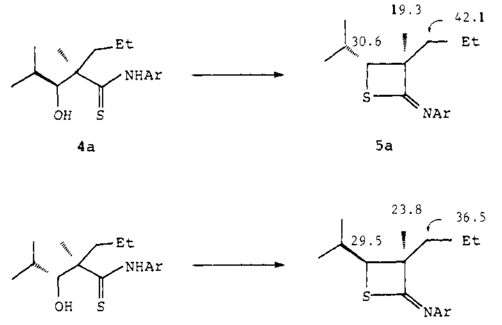
Table I. Tandem Michael Addition-Aldol Condensation of Thioamide **1**[a]

entry	Grignard, R^1MgBr	aldehyde, R^2CHO	conditions[b]	product distribution,[c] **2**:**3**	yield,[d] %
1	Et	Me	-78 °C, 2 min	>99:1	85
2	Et	*i*-Pr	-78 °C, 2 min	>99:1	86
3	*i*-Pr	Me	-78 °C, 2 min	>99:1	95
4	*i*-Pr	Et	-78 °C, 2 min	>99:1	86
5	Ph	Me	-78 °C, 2 min	>99:1	24
6	Ph	MeCH=CH	-78 °C, 2 min	>99:1	25
7	Ph	PhCH=CH	-78 °C, 2 min	>99:1	48
8	Et	Ph	-78 °C, 2 min	41:59	80
9	Et	Ph	-78 °C, 2 min; room temp, 18 h	8:92	80
10	*i*-Pr	Ph	-78 °C, 2 min	33:67	83
11	Ph	Ph	-78 °C, 2 min	17:83	81

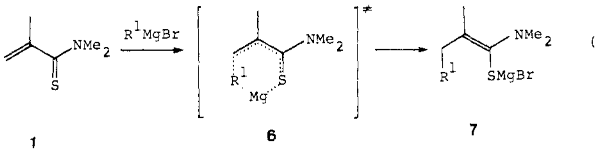
[a] For the structure of **2** and **3**, see eq 1. [b] Reaction conditions for the aldol condensation. [c] Distribution determined on the basis of HPLC, ^1H NMR, and/or ^{13}C NMR spectra. [d] Combined isolated yield of **2** and **3**.

transformations of **2** and/or **3** to the structurally defined authentic samples.[12] The structure of **2** and **3** was confirmed unequivocally by the procedure outlined in eq 2. *N*-(Trimethylsilyl)-*N*-(2,6-dimethylphenyl)-α-methacrylothioamide (generated in situ by treatment of *N*-(2,6-dimethylphenyl)-α-methacrylothioamide with NaH/trimethylsilyl chloride in THF at 0 °C)[14] was subjected to a tandem Michael addition-aldol condensation[15] under conditions similar to those in Table I and gave a single aldol-type product of secondary thioamide (**4a**). The product **4a** was then subjected to the Mitsunobu reaction[16] and the β-thioiminolactone **5a** was obtained in quantitative yield. The trans structure of **5a** was determined on the basis of the observations of the higher field resonances of the α-methyl signal in the ^{13}C NMR spectra of **5a** compared with that of the cis isomer **5b**.[17,18] Selected data (figures given in ppm relative to Me_4Si) are shown in eq 2.



4a **5a** **4b** **5b** (2)

The high erythro selectivity might be attributed to the high *Z* stereochemical purity of the enolate **7**,[1] which may stem from the Michael addition of Grignard reagents to **1** through a coordination of magnesium(II) to the sulfur atom to form a 6π-electron cyclic transition state **6** (eq 3).[19] The usefulness of the present Michael addition technique is furthermore augmented by the unsuccessful generation of tetrasubstituted enolate by treatment of *N*,*N*-dimethyl-2-methylvalerothioamide with bases (*i*-PrMgBr, *n*-BuLi, or LDA in THF either in the presence or absence of HMPA or TMEDA).[20]



1 **6** **7** (3)

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(12) For example, **2** (R^1 = Ph, R^2 = Me) underwent a C_2-C_3 bond cleavage in the attempts to obtain the corresponding amine (MeI-$NaBH_4$ in *i*-PrOH: Raucher, S.; Klein, P. *Tetrahedron Lett.* **1980**, *21*, 4061). Similarly bond cleavage took place in the thiolactonization of **3** (R^1 = *i*-Pr, R^2 = Ph, excess formalin, 2 N HCl in THF reflux).[13] The attempted reduction of *N*,*N*-dimethyl-2-methyl-2-benzoylbutyrothioamide to **2** and/or **3** (R^1 = Ph, R^2 = Me) resulted in a C_2-C_3 bond cleavage, giving *N*,*N*-dimethyl-2-methylbutyrothioamide ($NaBH_4$ in *i*-PrOH or Na in EtOH at 0 °C).

(13) α-Monosubstituted β-hydroxy thioamides can easily be converted to 4-oxa-δ-thiovalerolactones. The details will be reported shortly.

(14) Tamaru, Y.; Amino, Y.; Furukawa, Y.; Kagotani, M.; Yoshida, Z. *J. Am. Chem. Soc.* **1982**, *104*, 4018.

(15) For the tandem conjugate addition-alkylation of unsaturated amides, see: (a) Baldwin, J. E.; Dupont, W. A. *Tetahedron Lett.* **1980**, *21*, 1881. (b) Mpango, G. B.; Mahalanabis, K. K.; Mahdavi-Damghani, Z.; Snieckus, V. *Ibid.* **1980**, *21*, 4823. For unsaturated ketones, see: (c) Heng, K. K.; Simpson, J.; Smith, R. A. J.; Robinson, W. T. *J. Org. Chem.* **1981**, *46*, 2932.

(16) Mitsunobu, O. *Synthesis* **1981**, 1.

(17) Levy, G. C.; Lichter, R. L.; Nelson, G. N. "Carbon-13 NMR Spectroscopy", 2nd ed.; Wiley: New York, 1980.

(18) A 1:1 mixture of **4a** and **4b** was obtained by the reaction of *N*-(2,6-dimethylphenyl)-α-methacrylothioamide with 3 equiv of ethyllithium (THF, -78 °C, 5 h) followed by treatment with 3 equiv of isobutylraldehyde (-78 °C, 2 min): Tamaru, Y.; Kagotani, M.; Yoshida, Z. *Tetrahedron Lett.* **1981**, *22*, 3409, 3413.

(19) (a) Tamaru, Y.; Harada, T.; Nishi, S.; Yoshida, Z. *Tetrahedron Lett.* **1982**, *23*, 2383. (b) Beak, P.; Hunter, J. E.; Jun, Y. M. *J. Am. Chem. Soc.* **1983**, *105*, 6350.

(20) We acknowledge partial support for this work provided by the Ministry of Education, the Japanese Government (Grant in Aid for Special Project Research 58110005 and Scientific Research B 58470066).

Oxidation of Hydroxide Ion by Immonium Oxide

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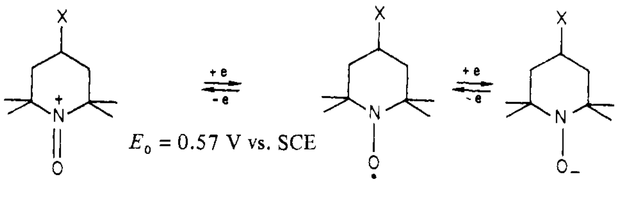
2,2,6,6-Tetramethylpiperidine-1-oxyl (I)[1] known as a stable radical has been widely used as a spin-labeling reagent in the field of biochemistry and applied as a spin trapping agent and antioxidant. A reversible redox system based on I is shown in eq 1.



II
IIa, X = OMe
I
Ia, X = OMe
(1)

1-Oxo-2,2,6,6-tetramethylpiperidinium salt (II)[1] used in this study is obtained by one-electron oxidation of I^2 with bromine.[3]

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(1) Golubev, V. A.; Rozantsev, E. G.; Neiman, M. B. *Izv. Akad. Nauk SSSR* **1965**, 1927-1936.

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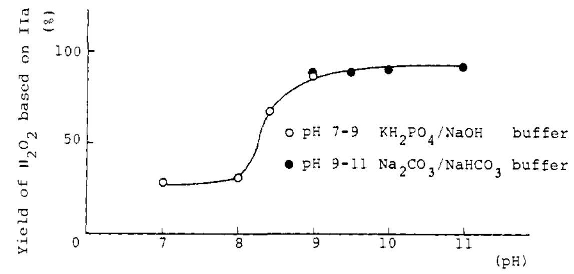
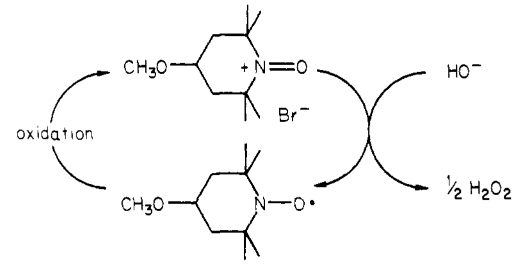


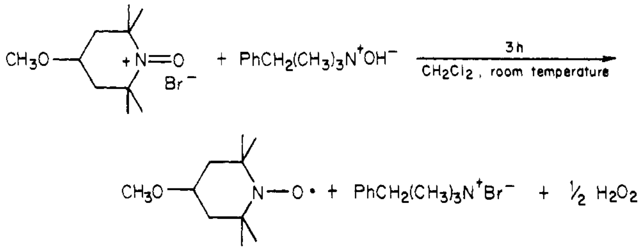
Figure 1. Influence of pH in the oxidation of H_2O by use of IIa.

During examination of II as an oxidizing agent for organic compounds such as amines and alcohols, we found that hydroxide ion undergoes one-electron oxidation by IIa to produce hydrogen peroxide,[4] and >N-O· was afforded quantitatively from IIa.

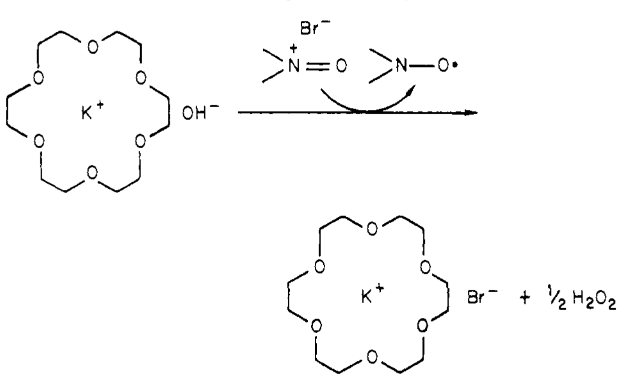


As shown in Figure 1, the amount of the produced hydrogen peroxide was only dependent on the pH and not the buffer composition. Especially in the range of pH 9–11 it was obtained in higher yields and >N-O· was recovered quantitatively.

Further, the oxidation of hydroxide ion was carried out in nonaqueous solvent. The hydroxide ion of anhydrous benzyltrimethylammonium hydroxide (Triton B) in methylene chloride[5] was oxidized by $>N^+=O$ at room temperature for 3 h to give hydrogen peroxide in 38% yield based on IIa.



The oxidation of potassium hydroxide,[6] which solubilized with 18-crown-6-ether into methylene chloride, was also carried out at room temperature to afford hydrogen peroxide (yield, 31% based on $>N^+=O$) and >N—O· (yield, 100%).



This method might be important in the chemical field using hydroxyl radical, because its generation from hydroxide ion in nonaqueous solvent should be useful in the organic chemistry.

Registry No. IIa·Br^-, 90246-27-8; HO^-, 14280-30-9; H_2O_2, 7722-84-1; $PhCH_2(CH_3)_3N^+OH^-$, 100-85-6; potassium hydroxide, 1310-58-3.

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(2) Ia was obtained by the reaction of 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl and methyl iodide. Ia: mp 35–36 °C; mass spectrum, *m/e* 186; IR (KBr) 2980, 2940, 2820, 1470, 1390, 1360, 1350, 1315, 1180, 1100 cm^{-1}. Anal. Calcd for $C_{10}H_{20}NO_2$: C, 64.48; H, 10.82; N, 7.52. Found: C, 64.11; H, 10.59; N, 7.64.

(3) IIa was obtained by the oxidation of 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl with bromine in CCl_4. IIa: mp 206–207 °C dec; IR (KBr) 2940, 2730, 2590, 2540, 1600, 1460, 1410, 1390, 1320, 1280, 1215, 1160, 1100 cm^{-1}. Anal. Calcd for $C_{10}H_{20}NO_2Br$: C, 45.12; H, 7.57; N, 5.26; Br, 30.02. Found: C, 45.11; H, 7.45; N, 5.29; Br, 29.59.

(4) After IIa (100 mg, 3.8 mmol) was dissolved in 50 mL of buffer solution (KH_2PO_4/NaOH or Na_2CO_3/$NaHCO_3$), the solution was stirred for 3 h at room temperature. The reaction mixture was washed with ether 3 times to remove the obtained nitroxyl radical (Ia), and the water layer was treated by iodometric titration to estimate the yield of hydrogen peroxide. Hydrogen peroxide derived from this method was detected by the mass spectrometry. The molecular ion peak at 34 was clearly observed.

(5) To a stirred solution of 940 mg (5.6 mmol) of anhydrous Triton B in 10 mL of methylene chloride was added 170 mg (0.64 mmol) of IIa at room temperature under nitrogen. After it was stirred for 3 h at room temperature, hydrogen peroxide was extracted with water from the methylene chloride solution and its amount was estimated by iodometry.

(6) IIa (69 mg, 0.26 mmol) was added to 5 mL of the supernatant of the KOH solution prepared from vigorous stirring of anhydrous 18-crown-6-ether (1.54 g, 5.8 mmol) and powdered KOH (3.25 g, 58 mmol) in 60 mL of methylene chloride. The obtained hydrogen peroxide was extracted with water from the reaction mixture and its amount was estimated by iodometry.

Synthesis, Reactivity, and Crystal and Molecular Structure of $Re(O)I(MeC{\equiv}CMe)_2$

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Oxide compounds are known for all of the transition metals, in fact for all the elements except the lighter noble gases.[1] However, transition-metal complexes with terminal, multiply bonded oxo ligands have been characterized only for Ti,[2] the elements in groups 5–7, and the iron triad.[1,3] These complexes have also been restricted to d^0, d^1, and d^2 electron configurations and therefore to the highest oxidation states of these elements. We wish to report the synthesis, structure, and reactivity of oxoiodobis(2-butyne)rhenium(III), $Re(O)I(MeC{\equiv}CMe)_2$ (**1**), the first well-characterized low-valent oxo complex.

Compound **1** is formed when excess 2-butyne is added to benzene solutions of $ReO_2I(PPh_3)_2$[4] or $ReOI_3(AsPh_3)_2$[5,6] (eq 1

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(1) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980.

(2) (a) Dwyer, P. N.; Puppe, L.; Buchler, J. W.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 1782–1785. Guilard, R.; Latour, J. M.; Lecomte, C.; Marchon, J. C.; Protas, J.; Ripoll, D. *Ibid* **1978**, *17*, 1228–1237. (b) See references and discussion in ref 3a, p 481.

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(4) (a) Freni, M.; Giusto, D.; Romiti, P.; Minghetti, G. *Gazz. Chim. Ital.* **1969**, *99*, 286–299. (b) Ciani, G. F.; D'Alfonso, G.; Romiti, P.; Sironi, A.; Freni, M. *Inorg. Chim. Acta* **1983**, *72*, 29–37.

(5) (a) $ReOI_3(AsPh_3)_2$ was prepared from $KReO_4$, aqueous HI, and $AsPh_3$, following the published procedure for $ReOBr_3(AsPh_3)_2$.[5b] Although we have as yet been unable to obtain analytically pure $ReOI_3(AsPh_3)_2$, the IR spectra of the iodide and bromide deriviatives are very similar (ν_{ReO}: 975 cm^{-1}). $Re(O)I(MeCCMe)_2$ was prepared by adding 1.5 g (28 mmol) of 2-butyne to a 10-mL benzene solution of 2 g (1.7 mmol) of $ReOI_3(AsPh_3)_2$ in a drybox. After stirring for 2 h 0.46 g (1.8 mmol) of I_2 in 50 mL of benzene was added and the mixture stirred another 0.5 h. After filtration the volatiles were removed and the residue recrystallized from hexane, yield 0.34 g of yellow crystals (47%). Anal. Calcd for $C_8H_{12}IORe$: C, 21.97; H, 2.77. Found: C, 22.22, 21.94; H, 2.76, 2.88. (b) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054–1066.

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