

Generation of nitryl chloride from chlorotrimethylsilane-acetyl nitrate reaction: A one-pot preparation of *gem*-chloronitro compounds from oximes

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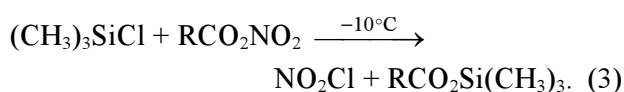
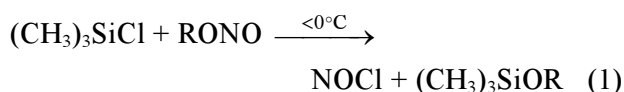
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Abstract. While *iso*-amyl nitrite reacts with chlorotrimethylsilane to give NOCl, *iso*-amyl nitrate does not yield NO₂Cl with silicon reagent. However, acetyl nitrate reacts successfully with chlorotrimethylsilane to give nitryl chloride, which is characterized by its UV spectrum. If it is generated in presence of ketoximes, *gem*-chloronitro as well as *gem*-chloronitroso compounds are formed in almost equal amounts, which together account for up to 80% yield. This is possibly the simplest one-pot reaction for the preparation of *gem*-chloronitro compounds which find several synthetic applications. If NO₂Cl is generated in presence of cycloalkenes, the corresponding 1,2-dichlorocycloalkanes are obtained. Considering the evidence in hand, it is proposed that NO₂Cl, initially formed by chlorotrimethylsilane-acetyl nitrate reaction, decomposes to Cl₂ and N₂O₄. Then chlorine reacts with oximes to produce first *gem*-chloronitroso compounds, which are oxidized by NO₂Cl or N₂O₄ to *gem*-chloronitro compounds, and with cycloalkenes it gives dichlorocycloalkanes.

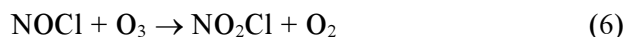
Keywords. Nitryl chloride; acetyl nitrate; chlorotrimethylsilane; *gem*-chloronitro compounds; *gem*-chloronitroso compounds; oximes; chlorination; cycloalkenes.

1. Introduction

The smooth and successful reaction of chlorotrimethylsilane (TMSCl) with amyl or *iso*-amyl nitrite to generate nitrosyl chloride *in situ* under anhydrous conditions either in the presence or in the absence of a solvent (1)¹ prompted us to attempt a similar reaction of TMSCl with amyl nitrate for the preparation of nitryl chloride. We found that this simple logic did not work the way it was expected to, as the starting compounds remained totally intact even after stirring for a long time at room temperature (2). However, we discovered that acetyl nitrate reacted efficiently with TMSCl to produce NO₂Cl, (3).



The only practical method of preparing nitryl chloride in the laboratory is by the reaction of chlorosulphonic acid with nitric acid² (4). An old method of its preparation consisted of passing chlorine gas on hot silver nitrate (5). It can be prepared by the oxidation of NOCl with ozone³ (6).



Nitryl chloride is widely recognised as an important product of interaction between chloride ions in sea salt aerosol and N₂O₅ present in marine atmosphere, particularly near urban centres that generate huge amounts of nitrogen oxides through fossil fuel burning. The nitryl chloride then dissociates into nitric oxide and chlorine, (7), the latter being responsible for the increased production of ozone in such marine environment.⁴

Nitryl chloride is known to react with unsaturated compounds^{5c,j,6} to give *vic*-chloronitro compounds and/or *vic*-dichloro compounds,^{2a,5} and to nitrate^{6e,7}

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as well as chlorinate⁷ aromatic compounds. It has been found to chlorinate carbonyl compounds⁸ and strained hydrocarbons.⁹ It is proposed that nitril chloride formed *in vivo* may be involved in tyrosine nitration as well as protein modification and tissue injuries.^{2c,10}

We found that nitril chloride can be conveniently generated under anhydrous conditions by the reaction of acetyl nitrate with chlorotrimethylsilane and present here the results of its reactions *in situ* with oximes and olefins.

2. Experimental

2.1 General

The NMR spectra were recorded on JEOL FX90Q or Bruker AC-250 instrument using CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard. The IR spectra were taken on Nicolet Impact 400D single beam instrument using KBr pellets for solids and as thin film between NaCl plates in case of liquids. Gas chromatographic (GC) analyses were carried out on a Varian Vista 6000 instrument using 15% of FFAP on Chromosorb-W column (2 × 2 mm i.d.).

Acetic anhydride and dichloromethane were distilled over P₂O₅ before use. Silica gel (Qualigens) used for column chromatography (60–120 mesh size) was activated by heating to 110°C before use.

Cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, cyclododecanone, norcamphor, camphor, 4-heptanone and propiophenone were obtained from Aldrich chemical company. Acetophenone was obtained from SD Fine Chemicals. Dibenzyl ketone was prepared by the literature procedure.¹¹ Hydroxylamine hydrochloride was of A.R. grade.

Cyclopentene, cyclohexene, and cycloheptene were prepared by dehydration of the corresponding alcohols. (Cyclopentanol and cycloheptanol were prepared by reducing cyclopentanone and cycloheptanone using sodium-wet ether.) Cyclooctene, cyclododecene (*cis-trans* mixture) and norbornene were purchased from Aldrich. Chlorotrimethylsilane, purchased from Spectrochem, was distilled over quinoline (1–2%).

Acetyl nitrate was prepared according to literature procedure¹² by adding conc HNO₃ (density 1.40) to acetic anhydride, freshly distilled over P₂O₅. The ketoximes 1–11 were prepared by known method.¹³

All the liquid starting compounds obtained from commercial sources were distilled and their purity was checked by GC before use.

2.2 General procedure for the reaction of oximes with TMSCl-AcONO₂

A solution of 10 mmol of oxime in 15 mL of CH₂Cl₂, distilled over P₂O₅, was placed in a 100 mL two-necked flask fitted with a CaCl₂ guard tube and a dropping funnel, and cooled to –10°C. Chlorotrimethylsilane (12–13 mmol) in 2 mL of CH₂Cl₂ was added drop-wise with stirring. Acetyl nitrate (12–13 mmol, prepared by mixing 12 mL of Ac₂O with 2 mL of conc. HNO₃ of density 1.40) was added cautiously over a period of 1–1.5 h. The solution turned blue indicating the formation of chloronitroso derivative. The blue colour persisted even after stirring the reaction mixture for an additional period of 1 h. The reaction mixture was then treated carefully with 20 mL of ice-cold water. After separating the organic layer, the aqueous layer was extracted with CH₂Cl₂ (2 × 15 mL). The CH₂Cl₂ layers were combined and washed with water (2 × 20 mL), 5% NaHCO₃ solution (2 × 20 mL), again water (20 mL), and finally with saturated NaCl solution (20 mL). After drying over Na₂SO₄, the solvent was removed and the residue was chromatographed on silica gel column using petroleum ether (b.p. 50–55°C) as eluant. The regenerated ketone (8–10%) passed through first, followed by *gem*-chloronitroso compound, and finally *gem*-chloronitro compound. The conversion is quantitative (table 1). The products were identified by their spectral data (see tables S1 and S2) (see supporting information). The spectral data of only **9a**, **3b** and **9b**, which are not reported in the literature, are tabulated in table 2 in the main text. *gem*-Chloronitroso compounds were found to be much less stable than the *gem*-chloronitro compounds.

2.3 Reaction of cycloalkenes with TMSCl-AcONO₂: Preparation of 1,2-dichlorocycloalkanes

2.3a General procedure: A solution of 10 mmol of cycloalkene in 5 mL of CH₂Cl₂, distilled over P₂O₅, was placed in a 100 mL round bottomed flask, and cooled to –10°C. Chlorotrimethylsilane (1.40 g, 10.94 mmol) was added drop-wise from a pressure equalizing dropping funnel fitted with a CaCl₂ guard tube. Acetyl nitrate (prepared freshly from 15 mL of acetic anhydride, distilled over P₂O₅ and 1.12 g of conc. HNO₃, *d*, 1.40), in 5 mL of CH₂Cl₂ was added slowly. The reaction mixture was allowed to stir for 2–3 h, and treated with 10 mL of cold water. The

Table 1. Reaction of ketoximes with ClSiMe₃-AcONO₂

Entry	Oxime of	Yield (%) ^a	
		<i>gem</i> -chloronitroso Compound	<i>gem</i> -chloronitro compound
1	Cyclopentanone	1a ^{14,15,29c,32} (45)	1b ^{14,22} (32)
2	Cyclohexanone	2a ^{14-16,29d} (40)	2b ^{14,22,28,29d} (30)
3	Cycloheptanone	3a ^{14,32d} (40)	3b ^b (32)
4	Cyclooctanone	4a ^{14,32d} (35)	4b ¹⁴ (42)
5	Cyclododecanone	5a ^{14,29c} (30)	5b ^{14,27} (33)
6	Norcamphor	6a ²⁵ (32)	6b ^{20,21} (35)
7	Camphor	7a ^{17,26} (30)	7b ^{18,21,26,29d} (37)
8	Acetophenone	8a ¹⁶ (34)	8b ^{19,20} (30)
9	Propiophenone	9a ^b (32)	9b ^b (35)
10	4-Heptanone	10a ²⁴ (45)	10b ²⁴ (33)
11	Dibenzylketone	11a ^{23,24} (40)	11b ²⁴ (43)

^aSome amount (8–10%) of regenerated parent ketone was also isolated.

^b**3b**, **9a** and **9b** are not known in the literature.

Table 2. Spectral data for **9a**, **3b** and **9b**.

Compd.	IR, ν (cm ⁻¹) (selected)	¹ H NMR (CDCl ₃), δ (ppm)	¹³ C NMR (CDCl ₃), δ (ppm)
9a	2974, 2937, 2886, 1624 1559, 1462, 1392, 1295, 1086, 891, 766, 678	(NMR was not done; oxidized to 9b)	
3b	2940, 2862, 1569, 1460, 1341, 1176, 1021, 969	2.65 (<i>m</i> , 2H), 2.36 (<i>m</i> , 2H), 1.58–1.65 (<i>m</i> , 8H).	22.76, 28.20, 42.39, 108.59
9b	3074, 2991, 2950, 2893, 1559, 1455, 1352, 1326, 1222, 912, 819, 721, 700	1.09 (<i>t</i> , 3H, <i>J</i> = 7.5 Hz), 3.02 (<i>q</i> , 2H, <i>J</i> = 7.5 Hz), 7.43–7.53 (<i>m</i> , 5H)	8.75, 29.11, 123.51, 128.16, 128.85, 129.17, 131.69

Table 3. Reaction of ClSiMe₃-AcONO₂ with olefins.

Entry	1,2-Dichloro-	Reaction time (h)	Yield (%)
1	-cyclopentane	2.0	60
2	-cyclohexane	2.5	76
3	-cycloheptane	2.5	70
4	-cyclooctane	3.0	73
5	-cyclododecane	3.0	83
6	2,3-dichloro-norbornane	2.5	75

layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 15 mL). The combined CH₂Cl₂ extracts were washed with water (2 × 15 mL), 5% NaHCO₃ solution (2 × 15 mL) and saturated NaCl solution (2 × 15 mL). After drying over Na₂SO₄, the solvent was removed and the residue was chromatographed on a silica gel column using petroleum ether (50–55°C) as eluant to obtain pure

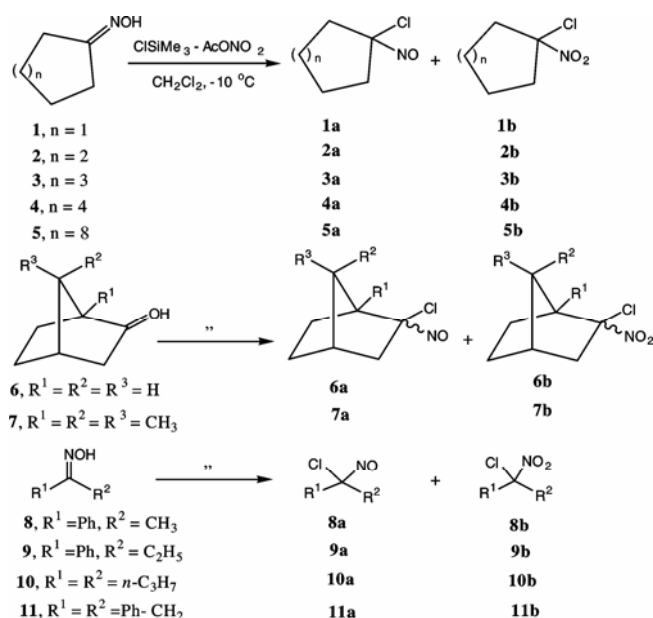
1,2-dichlorocycloalkanes, (table 3). The spectral data are given in table 4. (Authentic samples of 1,2-dichlorocycloalkanes **12a–17a** were prepared by passing chlorine to solutions of 1–6 in CH₂Cl₂ at –10°C).

3. Results and discussion

The principal aim of the present study was to know whether TMSCl would react with an organic nitrate to produce nitryl chloride which could be allowed to react *in situ* with oximes to obtain directly *gem*-chloronitro compounds which have many useful synthetic applications.²⁹ Based on the known fact that NOCl reacts with oximes to produce *gem*-chloronitroso compounds in almost quantitative yield,^{1a,c,30} we surmised that oximes when reacted with NO₂Cl might deliver *gem*-chloronitro compounds. If successful, this would be the simplest

Table 4. Spectral data of 1,2-dichloro compounds.

Entry	Compd.	IR	¹ H NMR (CDCl ₃) (δ)
1	1c	2955, 2859, 1457, 1448, 1322, 823, 743, 721, 695	3.97–4.04 (<i>m</i> , 2H), 1.42–2.15 (<i>m</i> , 6H)
2	2c	2950, 2862, 1455, 1445, 1347, 1212, 990, 845, 745, 738, 692	3.9–4.2 (<i>m</i> , 2H), 1.26–2.27 (<i>m</i> , 8H)
3	3c	2943, 2867, 1446, 1455, 1259, 1222, 778, 757, 695, 633	4.15–4.44 (<i>m</i> , 2H), 1.42–3.92 (<i>m</i> , 10H)
4	4c	2934, 2862, 1475, 1449, 1244, 1223, 869, 833, 776, 730, 678	4.21–4.29 (<i>m</i> , 2H), 1.35–2.30 (<i>m</i> , 12H)
5	5c	2934, 2872, 1471, 1445, 1284, 1248, 891, 767, 726, 736, 664	4.20–4.26 (<i>m</i> , 2H), 1.10–2.15 (<i>m</i> , 20H)
6	6c	2924, 2851, 1480, 1449, 1346, 1253, 865, 846, 782, 730, 668	3.87–3.91 (<i>m</i> , 2H), 1.11–2.51 (<i>m</i> , 8H)

**Scheme 1.**

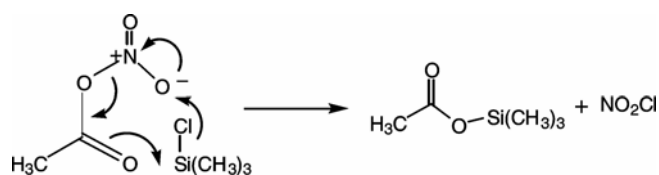
one-pot method to prepare *gem*-chloronitro compounds, as the other known methods involve more complicated two-step reactions.¹⁴

When the oximes **1–11** in CH₂Cl₂ were treated with TMSCl and AcONO₂, *gem*-chloronitro compounds **1b–11b** were obtained. However, they were accompanied by almost equal amounts of the corresponding chloronitroso derivatives **1a–11a** and small amounts of parent ketones (scheme 1, table 1). The products could be easily separated by chromatography on silica gel column using petroleum ether (b.p. 50–55°C) as eluant. They were identified by their spectral data (see tables S1 and S2, supporting

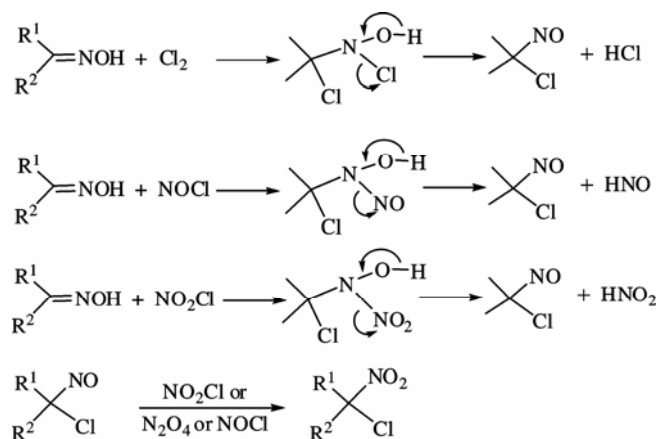
information). All the *gem*-chloronitroso and *gem*-chloronitro compounds, except **3b**, **9a** and **9b**, are known in the literature (see table 1 for references). The structural assignment of **3b**, **9a** and **9b** is tentative and is based on their spectral data (table 2), and similarity of their characteristics with those of other compounds in their respective group.

The chloronitroso compounds, except solids, decompose gradually even at room temperature. They can be oxidized to chloronitro compounds by treating them again with TMSCl and AcONO₂ or with cetyltrimethylammonium hypochlorite,³¹ thus increasing the total yield of the chloronitro compounds. The chloronitro compounds are far more stable than the chloronitroso compounds.

The formation of NO₂Cl in the mixture of TMSCl and AcONO₂ was indicated by the UV spectrum of the mixture. Literature reports describe two absorption peaks for NO₂Cl in various solvents. One of them is a weak band of fixed λ_{max} at 460 nm and the other one a strong absorption of variable λ_{max} , which depends on the solvent, ranges from 222 nm in MeCN to 373 nm in MeNO₂ including a 248 nm peak in MeCOOH.^{2b} When we measured the UV spectrum of TMSCl-AcONO₂ mixture, we observed a weak absorption at λ_{max} of 458 nm and six strong peaks between 202 and 267 nm including two peaks at 246 and 252 nm. One of the latter two absorptions can be assigned to NO₂Cl in MeCOOH and the remaining five can arise from various chromophoric groups present in the mixture. We presume that the presence of 458 nm peak and 246 or 252 nm peak is a good indication for the formation of NO₂Cl in the TMSCl-AcONO₂ mixture.



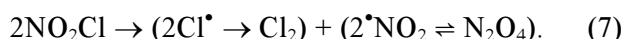
Scheme 2.



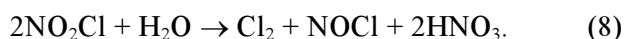
Scheme 3.

It is interesting to note that NO_2Cl is generated when TMSCl combines with AcONO_2 but not with *iso*- AmONO_2 . We attribute this to the stronger nucleophilicity of the carbonyl oxygen of AcONO_2 , in initiating the attack on silicon as shown in scheme 2, which is not possible by an alkyl nitrate.

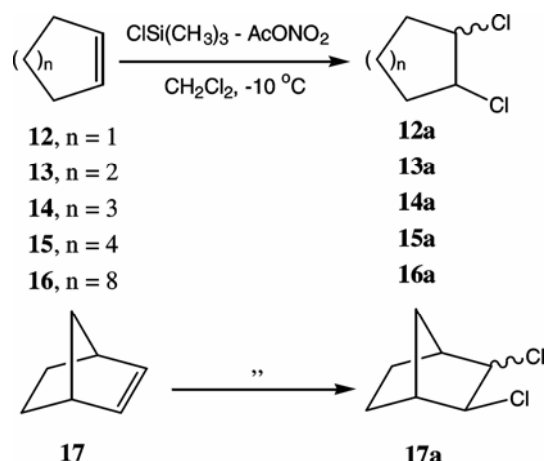
The nitryl chloride may or may not react directly with the oximes. It is well known to undergo spontaneous decomposition to chlorine and nitric oxide^{2b,c} (7).



The chlorine so formed would then react with oxime to produce *gem*-chloronitroso compounds³² (scheme 3), which are then oxidized by nitryl chloride or nitric oxide or even nitrosyl chloride which could form as shown in (8).



In separate experiments we found that treating *gem*-chloronitroso compounds with TMSCl and AcONO_2 converted them into *gem*-chloronitro compounds. This indicates that the chloronitroso compounds are initially formed, which are then oxidised in the second step (scheme 3).



Scheme 4.

3.1 Chlorination of olefins with TMSCl - AcONO_2 mixture

Since chlorine was suspected to be the main player in the conversion of oximes to *gem*-chloronitroso derivatives, we wanted to confirm its formation by trapping it through its addition to olefinic compounds. We treated six cycloalkenes **12**–**17** with chlorotrimethylsilane and acetyl nitrate. In each case we obtained the corresponding 1,2-dichlorocycloalkane as major product in good yield (scheme 4), accompanied by some minor products, which were not identified. The dichlorocycloalkanes were isolated in pure form by column chromatography and identified by their spectral characteristics (table 4) and comparing with authentic samples prepared by chlorination of the cycloalkenes with chlorine from an external source. We have not examined the stereochemistry of the dichloro compounds.

The formation of dichlorocycloalkanes **12a**–**17a** from the cycloalkenes **12**–**17** on treating with TMSCl and AcONO_2 is a clear indication that chlorine is formed, which then adds to the cycloalkenes.

Nitryl chloride is known to chlorinate olefins also by free radical mechanism.^{5d,33} However, in these cases the product is a mixture of several isomers, whereas in the present study we obtained essentially one isomer. Hence, we believe that here it is the addition of molecular chlorine by ionic mechanism.

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Supplementary information

For supplementary information tables S1 and S2 see www.ias.ac.in/chemsci website.

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