations. Obtained ρ values are as following; ρ=0.25 (*r*=0.97) for **9**, ρ=0.33 (*r*=0.96) for **11**. A positive Hammett correlations are obtained both in any denitration reaction with Bu_3SnH and reduction potentials of nitro compounds. However, ρ values for the reaction with tin radicals are larger than those for electrochemical reduction. This result suggests that the formation of the anion radicals is not so much affected by variation of substituents. Thus, the larger ρ values for denitration with tin radical also support that this denitration reaction with tin radical proceeds not via the electron-transfer pathway but via the nitroxyl radical intermediates.



As related reactions, reductive cleavage of alkyl halides, sulfides, selenides, and xanthates with Bu_3SnH is well-known. The formation of alkyl radicals by tin radicals may be considered as shown in Scheme 4, where abstraction of X by tin radicals takes place via S_H process.[18,19]

$$\text{R-X} + \text{Bu}_3\text{Sn}^\cdot \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R-X-SnBu}_3 \xrightarrow{k_2} \text{R}^\cdot + \text{Bu}_3\text{SnX}$$

X=Cl, Br, I

Scheme 4.

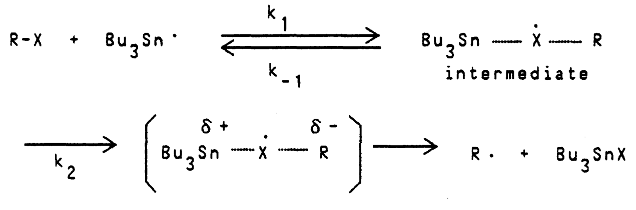
Hammett correlation for halogen abstraction with tin radical[19] and germyl radical[20] has been studied by Tanner and Sakurai, where positive ρ values are also obtained. They have concluded that these positive ρ values are attributed to following two reaction mechanism; an electron-transfer mechanism (Scheme 5) or polar effects on the halogen abstraction step (Scheme 6). In particular, carbon-halogen bond breaking step is considered as the rate-determining step of the reaction in the latter case.

$$\text{R-X} + \text{Bu}_3\text{Sn}^\cdot \xrightleftharpoons{\text{single electron transfer}} \underset{\text{anion radical}}{\text{R-X}^{\cdot -}} + \text{Bu}_3\text{Sn}^+$$

$$\longrightarrow \text{R}^\cdot + \text{X}^- + \text{Bu}_3\text{Sn}^+$$

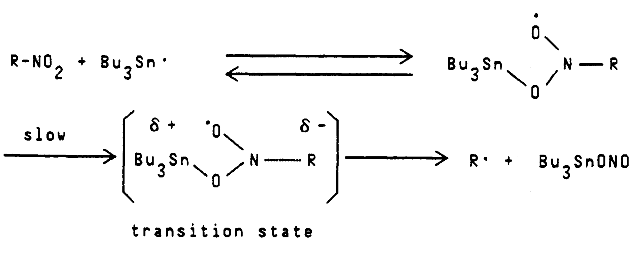
X=Cl, Br, I

Scheme 5.



Scheme 6.

The denitration with tin radicals are quite similar to these results. As the electron-transfer mechanism is excluded as discussed above, the positive ρ values are attributed to the polar effects on the carbon-nitrogen bond scission. Although carbon-halogen bonds are so weak as to give alkyl radicals very quickly, carbon-nitrogen bond cleavage is so difficult that nitroxyl radical intermediates are readily observed by ESR spectroscopy. Thus, the carbon-nitrogen bond scission may be the rate-determining step of the denitration reaction. Considerable reaction process is depicted in Scheme 7.



Scheme 7.

Experimental

Measurement. All melting points were uncorrected. ^{1}H NMR spectra were measured at 100 MHz with JEOL JNM-PS-100 spectrometer. IR spectra were recorded on Hitachi 215 spectrometer. GLC analyses were carried out with Shimadzu GC-8A gas chromatograph. Elemental analyses were performed by Kyoto University microanalyses center.

ESR Studies. ESR spectra were recorded using JEOL PX-3E spectrometer after mixing R-NO$_2$ (0.25 mmol), Bu$_3$SnH (0.25 mmol) and AIBN (0.05 mmol) in 0.5 ml of benzene under argon atmosphere, degassed and heating at 65 °C. ESR spectra were also recorded under irradiation of a solution of R-NO$_2$ (0.25 mmol) and Bu$_3$SnH (0.25 mmol) in 0.5 ml of benzene with high-pressure mercury lamp.

Polarography. PAR model 174 polarograph analyzer was used. The capillary constant for the dropping mercury electrode was 1.41 mg at −0.5 V vs. Ag/AgClO$_4$ in acetonitrile containing 2×10^{-2} M (1 M=1 mol dm^{-3}) Bu$_4$NClO$_4$. The anode was a 10 cm length of 1 mm diameter silver wire. All polarograms were determined at 25 °C with thoroughly deaerated solutions which was between 4×10^{-4} and 5×10^{-4} M in substrate and 2×10^{-2} M in Bu$_4$NClO$_4$.

Preparation of Nitro Compounds. α-Nitro sulfone **1** was prepared by the reaction of corresponding iodide with sodium benzenesulfinate.[21] α-Nitrocumene derivatives **2** substituted by electron-withdrawing groups were prepared by the reaction of the corresponding substituted nitrobenzenes with the lithium salt of 2-nitropropane in dimethyl sulfoxide (DMSO).[22] Other substituted nitrocumenes were prepared by the reaction of corresponding aryl lead(IV) compounds or diaryliodonium salts with the lithium salt of 2-nitropropane.[23] Physical properties of new compounds are summarized.

2c: ^{1}H NMR (CDCl$_3$) δ=1.91 (s, 6H), 3.72 (s, 3H), 6.83 (d, 2 H), 7.32 (d, 2H). IR (neat): 1250, 1350, 1530 cm^{-1}. Found: C, 61.38; H, 6.65; N, 7.13%. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18%.

2d: ^{1}H NMR (CDCl$_3$) δ=1.92 (s, 6H), 2.36 (s, 3H), 7.1—7.3 (m, 4H). IR (neat): 1350 and 1540 cm^{-1}. Found: C, 67.14; H, 7.39; N, 7.93%. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82%.

2e: ^{1}H NMR (CDCl$_3$) δ=1.98 (s, 6H), 7.1—7.6 (m, 4H). IR (neat): 1230, 1350, 1540 cm^{-1}. Found: C, 59.17; H, 5.45; N, 7.78%. Calcd for $C_9H_{10}NO_2F$: C, 59.01; H, 5.50; N, 7.65%.

2f: ^{1}H NMR (CDCl$_3$) δ=1.96 (s, 6H), 3.80 (s, 3H), 7.00 (m, 3 H), 7.36 (s, 1 H). IR (neat) 1220, 1350, 1530 cm^{-1}. Found: C, 61.47; H, 6.89; N, 7.13%. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.18%.

2g: ^{1}H NMR (CDCl$_3$) δ=1.98 (s, 6H), 7.40 (s, 4H). IR (neat): 1100, 1350, 1540 cm^{-1}. Found: C, 54.16; H, 5.08; N, 7.16%. Calcd for $C_9H_{10}NO_2Cl$: C, 54.15; H, 5.05; N, 7.02%.

2h: ^{1}H NMR (CDCl$_3$) δ=1.92 (s, 6H), 7.3—7.4 (m, 4 H). IR (neat): 1080, 1350, 1540 cm^{-1}. Found: C, 54.29; H, 5.08; N, 7.08%. Calcd for $C_9H_{10}NO_2Cl$: C, 54.15; H, 5.05; N, 7.02%.

2i: ^{1}H NMR (CDCl$_3$) δ=2.00 (s, 6H), 7.64—7.72 (m, 4H). IR (neat): 1120, 1350, 1540 cm^{-1}. Found: C, 51.38; H, 4.28; N, 6.17%. Calcd for $C_{10}H_{10}NO_2F_3$: C, 51.51; H, 4.32; N, 6.01%.

2l: Mp 41.5—42 °C. ^{1}H NMR (CDCl$_3$) δ=2.04 (s, 6 H), 7.56—7.80 (m, 4 H). IR (Nujol): 1140, 1350, 1540 cm^{-1}. α-Nitroethylbenzenes **9** except **9i** were prepared by the reaction of the corresponding bromides with IRA-900 (NO$_2^-$)

in 60—70% yield.[24] Compound **9i** was prepared by the reaction of *p*-nitrobenzonitrile with lithium salt of nitroethane in hexamethylphosphoric triamide (HMPA). Physical properties of new compounds are shown here.

9a: ^{1}H NMR ($CDCl_3$) δ=1.83 (d, 3 H, J=7 Hz), 3.80 (s, 3 H), 5.56 (q, 1 H, J=7 Hz), 6.80—7.00 (m, 2H), 7.28—7.68 (m, 2H). IR (neat): 1250, 1350, 1540 cm^{-1}. Found: C, 59.62; H, 6.08; N, 7.89%. Calcd for $C_9H_{11}NO_2$: C, 59.66; H, 6.12; N, 7.73%.

9b: ^{1}H NMR ($CDCl_3$) δ=1.84 (d, 3H, J=7 Hz), 2.34 (s, 3H), 5.55 (q, 1H, J=7 Hz), 7.30 (m, 4 H). IR (neat): 1350 and 1540 cm^{-1}. Found: C, 65.58; H, 6.68; N, 8.25%. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48%.

9c: ^{1}H NMR ($CDCl_3$) δ=1.80 (d, 3H, J=7 Hz), 2.21 (s, 3H), 5.51 (q, 1H, J=7 Hz), 7.16—7.38 (m, 4H). IR (neat): 1350 and 1540 cm^{-1}. Found: C, 65.26; H, 6.64; N, 8.67%. Calcd for $C_9H_{11}NO_2$: C, 65.43; H, 6.71; N, 8.48%.

9e: ^{1}H NMR ($CDCl_3$) δ=1.84 (d, 3H, J=7 Hz), 3.78 (s, 3H), 5.53 (q, 1H, J=7 Hz), 6.84—7.40 (m, 4H). IR (neat): 1250, 1350, 1540 cm^{-1}. Found: C, 59.79; H, 6.19; N, 7.90%. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73%.

9f: ^{1}H NMR ($CDCl_3$) δ=1.84 (d, 3H, J=7 Hz), 5.56 (q, 1H, J=7 Hz), 7.40 (m, 4 H). IR (neat): 1090, 1350, 1540 cm^{-1}. Found: C, 51.97; H, 4.54; N, 7.51%. Calcd for $C_8H_8NO_2Cl$: C, 51.77; H, 4.34; N, 7.55%.

9g: ^{1}H NMR ($CDCl_3$) δ=1.87 (d, 3 H, J=7 Hz), 5.56 (q, 1H, J=7 Hz), 7.36—7.48 (m, 4H). IR (neat): 1080, 1350, 1540 cm^{-1}. Found: C, 51.85; H, 4.38; N, 7.67%. Calcd for $C_8H_8NO_2Cl$: C, 51.77; H, 4.34; N, 7.55%.

9h: ^{1}H NMR ($CDCl_3$) δ=1.94 (d, 3H, J=8 Hz), 3.96 (s, 3H), 5.69 (q, 1 H, J=7 Hz), 7.58 (d, 2H, J=8 Hz), 8.12 (d, 2H, J=8 Hz). IR (neat): 1350, 1540, 1705 cm^{-1}. Found: C, 57.28; H, 5.53; N, 6.93%. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70%.

9i: ^{1}H NMR ($CDCl_3$) δ=1.93 (d, 3H, J=8 Hz), 5.69 (q, 1 H, J=8 Hz), 7.70 (d,d, 4H). IR (neat): 1350, 1540, 2200 cm^{-1}. Found: C, 61.16; H, 4.68; N, 16.00%. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90%.

Preparation of α-nitro ketones **11** was carried out by oxidation of the corresponding nitro alcohols, which were prepared by the reaction of aldehydes with nitroethane.[25] Physical properties of new compounds are shown here.

11e: mp 86—86.5 °C. ^{1}H NMR ($CDCl_3$) δ=1.81 (d, 3H, J=7 Hz), 3.92 (s, 3H), 6.13 (q, 1H, J=7 Hz), 8.08 (q, 4H). IR (Nujol): 1350, 1560, 1700, 1720 cm^{-1}. Found: C, 55.56; H, 4.72; N, 5.90%. Calcd for $C_{11}H_{11}NO_5$: C, 55.70; H, 4.67; N, 5.90%.

11f: mp 119—120 °C. ^{1}H NMR ($CDCl_3$) δ=1.86 (d, 3H, J=7 Hz), 6.16 (q, 1H, J=7 Hz), 7.86 (d, 2H, J=8 Hz), 8.08 (d, 2H, J=8 Hz). IR (Nujor): 1350, 1540, 1700, 2250 cm^{-1}. Found: C, 58.78; H, 3.92; N, 13.86%. Calcd for $C_{10}H_8N_2O_3$: C, 58.83; H, 3.95; N, 13.72%.

Denitration of Compounds 2, 9, and 11. Denitration of these compounds with Bu_3SnH was described in a previous paper.[26] Denitrated products were obtained in 80—90% yield in most cases.

Competitive Reactions of 2. The substituted α-nitrocumene (0.25 mmol), α-nitrocumene (0.25 mmol), AIBN (0.01 mmol), and Bu_3SnH (0.02 mmol) were dissolved in 0.2 ml of benzene. The solution was degassed and sealed in a Pyrex tube. The tube was heated at 80 °C for 30 min, then opened and the products **8** were analyzed by GLC. Other compounds **9** and **11** were treated in the same way. The results are summarized in Tables 2, 3, and 4, respectively.

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