Concerning the Synthesis of *N*-Methylputrescine and Its Homologues

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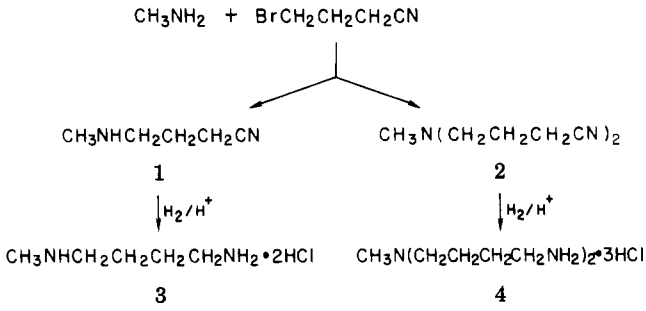
N-Methylputrescine **3** (Scheme I) has been extensively used as a biosynthetic precursor of the nicotine and tropane alkaloids.[1,2] It is also a natural product, since it is formed in tobacco roots by N-methylation of putrescine (1,4-butanediamine).[3] It was also recently shown to have a stimulatory effect on growth and protein synthesis of polyamine-depleted *Escherichia coli* cultures, while *N*-ethyl-, *N*-propyl-, and *N*-butylputrescine **13–15** (Scheme II) were without effect.[4] *N*-Methyl- (**3**), *N*-ethyl- (**13**), *N*-propyl- (**14**), and *N*-butylputrescine (*15*) were found to promote the growth of *Haemophilus parainfluenzae*,[5] although the synthetic procedures used to prepare **3** or **13–15** were not reported. The same *N*-alkylputrescines were recently found to be degraded (oxidized) by spermidine dehydrogenase from *Serratia marcescens*[6] and by putrescine oxidase from *Micrococcus rubens*.[7] The *N*-alkylputrescines **3** and **13–15** used in these last studies were obtained by direct alkylations of putrescine, but no evidence was given as to the homogeneity of the obtained products.

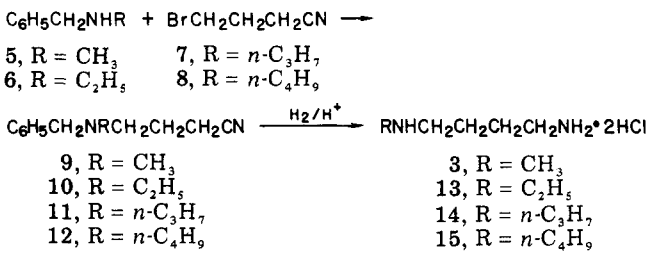
Although *N*-methylputrescine **3** and its homologues **13–15** are simple molecules, their synthesis is by no means straightforward. *N*-Methylputrescine **3** was first obtained by Duddley and Thorpe by reaction of benzoyl 5-iodobutylamine with methylamine followed by hydrolysis of the benzoyl residue.[8] A simpler synthesis was described by Kiel[9] by condensation of 4-chlorobutyronitrile with methylamine to give the 4-(methylamino)butyronitrile **1**, which was reduced to **3**. A similar condensation was again reported by Maier et al. (although without experimental detail) using 4-bromobutyronitrile[2] or 4-chlorobutyronitrile[10] in synthesis designed to obtain labeled **3**. A more elaborate synthesis of **3** was reported by Maier and Schutte[11] but could not be duplicated by Leete and McDonell,[1] who finally developed a new multistep synthesis of labeled **3** starting from ethyl 4-bromobutanoate.

The need for a simple and preparative synthesis of **3** led us to reexamine the condensation of 4-bromobutyronitrile with methylamine. We found that the reaction product was always a mixture of the expected nitrile **1** and the dinitrile **2** (Scheme I). Even at mild reaction conditions where unreacted 4-bromobutyronitrile was recovered, a GC analysis of the product mixture indicated the presence of equivalent amounts of **1** and **2**. Reduction of the mixture with hydrogen in the presence of hydrochloric acid afforded a mixture of the hydrochlorides **3** and **4** (with very similar melting points) that could only be separated by chromatography on cellulose.

Scheme I



Scheme II



To avoid the formation of a tertiary amine and since secondary amines (e.g., dimethylamine) are known to condense with 4-bromobutyronitrile,[9] we explored the preparative condensation of the latter with the alkylbenzylamines **5–8** (Scheme II). The condensation gave 85% yield for **9** and **10** when performed in tetrahydrofuran in the presence of triethylamine but only 35–40% yield for the higher homologues **11** and **12**. The condensation gave about 90% yield for **9–12** only when performed in the presence of an insoluble base (K_2CO_3), as observed in other alkylations.[12] The crude nitriles **9–12** were pure enough to be reduced directly with hydrogen over 10% palladium on charcoal in ethanol–hydrochloric acid to give **3** and **13–15** in about 90% yield. The synthetic procedure outlined in Scheme II also allowed the preparation of a number of higher homolgues of *N*-methylputrescine **3**.

The purity of the *N*-alkylputrescines was established by GC analysis of their ethyl carbamates (obtained by reaction of **3** and **13–15** with ethyl chloroformate) or by TLC analysis on cellulose plates.

Experimental Section

Melting points were determined on a Kofler melting point aparatus and are corrected. ^1H NMR spectra and ^{13}C NMR spectra were recorded on a FT-80A spectrometer. Mass spectra were obtained with a Varian CH-7 spectrometer. Analytical gas chromatography (GC) was performed on column A (6 ft × $^1/_8$ in., 15% Apiezon L on Chromosorb P (80–100) at 200 °C), column B (same as A at 250 °C), or column C (6 ft × $^1/_8$ in., 1.5% SE-30 and 0.3% Carbowax 20M on Chromosorb W HP (100/120) at 190 °C) on a Perkin-Elmer 900 instrument. The silica gel used in column chromatography was TLC Kieselgel (Merck). TLC was performed either on silica gel F-254 plaques (Merck, 0.25-mm-layer thickness), or on precoated cellulose plaques (Merck, 0.1-mm-layer thickness). TLC on cellulose was performed by using 2-propanol:concentrated hydrochloric acid:water (8:3:2) as developing solvent, and the substances were spotted by spraying with

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a ninhydrin solution (0.5% ninhydrin, 0.4% acetic acid, 5% 2,6-lutidine in acetone) followed by heat (100 °C).

Preparation of Alkylbenzylamines. General Procedure. A solution of the benzylidenalkylamine (170 mmol) in 200 mL of anhydrous methanol kept at 5 °C was reduced with sodium borohydride (500 mmol) added in small portions, while the reaction mixture was constantly stirred. After the addition was completed, the mixture was stirred for a further hour, when a concentrated hydrochloric acid solution in ice–water was added to obtain pH 2, the methanol was then evaporated in vacuo at 60 °C, and the residual aqueous solution was adjusted to pH 11 with a normal NaOH solution. It was then extracted twice with chloroform, the extracts were dried (Na_2SO_4) and evaporated to dryness, and the oily residue was distilled in vacuo.

Methylbenzylamine (5) was obtained (86%) from benzylidenmethylamine;[13] bp 128–129 °C (140 mm), lit.[14] bp 184–185 °C (749 mm); ^{13}C NMR ($CDCl_3$) δ 35.8 (CH_3), 55.8 (CH_2).

Ethylbenzylamine (6) was obtained (94%) from benzylidenethylamine (prepared following the procedure of ref 13); bp 136–137 °C (140 mm), lit.[14] bp 191–194 °C (740 mm); ^{13}C NMR ($CDCl_3$) δ 15.2 (CH_3), 43.5 (CH_2CH_3).

Propylbenzylamine (7) was obtained (96%) from benzylidenpropylamine (prepared following the procedure of ref 13); bp 129 °C (100 mm), lit.[14] bp 210 °C (741 mm); ^{13}C NMR ($CDCl_3$) δ 11.7 (CH_3), 23.3 (CH_2CH_3), 51.3 (-$NHCH_2CH_2CH_3$).

Butylbenzylamine (8) was obtained (94%) from benzylidenbutylamine (prepared following the procedure of ref 13); bp 180–182 °C (200 mm), lit.[15] bp 226–230 °C (715 mm); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 20.5 (CH_2CH_3), 32.4 ($CH_2CH_2CH_3$), 49.3 (-$NHCH_2CH_2CH_2CH_3$).

***N*-Methylputrescine Dihydrochloride (3).** 4-Bromobutyronitrile (14.8 g, 0.1 mol) was added in three portions over intervals of 1 h to a stirred mixture of 4 g (0.033 mol) of methylbenzylamine, 13.8 g (0.1 mol) of anhydrous potassium carbonate, and 1.6 g (0.01 mol) of potassium iodide in 100 mL of 1-butanol heated under reflux. After completion of the addition, the mixture was further heated under reflux during 20 h; the mixture was then cooled and filtered, and the solid was washed with ethyl ether. The filtrate was extracted with 2 N HCl (3 × 200 mL), and the aqueous extracts were washed with ethyl ether, adjusted to pH 10 with a concentrated sodium hydroxide solution, and extracted with ether (3 × 200 mL). The extracts were dried (Na_2SO_4) and evaporated to dryness in vacuo. The crude *N*-methyl-*N*-(3-cyanopropyl)benzylamine (**9**, 5,7 g, (92%); ^{13}C NMR ($CDCl_3$) δ 13.4 (CH_2CN), 22.3 (CH_2CH_2CN), 40.6 (NCH_3), 54.2 (-NCH_2CH_2–), 61.2 (NCH_2Ph), 118.8 (CN); retention time 3 min (column B); mass spectrum, *m/e* (relative intensity) 188 (M^+, 26)) was dissolved in 150 mL of ethanol containing 5mL of concentrated HCl and was reduced with hydrogen over 6 g of 10% Pd on charcoal at 50 psi during 17 h. The catalyst was filtered off, the solution evaporated to dryness in vacuo, and the residue was crystallized from anhydrous methanol; 4.8 g (90%); mp 176 °C (lit.[8] mp 179 °C, lit.[1] mp 179–181 °C); ^{13}C NMR (D_2O) δ 23.5 ($CH_3NHCH_2CH_2$-), 24.8 ($NH_2CH_2CH_2$-), 33.9 (CH_3NH), 39.9 (CH_2NH_2), 49.3 (CH_3NHCH_2-); ^1H NMR (D_2O) δ 2.2 (CH_2CH_2, m, 4 H), 3.15 (CH_3, s, 3 H), 3.5 (CH_2NH, m, 4 H); mass spectrum, *m/e* (relative intensity) 102 (M^+, 4). Anal. Calcd for $C_5H_{14}N_2$·2HCl; C, 34.3; H, 9.1; N, 16.0. Found: C, 34.2; H, 9.0; N, 16.1.

***N*-Ethylputrescine dihydrochloride (13)** was obtained by following the procedure described for the *N*-methyl derivative **3**. The condensation of 14.8 g (0.1 mol) of 4-bromobutyronitrile with 4.4 g (0.033 mol) of benzylethylamine afforded 5.9 g (90%) of crude *N*-ethyl-*N*-(3-cyanopropyl)benzylamine (**10**) (^{13}C NMR ($CDCl_3$) δ 10.7 (CH_3), 13.5 (CH_2CN), 22.5 (CH_2CH_2CN), 46.3 (CH_2CH_3), 50.3 ($NHCH_2CH_2$–), 57.1 ($NHCH_2Ph$), 118.8 (CN); retention time 3.6 min (column B); mass spectrum, *m/e* (relative intensity) 202 (M^+, 6)), which was reduced to give 4.8 g (87%) of the dihydrochloride **13**: mp 220–221 °C (absolute ethanol); ^{13}C NMR (D_2O) δ 11.7 (CH_3), 23.7 ($NHCH_2CH_2$-), 24.9 (-$CH_2CH_2NH_2$), 39.9 (CH_2NH_2), 43.9 (-$NHCH_2CH_3$), 47.3 (-$NHCH_2CH_2$-); ^1H NMR (D_2O) δ 1.7 (CH_3, t, 3 H), 2.15 (-CH_2CH_2-, m, 4 H), 3.4 (-CH_2NH-, -CH_2NH_2, m, 6 H); mass spectrum, *m/e* (relative intensity), 116 (M^+, 6). Anal. Calcd for $C_6H_{16}N_2$·2 HCl: C, 38.1; H, 9.5; N, 14.8. Found: C, 38.2; H, 9.6; N, 15.0.

***N*-Propylputrescine dihydrochloride (14)** was obtained by following the procedure described for **3** and **13**. The condensation of 14.8 g (0.1 mol) of 4-bromobutyronitrile with 4.9 g (0.033 mol) of benzylpropylamine afforded 6.1 g (86%) of crude *N*-propyl-*N*-(3-cyanopropyl)benzylamine (**11**) (^{13}C NMR ($CDCl_3$) δ 10.1 (CH_3), 14.1 (CH_2CN), 15.9 (CH_2CH_3), 19.2 (CH_2CH_2CN), 50.1 ($NCH_2CH_2CH_3$), 53.1 ($NCH_2CH_2CH_2CN$), 56.1 (CH_2Ph), 117.5 (CN); retention time 4.4 min (column B); mass spectrum, *m/e* (relative intensity) 216 (M^+, 2)), which was reduced to give 5.1 g (90%) of the dihydrochloride **14**: mp 272 °C (absolute ethanol); ^{13}C NMR (D_2O) δ 11.9 (CH_3), 20.0 (CH_3CH_2-), 23.6 (-$CH_2CH_2CH_2NH_2$), 24.8 (-$CH_2CH_2NH_2$), 39.8 (CH_2NH_2), 47.6 ($CH_3CH_2CH_2NH$), 50.1 (-$NHCH_2$); ^1H NMR (D_2O) δ 1.2 (CH_3, t, 3 H), 2.20 (-CH_2-, m, 6 H), 3.50 (m, 6 H, CH_2NH-); mass spectrum, *m/e* (relative intensity) 130 (M^+, 3). Anal. Calcd for $C_7H_{18}N_2$·2HCl: C, 41.4; H, 9.8; N, 13.8. Found: C, 41.3; H, 9.7; N, 13.6.

***N*-Butylputrescine dihydrochloride (15)** was obtained following the above-mentioned procedure. The condensation of 14.8 g (0.1 mol) of 4-bromobutyronitrile with 5.4 g (0.033 mol) of benzylbutylamine afforded 6.5 g (85%) of crude *N*-butyl-*N*-(3-cyanopropyl)benzylamine (**12**) (^{13}C NMR ($CDCl_3$) δ 12.9 (CH_3), 13.4 (CH_2CN), 19.4 (CH_3CH_2), 22.5 (CH_2CH_2CN), 28.1 ($CH_2CH_2CH_3$), 50.9 ($NCH_2CH_2CH_2CH_3$), 52.5 ($NCH_2CH_2CH_2CN$), 57.6 (CH_2Ph), 118.8 (CN); retention time 5.6 min (column B); mass spectrum, *m/e* (relative intensity 230 (M^+, 6)), which was reduced to give 5.2 g (85%) of the dihydrochloride **15**: mp 300 °C (absolute ethanol); ^{13}C NMR (D_2O) δ 13.6 (CH_3), 19.9 (CH_2CH_3), 23.5 (-$CH_2CH_2CH_2NH_2$), 24.8 ($CH_2CH_2NH_2$), 28.3 ($CH_3CH_2CH_2$-), 39.7 (CH_2NH_2), 47.8 ($CH_3CH_2CH_2CH_2NH$-), 48.3 (-$NHCH_2$-); ^1H NMR (D_2O) δ 1.3 (t, 3 H, CH_3), 2.15 (m, 8 H, CH_2CH_2), 3.45 (m, 6 H, CH_2NH-); mass spectrum, *m/e* (relative intensity) 144 (M^+, 4). Anal. Calcd for $C_8H_{20}N_2$·2HCl: C, 44.2; H, 10.1; N, 12.9. Found: C, 44.3; H, 10.2; N, 13.0.

Analytical Separation of the *N*-Alkylputrescines 3 and 13–15. The *N*-alkyputrescine dihydrochlorides **3** and **13–15** could be identified by TLC on cellulose. The following R_f values for putrescine (R_p) were determined; *N*-methyl (**3**), R_p 1.6; *N*-ethyl (**13**), R_p 2.0; *N*-propyl (**14**), R_p 2.1; *N*-butyl (**15**), R_p 2.6.

The bases were easily transformed into their diethyl carbamates by dissolution of 100 mg of the dihydrochlorides in 2 mL of 10% NaOH, stirring with 0.2 mL of ethyl chloroformate for 1 h, and extraction of the carbamates with chloroform (2 × 0.5 mL). The ethyl carbamates had the following retention times by GC (column C); *N*-methylputrescine diethylcarbamate, 2.8 min; *N*-ethyl, 3.1 min; *N*-propyl, 4.0 min; *N*-butyl, 5.2 min; putrescine diethylcarbamate, 3.4 min.

Condensation of Methylamine and 4-Bromobutyronitrile. A stream of dry methylamine was continuously bubbled during 4 h through a stirred solution of 5 g of 4-bromobutyronitrile in 100 mL of dry tetrahydrofuran in a moisture-proof vessel kept at 20 °C. After the stream of methylamine was interrupted, the solution was stirred for further 17 h. The solvent was then evaporated to dryness, the residue was dissolved in 100 mL of 2 N HCl, and the aqueous solution was extracted with chloroform (2 × 20 mL) to eliminate unreacted 4-bromobutyronitrile. It was then brought to pH 12 with a concentrated sodium hydroxide solution and extracted with chloroform (3 × 20 ml). The dried (Na_2SO_4) chloroform extracts were evaporated to dryness. The oily residue (3.5 g) was shown by GC/MS to consist of 4-(methylamino)butyronitrile (**1**, retention time 1.3 min (column A); mass spectrum, *m/e* (relative intensity) 98 (M^+, 30)) and bis(3-cyanopropyl)methylamine (**2**, retention time 6.2 min (column A); mass spectrum, *m/e* (relative intensity) 165 (M^+, 5)) in a proportion of 1/2 of 1/1. The mixture of nitriles was reduced with hydrogen as described for the obtention of *N*-methylputrescine **3** to a mixture of *N*-methylputrescine dihydrochloride (**3**) and bis(4-aminobutyl)methylamine trihydrochloride (**4**). They were separated by chromatography on a cellulose column (6 × 50 cm) using 2-propanol/hydrochloric acid/water (8:3:2) as solvent. *N*-Methylputrescine dihydrochloride (**3**) was eluted first (R_p 1.6); 1.5 g, mp 176 °C (methanol), followed by bis(4-aminobutyl)-methylamine trihydrochloride (**4**) (R_p 1.1); 1.6 g, mp 172 °C (methanol); ^{13}C NMR (D_2O) δ 21.7 (NCH_2CH_2), 24.7 (CH_2CH_2-

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NH_2), 39.7 (CH_2NH_2), 40.5 (CH_3), 56.2 (NCH_2); ^1H NMR (D_2O) δ 2.15 (m, 8 H, CH_2CH_2), 3.25 (s, 3 H, CH_3), 3.45 (m, 8 H, CH_2N); mass spectrum, m/e (relative intensity) 174 ($M^+ + 1$, 7). Anal. Calcd for $C_9H_{23}N_3 \cdot 3HCl$: C, 38.2; H, 9.2; N, 14.9. Found: C, 38.3; H, 9.3; N, 14.7.

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Registry No. 1, 31058-09-0; 2, 89690-18-6; 3, 89690-09-5; 4, 89690-17-5; 5, 103-67-3; 6, 14321-27-8; 7, 2032-33-9; 8, 2403-22-7; 9, 89690-05-1; 10, 89690-06-2; 11, 89690-07-3; 12, 89690-08-4; 13, 89690-10-8; 14, 89690-11-9; 15, 89690-12-0; *N*-ethylputrescine diethylcarbamate, 89690-13-1; *N*-propylputrescine diethylcarbamate, 89690-14-2; *N*-butylputrescine diethylcarbamate, 89690-15-3; *N*-methylputrescine diethylcarbamate, 89690-16-4; methylamine, 74-89-5; benzylidenemethylamine, 622-29-7; benzylideneethylamine, 6852-54-6; benzylidenepropylamine, 6852-55-7; benzylidenebutylamine, 1077-18-5; 4-bromobutyronitrile, 5332-06-9.

Oxidative Hydrolysis of γ-Thioacetalated Phosphonium Salts. Influence of the Counterion on the Course of the Reaction

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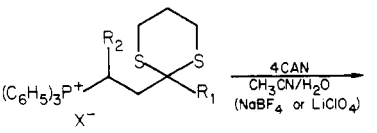
A fast reaction and an easy workup make cerium(IV) ammonium nitrate (CAN) an attractive reagent for oxidative hydrolysis of 1,3-dithianes to the corresponding carbonyl compounds.[1] We proposed a mechanism based on electron transfer from sulfur to the metal followed by chemical reaction with the medium[2] that is essentially identical with the one proposed for the electrochemical hydrolysis.[3] We have already stated[4] that the electrochemical oxidation can be complicated by the presence of halide counterions, and ion exchange with nonoxidizable counterions is advantageous. We report here on oxidative hydrolysis of γ-thioacetalated phosphonium fluoroborates, perchlorates, or nitrates with cerium(IV) and emphasize the "abnormal" oxidation of nitrate salts.

The oxidation of phosphonium fluoroborates **1a–e** or perchlorates **1a′–e′** by 4 equiv of cerium(IV) affords, in good yield, the expected γ-aldehydic or ketonic phosphonium salts **2a–e** and **2a′–e′** (Scheme I).

The oxidation of γ-thioacetalated ketonic or aldehydic phosphonium nitrates **3a–c** (Scheme II) does not consume 4 equiv of cerium(IV) but is complete after 2 equiv of reagent are added. The ^1H NMR spectra of isolated compounds **4** (Scheme II) indicate the presence of the dithiane group, and the IR spectra show a new strong absorption near 1030 cm^{-1} which can be attributed to a sulfoxide group. The elimination of the triphenylphosphonio group by a Wittig reaction with benzaldehyde affords the olefin **5** in which the presence of an oxygen was determined by mass spectrometry and evidence for a sulfoxide group was given by IR (strong absorption near 1030 cm^{-1}). Olefin **5a** also was independently prepared by a Wittig reaction of **3a** with benzaldehyde[5] followed by the oxidation of **6a** with sodium periodate to the corresponding monosulfoxide.[6]

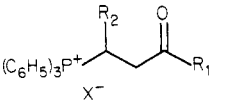
This is, to our knowledge, the first example of oxidation of a 1,3-dithiane to a monosulfoxide by cerium(IV). This "abnormal" oxidation pathway requires the presence of a phosphonium group with a nitrate counterion. Indeed, phosphine oxide **7** with only a partial positive charge on

Scheme I



1

a (X^- = BF_4^-), a′ (X^- = ClO_4^-): R_1 = CH_3; R_2 = H
b (X^- = BF_4^-), b′ (X^- = ClO_4^-): R_1 = CH_3; R_2 = CH_3
c (X^- = BF_4^-), c′ (X^- = ClO_4^-): R_1R_2 = $-(CH_2)_3-$
d (X^- = BF_4^-), d′ (X^- = ClO_4^-): R_1 = H; R_2 = CH_3
e (X^- = BF_4^-), e′ (X^- = ClO_4^-): R_1 = H; R_2 = C_6H_5

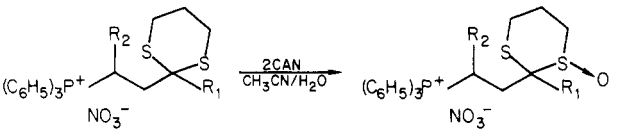


2

yield, %

a, 83	a′, 80
b, 87	b′, 75
c, 58	c′, 67
d, 68	d′, 74
e, 75	e′, 82

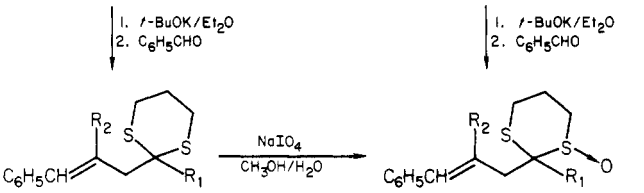
Scheme II



3 **4**

a, R_1 = CH_3; R_2 = H
b, R_1R_2 = $-(CH_2)_3-$
c, R_1 = H; R_2 = H

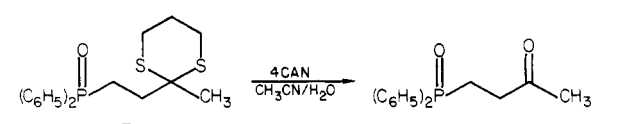
	IR(ν_{S-O}), cm^{-1}	yield (%)
a	1030	75
b	1030	68
c	1028	63



6a **5**

(yield = 93%)

	IR(ν_{S-O}), cm^{-1}	yield (%)
a	1052, 1041	70 ($NaIO_4$:80)
b	1050, 1032	75
c	1052, 1041	67



7 **8** (yield = 79%)

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