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Viologen-mediated Reductive Transformations of *gem*-Bromonitro Compounds and α-Nitro Ketones by Sodium Dithionite

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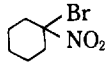
Received February 19, 1993

Reductive transformations of *gem*-bromonitro compounds and α-nitro ketones were carried out conveniently with sodium dithionite by using dioctyl viologen as an electron-transfer catalyst in dichloromethane-water two-phase system: the bromine atom in *gem*-bromonitro compounds and the nitro group in α-nitro ketones are replaced by hydrogen.

Introduction

Viologens (1,1'-dialkyl-4,4'-bipyridiniums, V^{2+}) undergo two consecutive one-electron reduction processes to the respective cationic radical ($V^{+\cdot}$) and quinoid (V) forms. The reduced forms are readily reoxidized to V^{2+}. They have at-

Table 1. Reductive Debromination of *gem*-Bromonitro Compounds to the Corresponding Nitro Compounds by Sodium Dithionite Using Dioctyl Viologen as an ETC in Dichloromethane-water Two-phase System at 35℃ [a]

Entry	Substrate[b]	Reaction time, h	Yield (%)[c]
1a		2	>98 (63)[d]
1b		2	>98
1c	$C_6H_5CH_2CH_2CBr(NO_2)CH_3$	1	90 (62)[d]
1d	$CH_3(CH_2)_6CBr(NO_2)CH_3$	1	80
1e	$C_6H_5CBr(NO_2)CH_3$	2	76
1f		1	80
1g		1	75

[a] The molar ratio of the viologen to the substrate was 1 : 10. [b] In the absence of the viologen the debrominated product was not detected. [c] From the ^{1}H-NMR analysis. [d] Numbers in parentheses are the isolated yields.

tracted much attention as herbicides[1] and electron mediators in solar energy conversion and storage.[2] Recently, the viologen-mediated reductions of organic compounds such as nitroalkenes,[3] 1,2-dibromides,[4] activated carbonyl compounds,[5] azobenzene,[6] acrylonitrile,[7] α-halogeno ketones,[8] and α-nitro sulfones[9] have been reported. We have been interested in the viologen-mediated reductions of organic compounds in the hope of providing a convenient and practical route for reductive transformations of synthetic intermediates. Previously, we demonstrated that reductive transformations of various α-halogeno ketones[8] and α-nitro sulfones[9] to the corresponding ketones and nitro compounds are achieved almost quantitatively with sodium dithionite by using dioctyl viologen (OcV^{2+}) as an electron-transfer catalyst (ETC) in organic-water two phase systems.

Reductive debromination of *gem*-bromonitro compounds is an useful pathway in the synthesis of nitro compounds.[10-13] Also, replacement of the nitro group by hydrogen has been a subject of many investigations in connection with the versatile utilities of nitro compounds in organic synthesis.[14-18] In this paper, we show that reductive debromination of *gem*-bromonitro compounds and denitration of α-nitro ketones can be conveniently achieved in good yields with sodium dithionite in the presence of OcV^{2+} as an ETC in dichloromethane-water two phase system.

Results and Discussion

Reductive Debromination of *gem*-Bromonitro Compounds. Several methods have been reported for preparation of *gem*-bromonitro compounds from oximes *via* a halogenation-oxidation sequence.[10-12,19] Compounds **1a-g** were made by the NBS procedure[10] (see Experimental section for details). Reductive debromination of *gem*-bromonitro compounds with sodium dithionite proceeded smoothly in good yields in the presence of OcV^{2+} in dichloromethane-water two phase system under nitrogen atmosphere. The results are summarized in Table 1. No appreciable reaction occurs when OcV^{2+} is excluded from the system. As in the desulfonylation reaction of α-nitro sulfones,[9] the nitro groups of the reaction products remain intact: it was reported that nitroalkenes undergo the viologen-mediated reduction to yield the corresponding oximes or carbonyl compounds.[3]

Table 2. Reductive Denitration of α-Nitro Ketones to the Corresponding Ketones by Sodium Dithionite Using Dioctyl Viologen as an ETC in Dichloromethane-water Two-phase System at 35 ℃ [a]

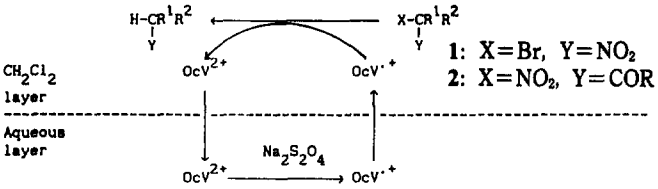
Entry	Substrate[b]	Reaction time, h	Yield (%)[c,d]
2a	$C_6H_5COCH_2NO_2$	9	0
2b	$C_6H_5COCH(NO_2)CH_3$	9	83
2c	$C_6H_5COC(CH_3)(NO_2)CH_2CH_2COCH_3$	9	>98 (80)[d]
2d	$C_6H_5COCH(NO_2)CH_2CH_2COCH_3$	9	>98 (73)[d]
2e	$C_6H_5COC(NO_2)(CH_2CH_2COCH_3)_2$	6	>98 (62)[d]

[a] The molar ratio of the viologen to the substrate was 1 : 10. [b] In the absence of the viologen the denitrated product was not detected. [c] From the ^{1}H-NMR analysis. [d] Numbers in parentheses are the isolated yields.

Several methods have been reported for the replacement of the bromine atom of *gem*-bromonitro compounds by hydrogen: sodium borohydride,[10,11] KOH in ethanol,[12] or 1-benzyl-1,4-dihydronicotinamide, BNAH,[13] has been used for the transformation. The reaction with KOH in alcohol or sodium borohydride suffers the incompatibility with other functional groups. The use of BNAH requires long reaction time[13] and excess of the reagent which is not readily available.[20] Therefore, we consider that the viologen-mediated reaction demonstrated here adds an alternative and convenient route to reductive debromination of α-bromonitro compounds, and will broaden versatility of α-bromonitro compounds as intermediates in the synthesis of nitro compounds.

Reductive Denitration of α-Nitro Ketones. Five α-nitro ketones **2a-e** were prepared (see Experimental section). The reaction of these compounds with sodium dithionite in the presence of OcV^{2+} in dichloromethane-water two-phase system under nitrogen atmosphere replaced the nitro group of α-nitro ketones **2b-e** by hydrogen almost quantitatively (Table 2). In the absence of the viologen, the reaction products were not detected. In the agreement with the dehalogenation reaction of α-halogeno ketones,[8] no reduction of carbonyl groups was observed. Primary α-nitro kethone **2a** was unreactive under the same reaction condition. The unreactiveness of primary α-nitro ketones was also observed in other methods of denitration:[14-18] the primary radical would be difficult to be formed from the radical anion by ejection of the nitrite ion, due to its relative instability compared with secondary and tertiary radicals (*vide infra*).

A number of methods for replacing a nitro group by hy-

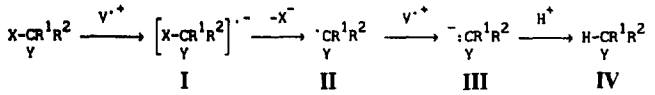


Scheme 1. Cyclic pathway for the dioctyl viologen-mediated reductive transformations of *gem*-bromonitro compounds **1** and α-nitro ketones **2** by sodium dithionite.

drogen have been described. These include the use of BNAH[14] or sodium salt of methyl mercaptan,[15] treatment with KOH in ethylene glycol,[16] and the use of tributyltin hydride[17] or sodium hydrogentelluride.[18] However, these methods have certain drawback such as the necessity of a large excess of reagents,[14,18] harsh reaction conditions,[16] chromatographic separation of the oxidized organometallic reagent,[17] or the formation of side products.[15] Moreover, some of theses methods are thought to be unsuitable for reduction of α-nitro ketones: the use of KOH causes the cleavage of the carbon-carbon bond;[22] treatment with sodium borohydride generally reduces keto groups to yield corresponding β-nitro alcohols;[23] reduction of **2b** by sodium borohydride gave benzyl alcohol;[14] reduction of **2b** by MeSNa gave the denitration product in poor yield and most of the starting **2b** was recovered.[14] Considering these, the present procedure apprears to provide a mild and convenient alternative route for the denitration of secondary and tertiary α-nitro ketones, and extends the utilities of nitro compounds.

Reduction Mechanism. In the debromination reaction of *gem*-bromonitro compounds and the denitration reaction of α-nitro ketones, we used the molar ratio of OcV^{2+} to the substrate of 1 : 10. Thus, it is clear that the viologen mediates the reaction and the active reductant produced from the dithionite reduction of the viologen is recycling. Little dependence of the reaction yield on the alkyl chain of viologen and organic phase in viologen-mediated reductions of α-halogeno ketones and α-nitro sulfones suggested that the active reductant could be one-electron reductant $OcV^{+\cdot}$ rather than the two-electron reductant OcV.[8,9] Persistence of the blue color, which arises from one-electron reduction product of the viologen, in organic phase during the reaction supports this. The overall reaction can be illustrated as Scheme 1.

Though the exact mode of the reactions is not clear at this point, the general mechanism shown in Scheme 2 is proposed for the viologen-mediated reductive transformations of *gem*-bromonitro compounds and α-nitro ketones. As proposed for the viologen-mediated reduction of α-halogeno ketones[8] and α-nitro sulfones,[9] and reduction of various organic compounds by BNAH,[13,14] the reaction is initiated by a single electron-transfer from the reduced viologen to the substrates to give the corresponding radical anions I. Better leaving group between X and Y is ejected from the radical anion to form radical II: bromide ion is expelled from **1**, while nitrite anion from **2**. This is reminiscent of the fact that viologen-mediated reduction of α-nitro sulfones gave rise to the replacement of phenylsulfonyl group.[9] The radical II is further reduced by viologen radical cation to produce a carbanion III. Protonation of the carbanion completes the



1: X=Br, Y=NO_2
2: X=NO_2, Y=COR

Scheme 2. Proposed mechanism for the viologen-mediated reduction of *gem*-bromonitro compounds **1** and α-nitro ketones **2**.

reduction.

In conclusion, α-bromonitro compounds are debrominated to give the corresponding nitro compounds and α-nitro ketones are denitrated to afford ketones by sodium dithionite with dioctyl viologen. We consider this method will extend the versatility of the nitro compounds in organic synthesis.

Experimental

NMR spectra were obtained with a Bruker FT NMR Aj 80 spectrometer in $CDCl_3$ (unless specified) using TMS as an internal standard. Dioctyl viologen (OcV^{2+}) was prepared from 4,4′-bipyridine and 1-bromooctane as described previously.[8]

Preparation of *gem*-Bromonitro Compounds 1a-g. 1-Bromo-1-nitrocyclohexane **1a**[10] and 2-bromo-2-nitrocamphane **1b**[24] were reported in literature. Others were made similarly from oximes *via* a halogenation-oxidation sequence.[10] The oximes for the preparation of **1c-g** were available from the corresponding ketones by reaction with hydroxylamine in the usual manner.[25] The yields and their physical data are the following: Benzylacetone oxime, yield 90%, mp. 87-88℃, ^{1}H-NMR δ 1.90 (s, 3H), 2.4-3.0 (m, 4H), 7.0-7.5 (m, 5H), and 8.0 (broad s, 1H); nonanone oxime, yield 70%, mp. 28-29℃, ^{1}H-NMR δ 0.88 (t, 3H, J=6), 1.2-1.8 (m, 10H), 1.87 (s, 3H), 2.19 (t, 2H, J=8), and 9.4 (broad s, 1H); acetophenone oxime, yield 79%, mp. 59-60℃, ^{1}H-NMR δ 2.28 (s, 3H), 7.2-7.8 (m, 5H), and 9.90 (broad s, 1H); α-tetralone oxime, yield 92%, mp. 106-107℃, ^{1}H-NMR δ 1.7-2.1 (m, 2H), 2.6-3.0 (m, 4H), 7.0-7.4 (m, 3H), 7.8-8.0 (m, 1H), and 8.4 (broad s, 1H); 1-indanone oxime, yield 81%, mp. 148-149℃, ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ 2.8-3.2 (m, 4H), 7.1-7.4 (m, 3H), 7.5-7.8 (m, 1H), and 10.3 (broad s, 1H).

gem-Bromonitro Compounds **1c-g** were prepared from the corresponding oximes by the NMS procedure.[10] Nitric acid treatment was necessary to convert *gem*-bromonitroso intermediates[10,19] formed from oximes and NBS to **1c-d**, while compounds **1e-g** did not require such treatment: the oxidation step could be easily detected since the bromonitroso intermediates retain blue-green color. Products were purified by column chromatography [silica gel; hexane-ethyl acetate (9 : 1)]. The yields, physical and analytical data of **1c-g** are the following: 3-Bromo-3-nitro-1-phenylbutane **1c**, yield 28%, mp. 31-32℃, ^{1}H-NMR δ 2.27 (s, 3H), 2.70 (broad s, 4H), and 7.0-7.5 (m, 5H), Anal. Calcd for $C_{10}H_{12}BrNO_2$: C, 46.53; H, 4.69; N, 5.43. Found: C, 46.4; H, 4.7; N, 5.6; 2-bromo-2-niotrononane **1d**, yield 20%, ^{1}H-NMR δ 0.88 (t, 3H, J=6), 1.1-2.0 (m, 10H), 2.23 (s, 3H), and 2.42 (t, 2H, J=7); 1-bromo-1-nitro-1-phenylethane **1e**, yield 25%, ^{1}H-NMR δ 2.64 (s, 3H) and 7.3-7.7 (m, 5H); 1-bromo-1-nitrotetralin **1f**, yield 23%, ^{1}H-NMR δ 1.8-2.4 (m, 2H), 2.5-3.4 (m, 4H), 7.0-7.5 (m, 3H),

and 7.6-7.8 (m, 1H); 1-bromo-1-nitroindan **1g**, yield 20%, ^{1}H-NMR δ 2.7-3.7 (m, 4H), 7.1-7.5 (m, 3H), and 7.6-7.8 (m, 1H).

Preparation of α-Nitro Ketones 2a-e. Compounds **2a-b** were prepared by the oxidation of the corresponding β-nitro alcohols with sodium dichromate.[14,26] **2c** and **2d-e** were prepared by the Michael addition of **2b** and **2a** to methyl vinyl ketone, respectively.

$C_6H_5COC(NO_2)(CH_3)CH_2CH_2COCH_3$ **2c**. A solution of **2b** (7.16 g, 40 mmol), methyl vinyl ketone (8.42 g, 120 mmol) and triethylamine (0.1 g) in tetranhydrofuran (THF) (15 mL) was stirred at 0℃ for 1 h and then at room temperature for 5 h. The reaction mixture was added to ice-water. After acidification (pH=1) the mixture was extracted with diethyl ether, and the extract was dried with sodium sulfate and concentrated. Recrystallization from 95% ethanol afforded compound **2c** in 52% yield, mp. 51℃; ^{1}H-NMR δ 1.91 (s, 3H), 2.14 (s, 3H), 2.4-2.8 (m, 4H) and 7.3-7.8 (m, 5H). Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.6; H, 6.0; N, 5.6.

$C_6H_5COCH(NO_2)CH_2CH_2COCH_3$ 2d and $C_6H_5COC(NO_2)(CH_2CH_2COCH_3)_2$ **2e**. A solution of **2a** (10 g, 60 mmol), methyl vinyl ketone (10.9 g, 150 mmol), and triethylamine (0.1 g) in THF (35 mL) was stirred at 0℃ for 1 h and then at room temperature for 23 h. The reaction mixture was added to ice-water. After acidification (pH=1) the mixture was extracted with diethyl ether, and the extract was dried with sodium sulfate and concentrated. Column chromatography [silica gel; hexane-ethyl acetate (8 : 2)] afforded compound **2d** in 60% yield and **2e** in 31% yield as separate fractions: compound **2d**, mp. 44-46℃, ^{1}H-NMR δ 2.18 (s, 3H), 2.3-2.9 (m, 4H), 6.30 (t, 1H, J=7) and 7.4-7.8 (m, 3H), and 8.0-8.2 (m, 2H). Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 61.2; H, 5.5; N, 5.9; compound **2e**, mp. 52-53℃, ^{1}H-NMR δ 2.12 (s, 6H), 2.2-2.8 (m, 8H), and 7.3-7.9 (m, 5H). Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 62.9; H, 6.3; N, 4.6.

Typical Procedures for Viologen-mediated Reductions. An aqueous solution (5 mL) containing K_2CO_3 (2-3 mmol) and $Na_2S_2O_4$ (4 mmol) was added dropwise to a mixture of substrate (2 mmol) and viologen (0.2 mmol) in CH_2Cl_2 (30 mL)-water (5 mL) under a nitrogen atmosphere. The mixture was sitrred for the reaction time indicated in Table 1 and 2 at 35℃ and then the aqueous layer was extracted with CH_2Cl_2 (2×30 mL). The combined organic layers were dried and concentrated. A control experiment was carried out without viologen. For isolated yields, the reactions were carried out with substrate (6 mmol), viologen (0.6 mmol), K_2CO_3 (9-10 mmol), and $Na_2S_2O_4$ (12-20 mmol) in CH_2Cl_2 (30 mL)-water (20 mL). After work-up, the products were purified by column chromatography. α-Nitroaryl compounds obtained from **1e-g** were hydrolytically unstable and transformed to the ketonic products. ^{1}H-NMR data of the reduced products are the following.

Debrominated Products from **1a-g** Nitrocyclohexane,[10] δ 1.1-2.5 (m, 10H) and 4.37 (m, 1H); 2-nitrocamphane,[13] δ 0.91 (s, 3H), 0.94 (s, 3H), 1.08 (s, 3H), 0.9-2.4 (m, 7H), and 4.68 (t, 1H, J=7); 3-nitro-1-phenylbutane, δ 1.52 (d, 3H, J=7), 1.8-2.8 (m, 4H), 4.54 (sextet, 1H, J=7), and 7.0-7.4 (m, 5H); 2-nitrononane, δ 0.87 (t, 3H, J=6), 1.51 (d, 3H, J=7), 1.5-2.1 (m, 12H), and 4.55 (sextet, 1H, J=7); 1-nitro-1-phenylethane, δ 1.84 (d, 3H, J=7), 5.59 (q, 1H, J=7), and 7.2-7.7 (m, 5H); 1-nitrotetralin, δ 1.6-3.2 (m, 6H), 5.64 (t, 1H, J=5), and 7.0-7.6 (m, 4H); 1-nitroindan, 2.2-3.6 (m, 4H), 5.85 (d of d, 1H, J=7 and 3), and 7.1-7.8 (m, 4H).

Denitrated Products from **2b-e** $C_6H_5COCH_2CH_3$, δ 1.23 (t, 3H, J=7), 3.00 (q, 2H, J=7), 7.3-7.7 (m, 3H), and 7.8-8.1 (m, 2H); $C_6H_5COCH(CH_3)CH_2CH_2COCH_3$, δ 1.20 (d, 3H, J=7), 2.10 (s, 3H), 1.6-2.6 (m, 4H), 3.56 (sextet, 1H, J=7), 7.3-7.6 (m, 3H), and 7.9-8.1 (m, 2H); $C_6H_5COCH_2CH_2CH_2COCH_3$, δ 2.01 (quintet, 2H, J=7), 2.16 (s, 3H), 2.57 (t, 2H, J=7), 3.01 (t, 2H, J=7), 7.3-7.6 (m, 3H), and 7.8-8.1 (m, 2H); $C_6H_5CO-CH(CH_2CH_2COCH_3)_2$, δ 2.08 (s, 6H), 1.6-2.8 (m, 8H), 3.56 (quintet, 1H, J=7), 7.4-7.6 (m, 3H), and 7.8-8.1 (m, 2H).

Acknowledgement. This work was supported by the Korea Science and Engineering Foundation through Center for Biofunctional Molecules and by the Ministry of Education of the Republic of Korea through the Basic Science Research Institute Program.

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Syntheses of Piperidinyloxyl Diradicals Containing Squaric Acid Moieties and Their Magnetic Properties

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Received February 19, 1993

Four compounds containing two 2,2,6,6-tetramethylpiperidin-1-yloxyl radicals were synthesized. They are all chemically bonded with squaric moieties. The diradical compounds show fundamentally the paramagnetic behaviors satisfying the theoretical magnetic susceptibility according to Curie's law. A diradical compound of salf-form **4** however shows a relatively strong antiferromagnetic interaction in comparison with other reported organic radicals. The antiferromagnetic interaction of diradical **4** approximates a value of $J/k = -50$ K by the theoretical analysis of its temperature dependence.

Introduction

Unpaired electrons in atoms and molecules cause several kinds of magnetic properties. They are divided into paramagnetism, ferromagnetism and antiferromagnetism according to the direction and strength among the individual magnetic moments. The ferromagnetism usually occurrs with the transition metals or their oxides. In the case of organic compounds, parallel arrangements of electron spins, which can eventually result in ferromagnetism, have usually no success because of their low symmetry and degeneracy. Several theoretical models solving these difficulties and aiming at the organic ferromagnetism are proposed in the literatures.[1-7] However no valuable pure organic ferromagnet has been reported yet.

McConnell noticed the possibility of organic ferromagnetism through the strong spin-polarization of crystalline radical compounds.[1] The magnetic properties of a few well-known stable radicals such as galvanoxyl, verdazyl and hydrazyl were reported to show only paramagnetism with weak antiferromagnetic interaction.[8-10] This paper is a part of our studies on the way toward organic ferromagnetism.[11,12] We report here the magnetic properties of a different type of stable radicals. The piperidinyloxyl radicals have been conventionally named as nitroxyl. Their derivatization with squaric acid was selected because it has the intrinsic polarity as well as aromaticity.[13-15]

Results and Discussion

Figure 1 shows the synthetic route for diradical compounds **4**, **5**, **6** and **7**, which contain nitroxyl diradical and cyclobutene skeleton from squaric acid **1**. 2,2,6,6-Tetramethylpiperidin-1-yloxyl radical is abbreviated into a TEMPO as in the conventional way. The reaction conditions to link the TEMPO unit were refered to the similar reaction of squaric acid with amine and alcohol in literatures.[16-19] In contrast with squaric acid which is a strong organic acid, the nitroxyl radical is weakly basic.[20] The salt form **4** is formed by simple mixing of squaric acid with H_2N-TEMPO under mild condition. However a direct condensations to obtain bisamide forms **5**, **6** and bisester form **7** are not successful because they cause the destruction of nitroxyl radical center. Consequently, 1,2-bisamide form **5** and 1,2-bisester form **7** were synthesized by the indirect condensation *via* diethyl ester **2**. 1,3-Bisamide form **6** was synthesized for the same reason by transamidization from compound **3**.

Hot DMSO around 100° *C* is the only solvent for bisamide compounds **5** and **6**. In comparison with that, the salt compound **4** is soluble in water and the bisester compounds