has to be carbon n because it is the only CH carbon that clearly shows a connection to two other CH carbons that are also connected to aromatic ring carbons. (c) Carbon i is then confirmed by the above connections and the connection to the quaternary carbon x at 62.5 ppm.

2. The assignments of the C4 ring carbons x, y, z, and o are confirmed by these facts: (a) The peak at 57.0 ppm is assigned to the CH carbon o because it shows no coupling in the proton spectrum and only couplings to quaternary carbons x and z at 62.5 and 61.6 ppm in the carbon 13 spectrum. (b) The peak 62.7 ppm is assigned to the quaternary carbon y because it is the only quaternary carbon that shows connections to two CH$_2$'s (j and e) and another quaternary carbon z. (c) The peak at 61.6 ppm is assigned to the quaternary carbon z because it shows connections to the two CH carbons n and o at 56.7 and 57.0 ppm. (d) The peak at 62.5 ppm is assigned to the quaternary carbon x because it is the only quaternary carbon to show coupling to a CH carbon that is also coupled to an aromatic ring carbon i at 42.9 ppm.

We also see an interesting proton coupling situation in the COSY spectrum for the CH carbons on the C7 ring. The formation of the C4 ring in this molecule locks the CH carbons h, n, and i into a configuration that results in the protons on carbons n and i being in the eclipsed position and therefore shows a strong coupling, while the dihedral angle between the protons on carbons h and n is locked at 90° and shows zero coupling.

Acknowledgment. We are indebted greatly to Kurt L. Loening of Chemical Abstracts who has suggested these names for the photoproduct **3**: (6α,7α,8β)-7-(5,5-dimethyl-3-oxo-1-cyclohexen-1-yl)-3,4,5,6,7,8-hexahydro-3,3-dimethyl-6,8-diphenyl-1(2*H*)-naphthalenone and (1α,2β,3a*S**,7aα,7bβ,11a*R**,12*R**)-hexahydro-5,5,10,10-tetramethyl-2,12-diphenyl-9*H*-1,7a-methano-1*H*-cyclopenta[*e*]biphenylene-7,8(4*H*,7b*H*)-dione; and to one of the reviewers for his suggestions concerning the NMR analysis.

Registry No. 1, 119680-89-6; 3, 119680-90-9; isophorone, 78-59-1; benzaldehyde, 100-52-7.

Supplementary Material Available: Crystallographic summary, tables of final atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and hydrogen final atomic coordinates (16 pages). Ordering information is given on any current masthead page.

Radical Reaction of Ketene Alkyl Trimethylsilyl Acetals with Divinyl Sulfone Promoted by Titanium(IV) Chloride

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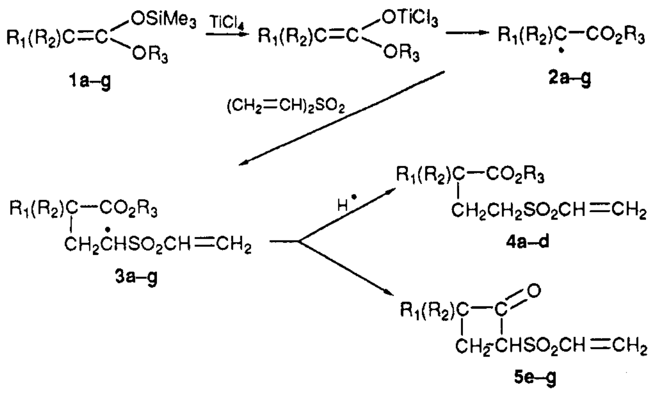
Received October 20, 1988

In the course of our studies on the synthetic utility of ketene alkyl trimethylsilyl acetals (**1**), we conducted the reaction of **1** with divinyl sulfone in the presence of titanium(IV) chloride. During the past decade several groups have demonstrated the synthetic utility of these ketene acetals.[1-4] Very recently we have accomplished the synthesis of α-nitroso esters, oximes of α-oxo esters, and malonic ester derivatives using **1**.[5,6] The usefulness of **1** would be more enhanced if they could be converted to new type of ester derivatives that are difficult to prepare by known methods. Thus, we have investigated the interaction between divinyl sulfone and the radical species derived from **1** and titanium(IV) chloride, because it was anticipated that the reaction would lead to the formation of either a simple addition product or a cyclobutanone derivative by subsequent cyclization.

Scheme I



a : R$_1$ = Me; R$_2$ = H; R$_3$ = Et
b : R$_1$ = Et; R$_2$ = H; R$_3$ = Et
c : R$_1$ = Pr; R$_2$ = H; R$_3$ = Me
d : R$_1$ = *i*-Pr; R$_2$ = H; R$_3$ = Et
e : R$_1$ = R$_2$ = Me; R$_3$ = Et
f : R$_1$ = Et; R$_2$ = Me; R$_3$ = Et
g : R$_1$ = R$_2$ = R$_3$ = Et

The reactions using several ketene alkyl trimethylsilyl acetals (**1a–g**) proceeded smoothly as anticipated, providing excellent yields of alkyl γ-(vinylsulfonyl)butyrate derivatives (**4a–d**) or 2-(vinylsulfonyl)cyclobutanone derivatives (**5e–g**) (Scheme I). The divergence in the formation of products, which is somewhat surprising, indicates that the reaction process is highly controlled by the number of alkyl substituents situated on the α-carbon of the starting acetals (**1a–g**). The products obtained have been characterized on the basis of spectral properties (IR, ^{1}H NMR, ^{13}C NMR, MS, and UV spectra), elemental analyses, chemical transformations, and further by comparison with reported data if available.

In a preliminary experiment, it was ascertained that divinyl sulfone shows no interaction with titanium(IV) chloride. The formation of radical species **2** from **1** and titanium(IV) chloride, followed by dimerization into alkyl succinate derivatives, is well documented.[7] In the present experiments, however, the reactions of divinyl sulfone with radical species **2** dominate over their dimerization and afford another intermediate, radical species **3**. It should be noted that, when both substituents (R$_1$ and R$_2$) of **3** are alkyl groups, **3** prefers cyclization to give the corresponding 2-(vinylsulfonyl)cyclobutanone derivatives (**5e–g**), and that when one of the above substituents is hydrogen, **3** abstracts a hydrogen radical to afford the corresponding alkyl γ-(vinylsulfonyl)butyrate derivatives (**4a–d**). Although the reason for this reactivity difference is not clear, it is thought that the steric requirements of two alkyl substituents of **3** cause the radical site and carbonyl group of **3** to approach each other and assist cyclization. The radical nature of reaction was further supported by experiments in which a small amount of hydroquinone or *p*-*tert*-butylpyrocatechol was added to the reaction mixture. In these cases, the yields of **4** and **5** were depressed to less

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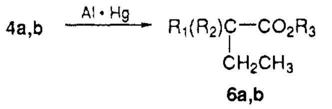
than 40% in every run. However, the process involving the conversion of **3e–g** into **5e–g** is uncertain. Two mechanisms can be proposed for the conversion of **3e–g** into **5e–g**. One involves the intermediacy of **4e–g** and subsequent cyclization with the release of alcohol. The other is that involving the attack of the radical in **3e–g** at the carbonyl carbon with the release of alkoxy radical. The latter process seems to be operating because of the complete absence of alkyl γ-(vinylsulfonyl)butyrate derivatives (**4e–g**) in the reaction mixture with **1e–g**. This was ascertained by ^{1}H NMR spectra of the crude products obtained.

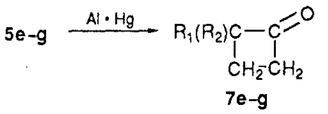
Further, several of the products obtained were reduced in order to convert them into the known alkyl butyrate derivatives (**6a,b**), or cyclobutanone derivatives (**7e–g**), with the cleavage of the vinyl sulfonyl group. The reductive fission of sulfones is well known.[8,9] The compounds **4a** and **4b** on reduction with aluminum amalgam gave the corresponding alkyl butyrate derivatives **6a** and **6b**, respectively. Also, the compounds **5e**, **5f**, and **5g** on similar reduction gave the corresponding cyclobutanone derivatives **7e**,[10] **7f**,[11] and **7g**.[12,13] These reduction products were identified by comparing their boiling points and spectral data with those reported in literature.



$\text{4a,b} \xrightarrow{\text{Al}\cdot\text{Hg}} \text{R}_1(\text{R}_2)\text{C(CH}_2\text{CH}_3)\text{—CO}_2\text{R}_3$

6a,b

a : R_1 = Me; R_2 = H; R_3 = Et
b : R_1 = Et; R_2 = H; R_3 = Et



7e–g

e : R_1 = R_2 = Me
f : R_1 = Et; R_2 = Me
g : R_1 = R_2 = Et

Experimental Section

Boiling points were determined on a glass tube oven by bulb-to-bulb distillation and were uncorrected. Microanalyses were performed with a Yanaco MT-3 elemental analyzer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian VXR-200 spectrometer in $CDCl_3$ with $SiMe_4$ as an internal standard. IR spectra were recorded on a JASCO IR-810 spectrophotometer. For UV spectra in ethanol a UVIDEC-610B double-beam spectrophotometer was used. Mass spectral data were obtained on a JEOL DMS-DX-300 spectrometer.

Reaction of Ketene Alkyl Trimethylsilyl Acetals (1a–g) with Divinyl Sulfone in the Presence of Titanium(IV) Chloride. To a stirred, cooled (0 °C) solution of **1** (10 mmol) and divinyl sulfone (1.18 g, 10 mmol) in dry dichloromethane (more than 50 mL)[14] was added, slowly, by syringe under nitrogen atmosphere, titanium(IV) chloride (1.09 g, 10 mmol). This was followed by stirring at room temperature for 3 h, whereupon the reaction mixture was quenched with 100 mL of water. It was extracted with dichloromethane (3 × 30 mL). The combined extracts were washed with water (100 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo to give a residue, which was subjected to column chromatography on silica gel using 30% ethyl acetate–70% hexane as eluent.

Ethyl α-methyl-γ-(vinylsulfonyl)butyrate (4a): 62% yield; bp 135 °C (4 mmHg); UV (EtOH) λ_{max} nm (ε) 205 (6240); IR (neat) 3050, 2970, 2860, 1730, 1610, 1450, 1380, 1310, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (d, 3 H, *J* = 7.4 Hz), 1.22 (t, 3 H, *J* = 7 Hz), 1.61 (m, 2 H), 2.27 (m, 1 H), 2.92 (t, 2 H, *J* = 7.4 Hz), 4.17 (q, 2 H, *J* = 7.2 Hz), 6.14 (d, 1 H, *J* = 9.6 Hz), 6.38 (d, 1 H, *J* = 16.4 Hz), 6.61 (dd, 1 H, *J* = 9.6, 16.6 Hz); mass spectrum M$^+$ 220 ($C_9H_{16}O_4S$). Anal. Calcd for $C_9H_{16}O_4S$: C, 49.07; H, 7.32. Found: C, 48.88; H, 7.30.

Ethyl α-ethyl-γ-(vinylsulfonyl)butyrate (4b): 78% yield; bp 210 °C (20 mmHg); UV (EtOH) λ_{max} nm (ε) 205 (7731); IR (neat) 3050, 2970, 2870, 1730, 1610, 1460, 1385, 1315, 1135 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3 H, *J* = 7.6 Hz), 1.22 (t, 3 H, *J* = 7.2 Hz), 1.61 (m, 2 H), 1.94 (m, 2 H), 2.39 (m, 1 H), 2.95 (t, 2 H, *J* = 7.6 Hz), 4.11 (q, 2 H, *J* = 7.0 Hz), 6.15 (d, 1 H, *J* = 9.6 Hz), 6.39 (d, 1 H, *J* = 16.6 Hz), 6.62 (dd, 1 H, *J* = 9.6, 16.4 Hz); ^{13}C NMR ($CDCl_3$) δ 174.46, 135.81, 130.75, 60.56, 51.92, 45.20, 25.13, 23.96, 14.21, 11.29; mass spectrum M$^+$ 234 ($C_{10}H_{18}O_4S$). Anal. Calcd for $C_{10}H_{18}O_4S$: C, 51.26; H, 7.74. Found: C, 51.16; H, 7.79.

Methyl α-propyl-γ-(vinylsulfonyl)butyrate (4c): 76% yield; bp 110 °C (2 mmHg); UV (EtOH) λ_{max} nm (ε) 205 (13077); IR (neat) 3050, 2950, 2870, 1725, 1610, 1460, 1380, 1320, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3 H, *J* = 6.5 Hz), 1.26 (m, 4 H), 1.58 (m, 2 H), 2.05 (m, 1 H), 2.26 (t, 2 H, *J* = 7.6 Hz), 3.63 (s, 3 H), 6.10 (d, 1 H, *J* = 9.4 Hz), 6.41 (d, 1 H, *J* = 16.6 Hz), 6.58 (dd, 1 H, *J* = 9.2, 16.6 Hz); mass spectrum M$^+$ 234 ($C_{10}H_{18}O_4S$). Anal. Calcd for $C_{10}H_{18}O_4S$: C, 51.26; H, 7.74. Found: C, 50.98; H, 7.74.

Ethyl α-isopropyl-γ-(vinylsulfonyl)butyrate (4d): 70% yield; bp 150 °C (2 mmHg); UV (EtOH) λ_{max} nm (ε) 205 (11354); IR (neat) 3050, 2960, 2880, 1725, 1610, 1470, 1385, 1315, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (d, 6 H, *J* = 6.6 Hz), 1.22 (t, 3 H, *J* = 7 Hz), 1.94 (m, 2 H), 2.21 (m, 1 H), 2.47 (m, 1 H), 2.92 (t, 2 H, *J* = 7.4 Hz), 4.10 (q, 2 H, *J* = 7 Hz), 6.15 (d, 1 H, *J* = 9.6 Hz), 6.39 (d, 1 H, *J* = 16.4 Hz), 6.59 (dd, 1 H, *J* = 9.6, 16.4 Hz); ^{13}C NMR ($CDCl_3$) δ 174.13, 135.82, 130.76, 60.52, 52.26, 50.63, 30.41, 21.68, 20.05, 19.78, 14.26; mass spectrum M$^+$ 248 ($C_{11}H_{20}O_4S$). Anal. Calcd for $C_{11}H_{20}O_4S$: C, 53.20; H, 8.12. Found: C, 52.95; H, 8.06.

4,4-Dimethyl-2-(vinylsulfonyl)cyclobutanone (5e): 68% yield; bp 128 °C (4 mmHg); UV (EtOH) λ_{max} nm (ε) 205 (44321); IR (neat) 3050, 2960, 2860, 1780, 1610, 1460, 1380, 1310, 1135 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 3 H), 1.28 (s, 3 H), 2.25 (d, 1 H, *J* = 10.4 Hz), 2.45 (d, 1 H, *J* = 7 Hz), 4.66 (dd, 1 H, *J* = 7.2, 10.2 Hz), 6.20 (d, 1 H, *J* = 9.8 Hz), 6.43 (d, 1 H, *J* = 16.6 Hz), 6.73 (dd, 1 H, *J* = 9.8, 16.4 Hz); ^{13}C NMR ($CDCl_3$) δ 202.28, 135.88, 131.43, 72.76, 61.08, 27.66, 23.09, 21.10; mass spectrum M$^+$ 188 ($C_8H_{12}O_3S$). Anal. Calcd for $C_8H_{12}O_3S$: C, 51.04; H, 6.43. Found: C, 51.01; H, 6.40.

4-Ethyl-4-methyl-2-(vinylsulfonyl)cyclobutanone (5f): 70% yield; bp 135 °C (4 mmHg); UV (EtOH) λ_{max} nm (ε) 205 (49995); IR (neat) 3050, 2960, 2855, 1775, 1610, 1460, 1380, 1320, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H, *J* = 7.2 Hz), 1.27 (s, 3 H), 1.63 (q, 2 H, *J* = 7 Hz), 2.33 (d, 1 H, *J* = 10.2 Hz), 2.40 (d, 1 H, *J* = 7.4 Hz), 4.59 (dd, 1 H, *J* = 10.2, 7.2 Hz), 6.21 (d, 1 H, *J* = 9.8 Hz), 6.45 (d, 1 H, *J* = 16.4 Hz), 6.75 (dd, 1 H, *J* = 9.8, 16 Hz); ^{13}C NMR ($CDCl_3$) δ 202.20, 135.90, 131.38, 72.83, 65.58, 27.01, 25.47, 20.95, 18.57; mass spectrum M$^+$ 202 ($C_9H_{14}O_3S$). Anal. Calcd for $C_9H_{14}O_3S$: C, 53.44; H, 6.98. Found: C, 53.48; H, 6.76.

4,4-Diethyl-2-(vinylsulfonyl)cyclobutanone (5g): 72% yield; bp 150 °C (2 mmHg); UV (EtOH) λ_{max} nm (ε) 207 (3092); IR (neat) 2970, 2880, 1780, 1605, 1460, 1380, 1315, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 6 H, *J* = 7.4 Hz), 1.66 (q, 4 H, *J* = 7.4 Hz), 2.21 (d, 1 H, *J* = 10.4 Hz), 2.42 (d, 1 H, *J* = 7.4 Hz), 4.54 (dd, 1 H, *J* = 7.4, 10.3 Hz), 6.19 (d, 1 H, *J* = 9.8 Hz), 6.41 (d, 1 H, *J* = 16.6 Hz), 6.72 (dd, 1 H, *J* = 9.8, 16.6 Hz); ^{13}C NMR ($CDCl_3$) δ 202.11, 136.11, 131.26, 72.29, 69.84, 26.10, 24.42, 23.54, 8.64, 8.16; mass spectrum M$^+$ 216 ($C_{10}H_{16}O_3S$). Anal. Calcd for $C_{10}H_{16}O_3S$: C, 55.53; H, 7.46. Found: C, 55.46; H, 7.51.

Reaction of the Compounds 4a, 4b, 5e, 5f, and 5g with Aluminum Amalgam. To a stirred solution of one of **4a**, **4b**, **5e**, **5f**, and **5g** (0.1 mol in 10% aqueous tetrahydrofuran (40 mL)) was added aluminum amalgam, prepared by immersing a small piece of aluminum foil in 2% aqueous $HgCl_2$ solution (20 mL) for 0.5 min, rinsing the amalgamated foil quickly with alcohol and

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[14] In order to avoid the dimerization of radical species **2** leading to the decreased yield of objective product, a relatively large amount of dichloromethane was employed.

ether, and drying it on filter paper. The addition of amalgamated foils was repeated until the weight of all pieces of aluminum foil employed totaled 1 g. After completion of the above addition, the reaction mixture was stirred at room temperature for 7–10 h. The resulting precipitate was filtered off. It was washed repeatedly with tetrahydrofuran. The combined washings and the filtrate were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure to afford a residue, which was subjected to column chromatography on silica gel with 50% ether–50% hexane as eluent. The isolated yields of **6a**, **6b**, **7e**, **7f**, and **7g** were 60, 64, 54, 62, and 58% based on the corresponding starting compounds **4a**, **4b**, **5e**, **5f**, and **5g**.

Acknowledgment. Financial support from the Ministry of Education (Japan) in the form of post doctoral fellowship to S.M.A. is gratefully acknowledged.

Registry No. **1a**, 80675-53-2; **1b**, 65946-52-3; **1c**, 84393-10-2; **1d**, 63547-55-7; **1e**, 31469-16-6; **1f**, 118646-01-8; **1g**, 31469-17-7; **2a**, 37999-08-9; **2b**, 105019-17-8; **2c**, 65364-88-7; **2d**, 105019-18-9; **2e**, 37999-09-0; **2f**, 41771-06-6; **2g**, 105019-20-3; **4a**, 119770-04-6; **4b**, 119770-05-7; **4c**, 119770-06-8; **4d**, 119770-07-9; **5e**, 119770-08-0; **5f**, 119770-09-1; **5g**, 119770-10-4; **6a**, 7452-79-1; **6b**, 2983-38-2; **7e**, 1192-14-9; **7f**, 75750-10-6; **7g**, 35358-42-0; $(CH_2{=}CH)_2SO_2$, 77-77-0; $TiCl_4$, 7550-45-0.

Electroorganic Chemistry. 116. Electrochemical Transformation of Aldoximes to Nitriles Using Halogen Ions as Mediators: Intermediary Formation of Nitrile Oxides

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Received December 8, 1988

In our continuing studies on electroorganic synthesis using mediators,[1] we have found that aldoximes 1 are converted to nitriles 2 by using halogen ions as mediators (eq 1). This transformation is interesting from both synthetic and mechanistic viewpoints since it is achievable under much milder reaction conditions than those used in hitherto-known methods,[2] and also, passing electricity is necessary for the formation of 2 from 1 although it is formally a simple dehydration process which is unrelated to oxidation and reduction. Both synthetic results and mechanistic discussion are described in this report.

$$\underset{1}{\text{R-CH=N-OH}} \xrightarrow[\substack{\text{supporting electrolyte}\\ \text{MeOH}}]{\text{electricity}} \underset{2}{\text{R-CN}} \qquad (1)$$

Electrochemical Transformation of Aldoximes 1 to Nitriles 2. Passing electricity through a solution of aldoximes 1 in methanol containing sodium chloride under conditions of constant current at room temperature using an undivided cell gave nitriles 2 in the yields shown in Table I after electricity of 2.5–8.0 F/mol was passed.

The yield of nitrile was found to be strongly dependent on the type of supporting electrolytes, as summarized in Table II. Sodium chloride gave the best result among the supporting electrolytes examined (run 2 in Table II), and the yields decreased in the order of $Cl^- > Br^- > I^- > ClO_4^- > TsO^-$ (runs 2–6 in Table II). Also, it was found that only a catalytic amount of sodium chloride was enough to transform 1 to 2 effectively as shown by a typical example in which 0.1 equiv of sodium chloride was used (run 1 in Table II).

Table I. Electrochemical Transformation of Aldoximes 1 to Nitriles 2

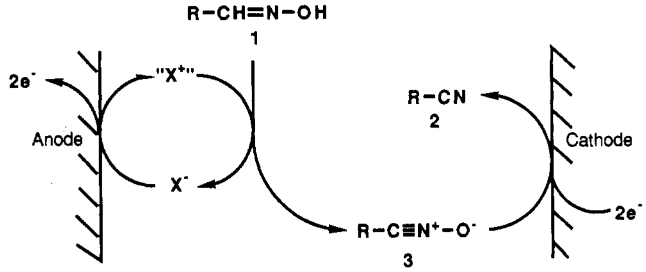
run	aldoximes 1; R	electricity, F/mol	isolated yields of nitriles 2, %
1	**1a**; $CH_3(CH_2)_5$	3.5	**2a**, 83
2	**1b**; $CH_3(CH_2)_8$	3.5	**2b**, 82
3	**1c**; cyclohexyl	3.5	**2c**, 71
4	**1d**; Ph(Me)CH	2.5	**2d**, 74
5	**1e**; $Ph(CH_2)_2$	3.8	**2e**, 73
6	**1f**; Ph	4.5	**2f**, 61
7	**1g**; *p*-ClPh	4.0	**2g**, 40
8	**1h**; *p*-MePh	3.0	**2h**, 54
9	**1i**; *p*-MeOPh	8.0	**2i**, 54
10	**1j**; 2,4,6-Me_3Ph	5.0	**2j**, 91

Table II. The Effect of Supporting Electrolytes

run	supporting electrolyte (SE)	molar ratio of SE to **1a**	yield (%) of **2a**[a]
1	NaCl	0.1	71
2	NaCl	0.5	83
3	NaBr	0.5	66
4	NaI	0.5	42
5	Et_4NOTs	0.5	16
6	$LiClO_4$	0.5	26

[a] Electricity, 5 F/mol, was passed at room temperature.

Scheme I



Reaction Mechanism. The transformation of 1 to 2 is formally a dehydration. An acid-catalyzed dehydration of 1 is one of the plausible mechanisms for the electrochemical formation of 2 from 1 since it has been suggested that some sort of acid is generated by passing electricity through a solution of a salt of a strong acid.[3] A small amount of 2 was indeed formed under such reaction conditions (runs 5 and 6 in Table II), but the high yields obtained under the reaction conditions using halogen ions cannot be explained by acid-catalyzed dehydration alone.

It is well-known that halogen anion (X^-) is oxidized to cationic active species ("X^+")[4] by electrochemical oxidation.[5] In this study, a mechanism involving "X^+" as an oxidizing agent[6] is proposed, as shown in Scheme I, where aldoximes 1 are oxidized to nitrile oxides 3[8] followed by

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[4] "X^+" denotes the cationic active halogen species generated by anodic oxidation of X^-.

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[6] The reactivity of "X^+" is generally highly influenced by the reaction conditions. It is much higher than that of the corresponding X_2 in some cases as exemplified by the direct aromatic iodination,[7] while in other cases, it is similar to that of the corresponding X_2. In the transformation of 1 to 3, the reactivity of "X^+" may belong to the latter.[8,9]

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