J. Chem. Sci. Vol. 123, No. 4, July 2011, pp. 433–441.

Oxidation of *gem*-chloronitroso- and *vic*-chloronitroso-alkanes and -cycloalkanes to respective chloronitro compounds by novel cetyltrimethylammonium hypochlorite reagent†

ABDULKARIM H A MOHAMMED[a,b] and GOPALPUR NAGENDRAPPA[a,*]

[a]Department of Chemistry, Bangalore University, (Central College Campus), Bangalore 560 001, India
[b]University of Sana'a, Sana'a, Yemen
e-mail: gnagendrappa@gmail.com

MS received 28 November 2010; revised 23 April 2011; accepted 3 May 2011

Abstract. Cetyltrimethylammonium hypochlorite (CTAHC) is prepared and used as an oxidizing agent for nitroso group to nitro group. The *gem*-chloronitroso and *vic*-chloronitroso compounds are prepared respectively from ketoximes and olefins by reacting with NOCl generated *in situ* from chlorotrimethylsilane (TMSCl) and *iso*-amyl nitrite. CTAHC oxidizes *gem*-chloronitroso and *vic*-chloronitroso compounds to the corresponding chloronitro derivatives. While *gem*-chloronitro compounds are obtained in good yields, the *vic*-chloronitro derivatives are formed in moderate yields, because of the propensity of the *vic*-chloronitroso group to tautomerize to α-chlorooxime. The present method is simple and practical, particularly for the preparation of *vic*-chloronitro compounds, considering the fact that the known methods of their preparation are few and quite involved.

Keywords. Cetyltrimethylammonium hypochlorite; oxidation; *gem*-chloronitroso compounds; *vic*-chloronitroso compounds; *gem*-chloronitro compounds; *vic*-chloronitro compounds; nitroso-to-nitro conversion; nitrosyl chloride; oxime.

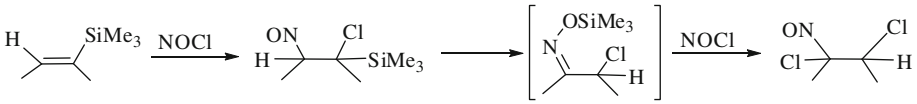
1. Introduction

gem-Chloronitro-alkanes and -cycloalkanes are valuable starting compounds in organic synthesis. They are used to prepare nitroalkanes and nitrocycloalkanes[1] by reductive dechlorination,[2] and find other useful applications in organic synthetic procedures.[3] They are generally prepared by the oxidation of the corresponding *gem*-chloronitroso compounds using oxidizing agents, such as ozone,[4] oxone,[5] chlorotriazines,[2a] chloroperoxidases,[6] peroxyacetic acid,[2b] trifluoroperoxyacetic acid,[7] nitric acid,[8] hydrogen peroxide,[9] N-bromosuccinimide,[10] and sodium hypochlorite alone[11] or with tetrabutylammonium hydrogen sulphate as phase transfer catalyst in a biphasic system.[2d] Recently, we have shown that nitryl chloride produced *in situ* oxidizes the nitroso group to nitro group.[12]

The required starting *gem*-chloronitroso compounds are prepared by the chlorination of oximes using elemental chlorine,[13] *t*-butylhypochlorite as well as hypochlorous acid,[11,14] N-*t*-butyl-N-chlorocyanamide,[15] hydrogen peroxide-hydrochlric acid,[2b] N-chlorourea,[16] and N,N'-dichlorobis(2,4,6-trichlorophenyl)urea.[17] Nitrosyl chloride[18] and nitryl chloride[12] are found to be efficient reagents to convert oximes to *gem*-chloronitroso compounds.

vic-Chloronitro compounds exhibit a variety of biological activities.[19] They are found to act as insecticides,[20] fungicides,[21] bactericides,[22] miticides,[23] and herbicides.[21b] Vinylic nitroolefins, obtained by the elimination of HCl from *vic*-chloronitro compounds, have been used as dienophiles in several synthetically useful Diels–Alder reactions, and undergo Michael addition with a variety of nucleophiles.[1d, 24d, 25] In spite of their many applications, to our knowledge, there are only two methods of synthesis of *vic*-chloronitro compounds. One is by a free radical addition of NO_2Cl or N_2O_4-chlorine mixture with olefins, especially in the gas phase, which leads to a mixture of several nitration products including the *vic*-chloronitro derivatives.[24] The second one is the addition of nitrosyl chloride to alkenes first to form *vic*-chloronitroso compounds, the latter are then allowed to stand for several days with excess nitrosyl chloride which slowly oxidizes them to *vic*-chloronitro derivatives.[26] Both these methods pose problems of purification and give poor yields.

*For correspondence
†Extracted from the Ph D Thesis of AHAM.



Scheme 1. Reaction of NOCl with vinylsilanes.

While NOCl reacts with oximes to produce *gem*-chloronitroso derivatives, it adds to alkenes and cycloalkenes to give *vic*-chloronitroso compounds.[18b, 27] We have shown earlier that NOCl, conveniently generated *in situ* by the reaction of amyl or *iso*-amyl nitrite with TMSCl under anhydrous conditions, brings about both these reactions in tandem in its reaction with vinylsilanes[18a,b] (scheme 1).

Since the methods employed for the oxidation of both *gem*- and *vic*-chloronitro compounds, especially the latter ones, are beset with deficiencies, we thought that introducing more efficient alternative routes for the preparation of chloronitrocycloalkanes and -alkanes would be useful.

We have developed cetyltrimethylammonium hypochlorite (CTAHC) as a novel oxidant for conversion of both *gem*- and *vic*-chloronitroso compounds to their corresponding chloronitro derivatives. This was formulated based on the fact that cetyltrimethylammonium group is an efficient and supportive countercation in such successful reagents as cetyltrimethylammonium permanganate (CTAP)[28] and dichromate (CTAD),[29] and that hypochlorite is a good oxidant for conversion of nitroso to nitro group.[2d, 11] We have prepared CTAHC and found it to be a handy, practical oxidizing agent in homogeneous organic solvent media for oxidizing both *gem*-chloronitroso and *vic*-chloronitroso compounds, prepared respectively by reacting oximes and olefins with NOCl generated *in situ*.[18a,b,g] The results are reported here.

2. Experimental

2.1 *General*

The NMR spectra were recorded on a JEOL FX90Q or Bruker AC-250 instrument using $CDCl_3$ 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 thin film between NaCl plates for liquids. GC analyses were carried out on a Varian Vista 6000 instrument using 15% of FFAP on chromosorb-W column (2 × 2 mm i.d.). The solvents were distilled before use. Diethyl ether was washed with 10% $FeSO_4$ solution, dried over $CaCl_2$, refluxed over sodium wire-benzophenone and distilled. 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, and propiophenone were obtained from Aldrich Chemical Company. Acetophenone was obtained from SD Fine Chemicals. Dibenzyl ketone was prepared by the literature procedure.[30a] Hydroxylamine hydrochloride was of A.R. grade. The oximes were prepared following the known procedure.[30b]

Cyclopentene, cyclohexene, cycloheptene and 1-heptene 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 (TMSCl) and cetyltrimethylammonium bromide were purchased from Spectrochem, and TMSCl was distilled over quinoline (1–2%). *iso*-Amyl nitrite was prepared by the literature procedure.[30c] The liquid starting compounds obtained from commercial sources were distilled and their purity checked by G.C. before use.

2.2 *Preparation of cetyltrimethylammonium hypochlorite*

A solution of cetyltrimethylammonium bromide (CTAB, 21.0 g, 62.5 mmol) in 100 mL of dichloromethane was placed in a 1 L 2-necked round bottomed flask equipped with a mechanical stirrer and a dropping funnel. Sodium hypochlorite solution (120 mL) containing 4% chlorine (only Merck company NaOCl worked well; NaOCl solution from other two commercial sources did not give CTAHC) was added over 5 min. The mixture was stirred for 3–4 h; it was then transferred to a separating funnel and allowed to stand until the layers separated (there was frothing that took time to settle). The organic layer was collected, the solvent was removed on a rotary evaporator and the white residue was dried over P_2O_5 under vacuum, yield, 15.6 g (81%). It was recrystallised from hot ethyl acetate. It decomposed on heating above 200°C without melting, and was found to be soluble in chlorohydrocarbons and also water.

2.3 *Synthesis of gem-chloronitroso compounds: General procedure*

A solution of 10 mmol of oxime in 10 mL of dry diethyl ether was taken in a two-necked flask equipped with a short condenser fitted with a $CaCl_2$ guard tube, and a dropping funnel. It was cooled to −10°C with stirring, and 1.03 g (12 mmol) of TMSCl was introduced. *iso*-Amyl nitrite (1.40 g, 12 mmol) was added over a period of 15 min. The reaction mixture was kept stirred for 1.0–2.5 h depending on the oxime (table 1), and as determined by TLC analysis. Water (10 mL) was added and the contents of the flask were transferred to a separating funnel (the flask was rinsed with 5 mL ether). The organic layer was separated and washed successively with water (2 × 15 mL), saturated NaCl solution (2 × 15 mL), and dried over Na_2SO_4. The solvent was removed on a rotary evaporator under reduced pressure and the residue was chromatographed on silica gel (60–120 mesh) using petroleum ether (b.p. 50–55°C) as eluant. The pure *gem*-chloronitroso products **1a**–**10a** eluted as blue band. The compounds **5a**, **6a**, and **11a** were solids, and were recrystallised from ethanol. The yields were 93–97% (table 1). Their identity was established by comparing their spectral properties with those we reported previously in the case of the reaction of NO_2Cl with the same oximes.[12] We have reported the crystal structure the compound **5a**.[18d]

2.4 *Preparation of gem-chloronitro compounds: General procedure*

A solution of 10 mmol of *gem*-chloronitroso compound in 10 mL of dichloromethane was placed in a 100 mL two-necked flask equipped with dropping funnel and a condenser fitted with a $CaCl_2$ guard tube. A solution of 4.9 g (14 mmol) of CTAHC in 15 mL of dichloromethane was added over 15 min. The mixture was stirred until the chloronitroso compound disappeared, as confirmed by GC analysis. The reaction needed 3–13 h for completion depending on the chloronitroso compound (table 2). The solvent was removed on a rotary evaporator under vacuum; the residue was dissolved in 50 mL of ether. The ensuing solution was washed with water (30 × 20 mL) and saturated NaCl solution (3 × 20 mL), and dried over Na_2SO_4. After removing the solvent the product was chromatographed on silica gel (60–120 mesh) using petroleum ether (50–55°C) as eluant. The isolated yields of the *gem*-chloronitro compounds varied from 50–70% (table 2).

2.5 *Oxime to gem-chloronitro compound: One-pot reaction*

In a 100 mL two-necked flask, equipped with a dropping funnel and condenser fitted with a $CaCl_2$ guard tube, was placed 10 mmol of oxime, 5 mL of dry ether was added and the solution was cooled to −10°C with stirring. TMSCl (1.2 g, 13 mmol) was added dropwise, the solution was stirred for further 10–15 min, and then 1.4 g (12 mmol) of *iso*-amyl nitrite was added over 15–20 min. The reaction mixture was stirred for 1–2.5 h (as mentioned in table 1), and allowed to attain room temperature. To this was added a solution of 6.0 g (17.8 mmol) of CTAHC in 25 mL of dichloromethane and the mixture was stirred until the chloronitroso compound disappeared (TLC analysis). The volatile substances were removed on a rotary evaporator under

Table 1. Preparation of *gem*-chloronitroso compounds form oximes and NOCl.

Entry	Oxime of	*gem*-Chloronitroso Compds[a]		Reaction time (h)	Yield (%)	m.p. (°C)[b]
1	Cyclopentanone	1-Chloro-1-nitrosocyclopentane	(**1a**)	1.5	93	
2	Cyclohexanone	1-Chloro-1-nitrosocyclohexane	(**2a**)	1.0	95	
3	Cycloheptanone	1-Chloro-1-nitrosocycloheptane	(**3a**)	1.5	95	
4	Cyclooctanone	1-Chloro-1-nitrosocyclooctane	(**4a**)	1.5	96	
5	Cyclododecanone	1-Chloro-1-nitrosocyclododecane	(**5a**)	1.5	98	50–52
6	Norcamphor	2-Chloro-2-nitrosonorbornane	(**6a**)	1.0	98	42–44
7	Acetophenone	1-Chloro-1-nitroso-1-phenylethane	(**7a**)	2.5	93	
8	Propiophenone	1-Chloro-1-nitroso-1-phenylpropane	(**8a**)	2.0	94	
9	4-Heptanone	4-Chloro-4-nitrosoheptane	(**9a**)	1.0	96	
10	Dibenzoyl ketone	2-Chloro-2nitroso-1,3-diphenylpropane	(**10a**)	1.0	97	93–95

[a]We had earlier obtained the compounds **1a**–**10a** by reacting oximes with NO_2Cl[12]
[b]Except **5a**, **6a**, and **10a**, the others are liquids, and decompose rapidly on heating

Table 2. Oxidation of *gem*-chloronitroso to *gem*-chloronitro compounds by CTAHC.

Entry	*gem*-Chloronitro compound		From 1a–10a (Two steps)		From 1a–10a (One-pot)	
			Reaction time (h)	Yield (%)	Reaction time (h)	Yield (%)
1	1-Chloro-1-nitrocyclopentane	(**1b**)	13	70	16	72
2	1-Chloro-1-nitrocyclohexane	(**2b**)	13	74	16	77
3	1-Chloro-1-nitrocycloheptane	(**3b**)	12	70	14	71
4	1-Chloro-1-nitrocyclooctane	(**4b**)	13	68	15	73
5	1-Chloro-1-nitrocyclododecane	(**5b**)	4	70	5	78
6	2-Chloro-2-nitronorbornane	(**6b**)	10	70	13	75
7	1-Chloro-1nitro-1-phenylethane	(**7b**)	3	50	5	51
8	1-Chloro-1-nitro-1-phenylpropane	(**8b**)	3	50	5	53
9	4-Chloro-4-nitroheptane	(**9b**)	14	53	16	60
10	2-Chloro-2-nitro-1,3-diphenylpropane	(**10b**)	12	60	14	65

vacuum, the residue was dissolved in 50 mL of ether, and the solution was washed with water (3 × 25 mL), saturated NaCl (3 × 20 mL), and dried over Na_2SO_4. After removing the solvent, *gem*-chloronitro product was obtained as mentioned in the previous experiment. The yields were in the range of 51–78% (table 2).

2.6 *Preparation of vic-chloronitroso compounds: General procedure*

2.6a *Method A—without solvent*: In a 100 mL two-necked flask equipped with a dropping funnel and a condenser fitted with a guard tube were placed 10 mmol of cycloalkene and cooled to −10°C. TMSCl was added drop-wise with stirring, followed by *iso*-amyl nitrite (12 mmol) over a period of 20 min. The reaction was followed by GC. The time taken for completion of the reaction varied widely depending on the cycloalkene, (table 3). When the cycloalkene had disappeared water (10 mL) was added, the white dimeric solid product was filtered off, washed with 10 mL of 10% $NaHCO_3$ solution, water (10 mL), and carefully with a little alcohol (under vacuum). The *vic*-chloronitroso compound was separated from the byproduct α-chlorooxime by chromatographing on silica gel. (Eluant: petroleum ether, b.p. 50–55°C, followed by 5% ethyl acetate in petroleum ether). The dimers were carefully (they are fairly soluble in ethanol) recrystallized from ethanol. We have reported the *vic*-chloronitroso compounds **11a–17a** in an earlier paper,[18g] where the preparation method was slightly different.

2.6b *Method B—in dichloromethane*: The above reaction was conducted under the same conditions by taking the solution of cycloalkene in 10 mL of dry dichloromethane. At the end of the reaction, 10 mL of water was added, the layers were separated; organic layer was washed with water (2 × 15 mL), 10% $NaHCO_3$ solution (15 mL), water (15 mL), saturated

Table 3. Preparation of *vic*-chloronitroso compounds by adding NOCl to olefins.

Entry	*vic*-Chloronitroso compd[a]		Solvent-free reaction		In CH_2Cl_2	
			Reaction time (h)	Yield (%)[a]	Reaction time (h)	Yield (%)[b]
1	1-Chloro-2-nitrosocyclopentane	(**11a**)	1.0	70 (+20)	1.5	60 (+30)
2	1-Chloro-2-nitrosocyclohexane	(**12a**)	1.5	65 (+15)	1.8	63 (+30)
3	1-Chloro-2-nitrosocycloheptane	(**13a**)	2.0	65 (+13)	2.5	60 (+25)
4	1-Chloro-2-nitrosocyclooctane	(**14a**)	2.5	60 (+20)	2.8	55 (+25)
5	1-Chloro-2-nitrosocyclododecane	(**15a**)	4.0	80 (+10)	4.0	70 (+20)
6	2-Chloro-3-nitrosonorbornane	(**16a**)	0.5	75 (+10)	0.5	70 (+15)
7	2-Chloro-1-nitrosoheptane	(**17a**)	3.0	57 (+10)	3.0	55 (+15)

[a]We have described the *vic*-chloronitroso compounds **11a–17a** in an earlier paper[18g]
[b]Yield of the corresponding α-chlorooxime, the product of tautomerisation

Table 4. Oxidation of *vic*-chloronitroso to *vic*-chloronitro compounds.

Entry	Compound[a]		Reaction time (h)	Yield (%)
1	1-Chloro-2-nitro-cyclopentane	(**11b**)	12	40 (+10)[c]
2	1-Chloro-2-nitro-cyclohexane	(**12b**)[b]	15	35 (+12)[c]
3	1-Chloro-2-nitro-cycloheptane	(**13b**)	13	37 (+10)[c]
4	1-Chloro-2-nitro-cyclooctane	(**14b**)	10	30 (+10)[c]
5	2-Chloro-3-nitro-norbornane	(**16b**)[b]	11	40 (+15)[c]
6	2-Chloro-1-nitro-heptane	(**17b**)[b]	10	35 (+15)[c]

[a] 1-chloro-2-nitrosocyclododecane (**15a**) did not get oxidized
[b] **12b**,[31a] **16**[31b] and **17b**[31c] are known in the literature; the other three are not
[c] The numbers in parentheses are yields of the respective α-chlorooximes

NaCl solution (15 mL), and dried over Na_2SO_4. In this case the byproduct α-chlrooxime was formed in slightly higher proportion than in the previous case, and was separated by chromatography as in the previous experiment, (table 3).

2.7 *Oxidation of vic-chloronitroso to vic-chloronitro compounds*

A solution of 4.2 g (12 mmol) of CTAHC in 10 mL of CH_2Cl_2 was added to a solution of 10 mmol of *vic*-chloronitroso compound in 10 mL of CH_2Cl_2 stirred vigorously in a 100 mL two-necked flask equipped with a dropping funnel and a condenser fitted with a $CaCl_2$ guard tube. The reaction mixture was kept stirred until the starting compound had disappeared, which took 10–15 h depending on the starting compound. All the *vic*-chloronitroso compounds, except 1-chloro-2-nitrosocyclododecane, underwent oxidation. The solvent was removed on a rotary evaporator, the residue was dissolved in 50 mL of diethyl ether, and the resulting solution was washed with water (2 × 30 mL), saturated NaCl solution (2 × 20 mL), and dried over Na_2SO_4. After removing the solvent, the residue was chromatographed on a silica gel column using petroleum ether (b.p. 50–55°C) as eluant. The yields of *vic*-chloronitro derivatives are modest, as α-chlorooxime was formed as a by-product in each case (table 4). The spectral data of *vic*-chloronitro compounds are recorded in table 5.

Table 5. IR, ^{1}H NMR and ^{13}C NMR spectral data for *vic*-chloronitro compounds.

Compd	IR (neat), ν (cm^{-1}) (selected)	^{1}H NMR ($CDCl_3$) δ (ppm)	^{13}C NMR ($CDCl_3$) δ (ppm)
11b	2976, 2903, 1564, 1471, 1440, 1140, 1357, 1140, 1078, 964, 788, 648	4.532 (m, 1H), 3.079 (m,1H), 1.94-2.644 (m, 6H).	19.13, 32.07, 35.25, 65.17, 107.01
12b	2955, 2878, 1569, 1455, 1440, 1372, 1191, 1000, 984, 866, 762, 695, 545	4.76 (m, 1H), 2.56-2.66 (m, 1H), 1.52-2.43 (m, 8H)	17.84, 21.81, 29.77, 30.73, 60.21, 101.73
13b	2966, 2929, 2857, 1564, 1481, 1450, 1362, 1134, 1072, 814, 788, 643	4.85 (m, 1H), 2.49-2.68 (m, 1H), 1.522-2.37 (m, 10H)	20.74, 21.00, 25.10, 29.26, 34.90, 64.87, 107.77
14b	2929, 2862, 1636, 1564, 1466, 1460, 1352, 1222, 1186, 1021, 881, 721, 643	5.15-5.30 (m, 1H), 2.84-2.97 (m, 1H), 2.55-1.51 (m, 12H)	21.81, 24.59, 25.31, 25.96, 30.72, 32.80, 57.63, 103.74
16b	2981, 2888, 1693, 1569, 1455, 1347, 1316, 995, 953, 850, 819, 772, 736	4.95-4.92 (m, 1H), 4.74-4.77 (m, 1H), 2.20-3.14 (m, 3H), 1.57-1.80 (m, 6H)[a]	23.51, 26.91, 35.71, 48.31, 53.46, 65.63, 105.52, and 23.46, 26.57, 36.07, 47.98, 52.90, 64.22, 105.52[a]
17b	2976, 2940, 2883, 1647, 1569, 1471, 1393, 1352, 1093, 866, 783, 674	4.2-4.6 (m, 2H), 2.25-2.46 (m, 1H), 1.15-1.80 (m, 11H)	13.61, 12.76, 23.12, 28.63, 23.19, 64.92, 104.05.

[a] Mixture of two isomers

3. Results and discussion

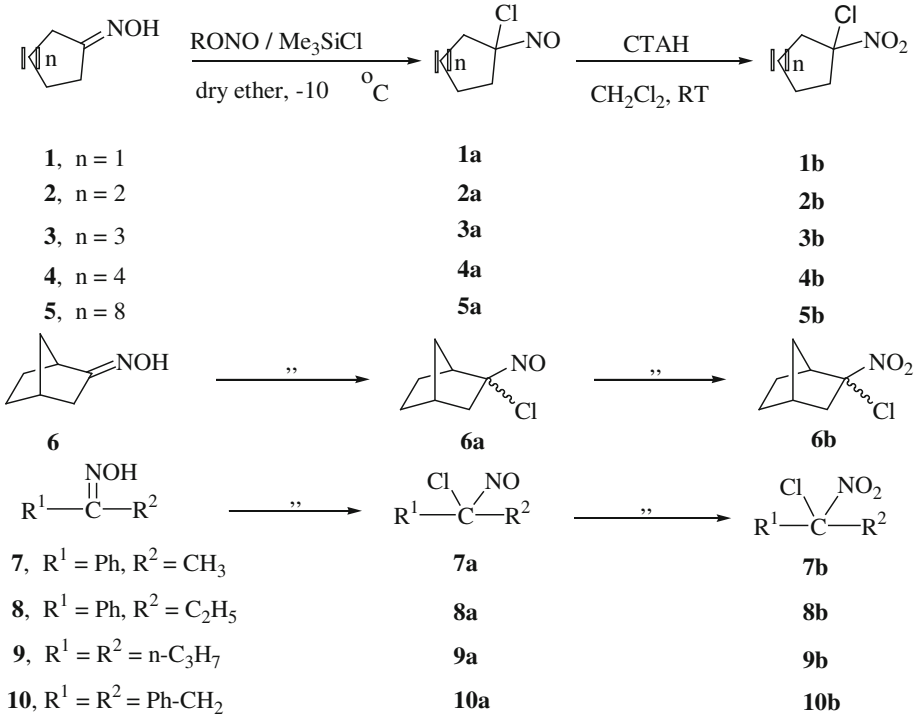
3.1 *gem-Chloronitro compounds*

Cetyltrimethylammonium hypochlorite (CTAHC) was prepared by a procedure similar to the one used for the preparation of CTAP.[28] When cetyltrimethylammonium bromide in dichloromethane and commercially available sodium hypochlorite solution are mixed and mechanically stirred at room temperature, they undergo double displacement, and CTAHC accumulates in the dichloromethane phase, which is separated and worked up to get the white solid. However, CTAHC is relatively more soluble in water than CTAP, hence needs more careful work-up. It decomposes without melting above 200°C, but can be stored intact in refrigerator for several months.

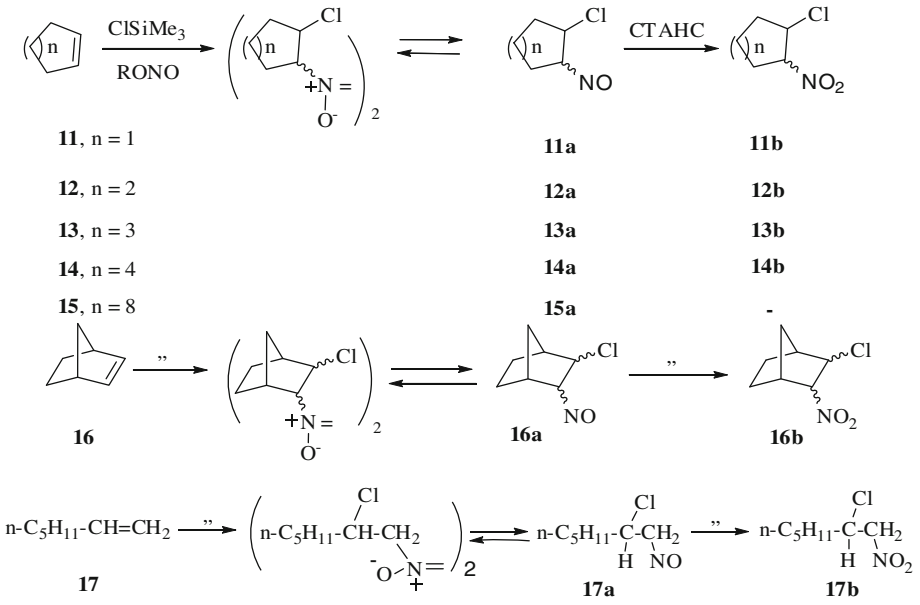
$$CH_3\text{-}(CH_2)_{15}\overset{+}{N}(CH_3)_3\,\overset{-}{Br}(CH_2Cl_2) + NaOCl\ (aq) \longrightarrow CH_3\text{-}(CH_2)_{15}\overset{+}{N}(CH_3)_3\,\overset{-}{O}Cl(CH_2Cl_2) + NaBr\ (aq) \quad \text{(eq 3)}$$

Ten ketoximes **1–10** were treated with TMSCl and *iso*-amyl nitrate at −10°C. The NOCl generated *in situ* reacted with oximes to produce the corresponding blue coloured *gem*-chloronitroso derivatives **1a–10a** (scheme 2), which were obtained in pure form by passing through silica gel column in almost quantitative yield (table 1). They were identified by their spectral data as described in our previous paper.[12] 1-Chloro-1-nitrosocyclododecane (**5a**), 2-chloro-2-nitrosonorbonane (**6a**) and 2-chloro-2-nitroso-1,3-diphenylpropane (**10a**) are stable solids. We have earlier reported the crystal structure of the compound **5a**.[18d] The others (**1a–4a** and **7a–9a**) are liquids, which decompose slowly at room temperature, and rapidly on heating. Their blue colour indicates that they exist in monomeric form. The dimerisation, which is a common feature of nitroso compounds,[18a,b] is prevented because of electronegative effect and steric hindrance of the geminal chlorine group. In contrast, the *vic*-chloronitroso compounds dimerise[18g] easily (scheme 3).

The oxidation of *gem*-chloronitroso compounds **1a–10a** was carried out in dichloromethane at room temperature by using about a 40% excess of CTAH. The reaction takes 3–13 h for completion depending on the structure of the starting compound (table 2). The *gem*-chloronitro derivatives **1b–10b** (scheme 2), after isolation by usual work-up and purification by chromatographing on silica gel, were identified by comparing their spectral data with those described previously.[12]



Scheme 2. Preparation of *gem*-chloronitro compounds.



Scheme 3. Preparation of *vic*-chloronitro compounds.

3.2 *One-pot procedure for oxime to gem-chloronitro compound*

The oximes could also be converted to their respective *gem*-chloronitro derivatives by a one-pot process. In this method, each oxime in ether solution at −10°C was first treated with TMSCl and *iso*-amyl nitrite to form *gem*-chloronitroso compound, after the mixture attained room temperature, it was treated with the required quantity of CTAHC in ether solution, stirred until the chloronitroso compound disappeared, and worked-up to get the *gem*-chloronitro derivative. The yields were slightly better (table 2) than in the case of the reactions carried out in two separate steps, which is attributable to single work-up step.

3.3 *vic-Chloronitro compounds*

Six *vic*-chloronitro compounds, **11b–14b**, **16b** and **17b** were prepared by a two-step procedure. In the first step, *vic*-chloronitroso compounds **11a–17a** were prepared by adding NOCl, generated *in situ*, to cycloalkenes and alkenes **11–17** (scheme 3). While 1-chloro-2-nitrosocycloheptane (**13a**) remained as blue monomer, the other adducts, **11a**, **12a**, and **14a–17a**, were obtained as white dimeric diazine dioxide products,[18g] which exhibited widely varying stability. The dimer of 2-chloro-3-nitrosonorbornene (**16a**) is quite stable even in solution, whereas the other dimers dissociate into monomers in solution resulting in monomer–dimer equilibrium.[18b,d,g]

The *vic*-chloronitroso compounds were treated at room temperature, with 20% excess of CTAHC. This produced 1-chloro-2-nitro compounds **11b–14b**, **16b** and **17b**, which were obtained after usual work-up and purification by chromatographing on silica gel column (table 4). They were identified by their spectral data (table 5). 1-Chloro-2-nitroso-cyclododecane (**15a**) did not undergo oxidation. The ^{1}H and ^{13}C NMR data (table 5) clearly indicated that each monocyclic *vic*-chloronitro derivative (**11b–14b**) was a single stereoisomer and most likely *trans*. However, 2-chloro-3-nitronorbornane was a mixture of a major and a minor component, the major one being the *exo*, *cis* derivative.[18a,b, 27l] The chloronitroheptane (**17b**) contained 10–15% of probably a regioisomeric impurity. Three of these, i.e., **12b**, **16b** and **17b** are known in the literature, while the other three are not.

The monomeric adducts with α-hydrogen tend to tautomerise to give chlorooximes fairly rapidly particularly in the presence of acidic or basic impurities.[18g] If excess NOCl is generated, the initially formed monomer produces α-chlorooxime as intermediate which further reacts with NOCl to finally give 1,2-dichloro-1-nitroso derivatives.[18b] Actually, in these reactions some amount of α-chlorooximino derivatives were isolated (table 4). Even during CTAH oxidation of the pure *vic*-chloronitroso compounds, some further quantity of chlorooxime was isolated as by-product in each case. As a result, the yields of *vic*-chloronitro derivatives were less than expected.

4. Conclusions

The oxidation of 1-chloro-1-nitroso and 1-chloro-2-nitroso compounds can be efficiently carried out using the novel cetyltrimethylammonium hypochlorite (CTAHC) reagent to the corresponding chloronitro derivatives. Considering the fact that CTAHC is easy to prepare and to handle, the method offers an easy access to the *gem*-chloronitro and *vic*-chloronitro compounds, which have many useful synthetic as well as other applications. The present method is promising particularly for the preparation of *vic*-chloronitro compounds, as the literature methods involve the complicated free radical reactions of NO_2Cl or N_2O_4+Cl_2 mixture with olefins, which require extensive purification and give low yields of the desired products.

Acknowledgements

AHAM thanks Indian Council for Cultural Relations (ICCR), NewDelhi, for a fellowship under Cultural Exchange Programme. The work was partly supported by UGC-DRS and UGC-COSIST programmes, NewDelhi. Some equipment used for the work is a donation to GN by the Alexander von Humboldt Foundation, Germany.

References

1. For a comprehensive account on nitroso and nitro compounds see, (a) Patai S (ed) 2003 *The chemistry of amino, nitroso, and nitro compounds and related groups* (Wiley-Interscience), (and its earlier editions); (b) Ono N 2001 *Nitro group in organic synthesis* (Wiley-VCH); (c) Feuer H and Nielsen A 1990 *Nitrocompounds: recent advances in synthesis and chemistry* (New York: VCH); (d) Feuer H 1969 *The chemistry of nitro and nitroso groups* (New York: Interscience Publishers); (e) Agarwal J P and Hodgson R D 2007 *Organic chemistry of explosives* (John-Wiley); (f) Shvekhgeimer G A, Zvoliniskii V I and Kobrakou K I 1986 *Chem. Hetero. Comp.* **22** 353
2. (a) Walters T R, Zajac W W and Woods J M 1991 *J. Org. Chem.* **56** 316; (b) Terent'ev A O, Krylov I B, Ogibin Y N and Nikishin G I 2006, *Synthesis* 3819; (c) Amrolla-Madjdabadi A, Beugelmans R and Lechevallier A 1986, *Synthesis* 826; (d) Corey E J and Estreicher H 1980, *Tetrahedron Lett.* **21** 1117; (e) Sakai I, Kawabe N and Ono M 1979, *Bull. Chem. Soc. Jpn.* **52** 3381
3. (a) Ono N, Tamura R, Hayami J-i and Kaji A 1977, *Chem. Lett.* 189; (b) Russell G A, Mudryk B and Jawdosiuk M 1981 *Synthesis* 62; (c) Ono N, Tamura R, Eto H, Hamamoto I and Nakatsuka T 1983 *J. Org. Chem.* **48** 3678; (d) Russell G A and Hershberger J 1980 *J. Chem. Soc. Chem. Commun.* 216; (e) Russell G A, Mudryk B, Ros F and Jawdosiuk M 1982 *Tetrahedron* **38** 1059; (f) Fridman A L, Surkov V D and Novikov S S 1980 *Russ. Chem. Rev.* **49** 1068
4. Barnes M W and Patterson J M 1976 *J. Org. Chem.* **41** 733
5. Ceccherelli P, Curini M, Epitano F, Marotullio M C and Rosati O 1998 *Tetrahedron Lett.* **39** 4385
6. Zaks A, Yabannavar A V, Dodds D R, Evans C A, Das P R and Malchow R 1996 *J. Org. Chem.* **61** 8692
7. (a) Marchand A P and Suri S C 1984 *J. Org. Chem.* **49** 2041; (b) Nielsen A T 1962 *J. Org. Chem.* **27** 1993; (c) Paquette L A, Fischer J. W and Engel P J 1985 *J. Org. Chem.* **50** 2524; (d) Marchand A P and Reddy D S 1984 *J. Org. Chem.* **49** 4078
8. Iffland D C and Criner G Y 1953 *J. Am. Chem. Soc.* **75**, 4047
9. Paquette L A, Waykole L M and Shen C-e 1988 *J. Org. Chem.* **53** 4969
10. (a) Marchand A P, Arney Jr B E and Dave P R 1988 *J. Org Chem.* **53** 443; (b) Baum K and Archibald T G 1988 *J. Org. Chem.* **53** 4645
11. (a) Archibald G A, Garver G, Baum K and Cohen M C 1989 *J. Org. Chem.* **54** 2869; (b) Eiserich J P Cross C E, Jones A D, Halliwell B and van der Vliet A 1996 *J. Biol. Chem.* **271** 19199
12. Abdulkarim A H A and Nagendrappa G 2010 *J. Chem. Sci.* **122** 571
13. (a) Kresze G, Mayer N M and Winkler J 1971 *Ann. Chem.* **747** 172; (b) Bosch T, Kresze G and Winkler J 1975 *Ann. Chem.* 1009; (c) Sakai I, Kawabe N and Ohno M 1979 *Bull. Chem. Soc. Jpn.* **52** 3381; (d) Tordeux M, Boumizane K and Wakselman C 1995 *J. Fluorine Chem.* **70** 207; (e) Müller E, Fries D and Metzger H 1955 *Chem. Ber.* **88** 1891; (f) Mackor A and de Boer T J 1970 *Recl. Trav. Chem. Pays-Bas* **89** 151; (g) Hammick D L and Lister M W 1937 *J. Chem. Soc.* 489
14. (a) Defoin A, Joubert M, Heuchel J M, Strehler C and Streith J 2000 *Synthesis* 1719; (b) Davis P, Vogt H C, Deck C F 1976 US Patent 3,960,822; (c) Diekmann H and Lüttke W 1968 *Angew. Chem. Int. Ed.* **7** 387; (d) Nacef B, Daudon M and Pinatel H 1977 *Synth. Commun.* **7** 153; (e) Nitsch H and Kresze G 1976 *Angew. Chem. Int. Ed.* **15** 760; (f) Sabuni M, Kresze G and Braun H 1984 *Tetrahedron Lett.* **25** 5377; (g) Felber H, Kresze G, Braun H and Vasella A 1984 *Tetrahedron Lett.* **25** 5381
15. Kumar V and Kaushik M P 2005 *Tetrahedron Lett.* **46** 8121
16. Wichterle O and Hudlicky M 1947 *Collect. Czech. Chem. Commun.* **12** 661
17. Gupta A K, Acharya J, Pardasani D and Dubey D K 2007 *Tetrahedron Lett.* **48** 767
18. (a) Mallya M N, Nagendrappa G, Prasad J S, Sridhar M A, Lokanath N K and Begum, N S 2001 *Tetrahedron Lett.* **42** 2565; (b) Mallya M N and Nagendrappa G 2006 *Arkivoc* 155; (c) Kyung J H and Clapp L B 1976 *J. Org. Chem.* **41** 2024; (d) Girija C R, Begum N S, Karim H A M A and Nagendrappa G 2004 *Acta Cryst.* **E60** 1764; (e) Kugelman M, Mallams A K and Vernay H F 1976 *J. Chem. Soc. Perkin Trans.* **1** 1113; (f) Bozzi E G, Shiue Ch. Y and Clapp

L B 1973 *J. Org. Chem.* **38** 56; (g) We have used α-chlorooximes to prepare α-chloroketones under solvent-free conditions, see Vimala B C and Nagendrappa G 2009 *J. Chem. Sci.* **121** 1011
19. Colonge J and Lartigau G 1965 *Bull Soc. Chim. France.* 738
20. Yakubovich A Ya, Shpanskii V A and Lemke A L 1954 *Dokl. Akad. Nauk USSR* **96** 773; (b) Hass H B and Whitaker A C 1948 US Patent 2,447,504 (*Chem. Abstr.* 1949 **43** 3024i); (c) Mark V 1956 US Patent 2,771,470 (*Chem. Abstr.* 1957 **51** 6686)
21. (a) Spencer A N and Wain R L 1963 *Ann. Appl. Biot.* **51** 153; (b) Mowry D T 1952 US Patent 2,591,589 (*Chem. Abstr.* 1954 **48** 11485)
22. (a) Bachman G B and Standish N W 1959 US Patent 2,999,118 (*Chem. Abstr.* 1962 **56** 2331d); (b) Nishimura T 1954 *Bull. Chem. Soc. Jpn.* **27** 617
23. Herzog L 1957 US Patent 3,000,933 (*Chem. Abstr.* 1962 **56** 1346a)
24. (a) Shechter H, Conrad F, Daulton A and Kaplan R 1952 *J. Am. Chem. Soc.* **74** 3052; (b) Goddard D R 1958 *J. Chem. Soc.* 1955; (c) Schlubach H H and Braun A 1959 *Ann Chem.* **627** 28; (d) Shin C, Yamaura M, Inui E, Ishida Y and Yoshimura J 1978 *Bull. Chem. Soc. Jpn.* **51** 2618; (e) Bachmann G B and Chupp J P 1956 *J. Org Chem.* **21** 465; (d) Bachmann G B and Hokama T 1960 *J. Org. Chem.* **25** 178
25. (a) Seebach D, Colvin E W, Lehr F and Weller T 1979 *Chimia* **31** 1; (b) Rajappa S 1981 *Tetrahedron* **37** 1453; (c) Barrett A G M and Graboskii G G 1986 *Chem. Rev.* **86** 751; (d) Barrett A G M 1991 *Chem. Soc. Rev.* **20** 95; (e) Perekalin V V, Lipina E S, Berestovitskaya V M and Effremov D A 1994 *Nitroalkenes: Conjugated Nitro Compounds* (New York: John Wiley); (f) Michael J P and Blom N F 1989 *J. Chem. Soc. Perkin Trans* **1** 623; (g) Clive D L J, Bo Y, Tao Y, Daigneault S, Wu Y J and Meignan G 1996 *J. Am. Chem. Soc.* **118** 4904; (h) Trost B M and Hitce J 2009 *J. Am. Chem. Soc.* **131** 4572; (i) Watanabe N, Ikagawa A, Wang H, Murata K and Ikariya T 2004 *J. Am. Chem. Soc.* **126** 11148; (j) Pansare S V and Pandya K 2006 *J. Am. Chem. Soc.* **128** 9624; (k) Yoshida M, Sato A and Hara S 2010 *Org. Biomol. Chem.* **8** 3031; Palomo C, Vera S, Mielgo A and G_mez-Bengoa 2006 *Angew. Chem. Int. Ed.* **45** 5984; (l) Wiesner M, Revell J D and Wennemers H 2008 *Angew. Chem. Int. Ed.* **47** 7539; (m) Rasappan R and Reiser O 2009 *Eur. J. Org. Chem.* 1305; (n) Luo J, Xu L W, Hay R A S and Lu Y X 2009 *Org. Lett.* **11** 437; (o) Alcaine A, Marques-Lopez E, Merino P Tejero T and Herrera R P 2011 *Org. Biomol. Chem.* **9** 2777; (p) Williams D R, Cullen Klein J and Chow N S C 2011 *Tetrahedron Lett.* **52** 2120
26. (a) Ogloblin K A, Grigorova T H and Potekhin A A 1969 *Zh. Org. Khim.* **5** 1360; (b) Khristov V Kh, Angelov Kh M, Petrov A A 1991 *Russ. Chem. Rev.* **60** 39; (c) Ogloblin A A and Samartsev M A 1964 *Zhur. Obshch. Khim.* **34** 1530
27. (a) Closs G L and Brois S I 1960 *J. Am. Chem. Soc.* **82** 6068; (b) Tanabe K and Hayashi R 1962 *Chem. Pharm. Bull. Japan* **10** 1177; (c) Leminer R U, Nagabhushan T L and Neill I K O 1964 *Tetrahedron Lett.* 1909; (d) Serfortein W J, Jordan J H and White J I 1964 *Tetrahedron Lett.* 1069; (e) Hassner A and Heathcock C 1964 *J. Org. Chem.* **29** 1350; (f) Ponder B W and Walker D P 1967 *J. Org. Chem.* **32** 4136; (g) Paul P 1993 *Polyhedron* **12** 2057; (h) Chaudhury P K; Barbaruah M and Sharma P P 1994 *Indian J. Chem.* **33B** 71; (i) Meinwald J, Meinwald Y C and Baker T N 1963 *J. Am. Chem. Soc.* **85** 2513; (j) Beier T, Hauthal H G and Pritzkow 1964 *J. Prakt. Chem.* **26** 304; (k) Freeman F 1975 *Chem. Rev.* **75** 471; (l) Gowenlock B G and Richter-Addo G B 2004 *Chem. Rev.* **104** 3315; (m) Boyer H J 1969 *The chemistry of nitro and nitroso groups* (eds) H Feuer and S Patai (New York: Interscience) part 1; (n) Glaser R, Murmann R K and Barnes C L 1996 *J. Org. Chem.* **61** 1047; (o) Chow Y L, Pallay K S and Richard R 1979 *Can. J. Chem.* **57** 2923; (p) Nelson D J 1999 *Tetrahedron Lett.* **40** 5823; (q) Kadzyauskas P P and Zefirov N S 1968 *Russ. Chem. Rev.* **37** 543
28. (a) Bhusan V, Rathore R and Chandrasekaran S 1984 *Synthesis* 431; (b) Freeman F and Kappos J C 1989 *J. Org. Chem.* **54** 2730; (c) Mallya M N and Nagendrappa G 1999 *Synthesis* 37; (d) Mallya M N and Nagendrappa G 2001 *J. Chem. Soc. Perkin Trans.* **2** 1099; (e) Begum N S, Girija C R, Mallya M N and Nagendrappa G 2005 *J. Mol. Struct.* **229** 31; (f) Bickley J F, Gilchrist T L and Mendonca R 2002 *Arkivoc* 192; (g) Rathore R, Vankar P S and Chandrasekaran S 1986 *Tetrahedron Lett.* **27** 4079; (h) Vankar P S, Rathore R and Chandrasekaran S 1987 *Synth. Commun.* **17** 195; (i) Holba V and Sumichrast R 1995 *Monats. Chem.* **126** 681; (j) Shukla R, Sharma P K, Kotai L and Banerji K L 2003 *Proc. Indian Acad. Sci. (J. Chem. Sci.)* **115** 129; (k) Vankar P S, Rathore R and Chandrasekaran S 1986 *J. Org. Chem.* **51** 3063
29. (a) Vimala B C 2004 Ph D Thesis Bangalore University; (b) Vimala B C and Nagendrappa G 2009 *Saudi J. Chem.* **13** 169; (c) Sahu S, Patel S and Mishra B K 2005 *Synth. Commun.* **35** 3123; (d) Patel S and Mishra B K 2007 *Tetrahedron* **63** 4367; (e) Patel S and Mishra B K 2006 *J. Org. Chem.* 71 3522; (f) Patel S and Mishra B K 2004 *Tetrahedron Lett.* **45** 1371
30. Furniss B S, Hannaford A J, Smith P W G and Tatchell A R 2004 *Vogel's textbook of practical organic chemistry* (Singapore: Pearson Education) 5th edn, (a) p. 1019; (b) p. 1259; (c) p. 413
31. (a) Brand J C D and Stevens I D R 1958 *J. Chem. Soc.* 629; (b) Chauvet F, Heumann A and Waegell B 1987 *J. Org. Chem.* 1916; (c) Ogloblin K A 1964 *Zh. Obsh. Khim.* **34** 170