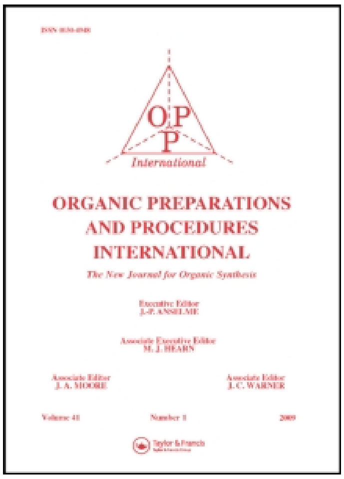

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RAPID AND SELECTIVE REGENERATION OF CARBONYL COMPOUNDS FROM THEIR OXIMES UNDER MILD. NEUTRAL AND SOLVENT-FREE CONDITIONS

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RAPID AND SELECTIVE REGENERATION OF CARBONYL COMPOUNDS FROM THEIR OXIMES UNDER MILD, NEUTRAL AND SOLVENT-FREE CONDITIONS

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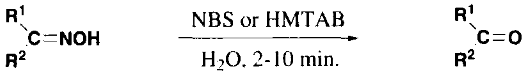
The development of efficient and mild methods for the selective cleavage of C=N containing derivatives to afford carbonyl compound continues to be a significant aspect of experimental organic chemistry.[1] Oximes are extensively used for purification and characterization of carbonyl compounds and in the preparation of amides *via* the Beckmann rearrangement. [2] Their synthesis from non-carbonyl compounds[3] provides potential alternative pathway to aldehydes and ketones, if selective cleavage can be worked out. The important role of oximes as protecting groups[4] owing to their hydrolytic stability has inspired the development of newer deoximation reagents such as Raney nickel,[5a] cetyltrimethylammonium permanganate,[5b] Dowex-50,[5c] ultrasonically stimulated baker's yeast,[5d] iron (III) perchlorate,[5e] zirconium sulfophenyl phosphate,[5f] ammonium persulfate-silica gel[5g] and manganese triacetate.[5h] The use of dimethyl dioxirane[6a] and silica supported periodate[6b] is restricted to ketoximes whereas pyridium chloroformate - H_2O_2,[6c] ozone[6d] and TBHP[6c] suffer from the disadvantage of over oxidation of ensuing aldehydes. Only a limited number of methods are thus available for this cleavage under mild reaction conditions.[5h, 6a,6d] We now report a remarkably rapid deoximation reaction under mild, neutral and solvent-free conditions (*Scheme*).



When an oxime was mixed with hexamethylenetetramine-bromine (HMTAB) or N-bromosuccinimide (NBS) in the presence of a few drops of water at room temperature, a spontaneous reaction took place. First the reaction mixture became yellow-brown and then colorless when the reaction was complete. Various aldoximes and ketoximes underwent smooth deoximation under this protocol in a very short time (2-10 min). The most remarkable advantage of this methodology is that no trace of acid was formed owing to over-oxidation of regenerated aldehyde. HMTAB[7] and NBS[8] are used as oxidizing agents. It is worth commenting that the oxime group was selectively cleaved without interfering with other sensitive functional groups, including phenols (entries **2c**, **d**, **o**), secondary alcohols (entry **2e**) and carbon-carbon double bonds (entry **2g**). This competitive deoximation was supported by the fact that when benzoin or cinnamaldehyde was mixed with HMTAB/NBS in the presence of a few drops of water, the mixture did not become brown and the secondary alcohol group of benzoin and the alkene unit of cinnamaldehyde remained intact. Furthermore, no α-bromination was observed (entries **2h-j**) and heterocyclic aldoximes (entry **2n**) - and even sterically hindered oximes- underwent smooth deoximation (entries **2k-l**). It is important to note that the ketoxime group was selectively cleaved in the presence of an aldoxime (entries **2o-p**) and TBDMS ether (entry **2p**). IR and ^{1}H NMR spectra of **2o** and **2p** indicated the absence of aldehydic hydrogen.

We believe that the present deprotection methodology for oximes should find wide use in organic synthesis.

TABLE. Selective and Rapid Deprotection of Oximes using NBS and HMTAB

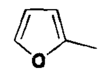
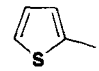
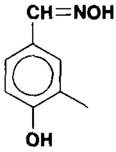
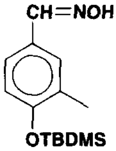
Entry	R1	R2	Reagent	Reaction Time (min.)	Yield[a,b] (%)
2a	H	4-Cl-C_6H_4–	NBS	4	95
			HMTAB	10	96
2b	H		NBS	3	61
			HMTAB	4	70
2c	H	2-HOC_6H_4–	NBS	6	78
			HMTAB	6	83
2d	H	4-HO, 3-$MeOC_6H_3$–	NBS	2	96
			HMTAB	5	90
2e	H	4-$NO_2C_6H_4$–	NBS	4	91
			HMTAB	5	80
2f	H	3,4,5-$(MeO)_3C_6H_2$–	NBS	5	93
			HMTAB	6	90
2g	H	$C_6H_5CH = CH$–	NBS	2	63
			HMTAB	2	72
2h	–$(CH_2)_4$–		NBS	2	78
			HMTAB	2	81
2i	–$(CH_2)_5$–		NBS	4	75
			HMTAB	5	76
2j	CH_3	C_6H_5–	NBS	2	86
			HMTAB	2	82
2k	C_6H_5	C_6H_5–	NBS	2	80
			HMTAB	2	89
2l	C_6H_5	C_6H_5CHOH–	NBS	4	69
			HMTAB	3	79
2m	H	$CH_3(CH_2)_7$–	NBS	2	63
			HMTAB	2	59
2n	H		NBS	2	62
			HMTAB	2	52

TABLE. Continued...

Entry	R_1	R_2	Reagent	Reaction Time (min.)	Yield[a,b] (%)
2o	Ph		NBS HMTAB	2 2	72 81
2p	Ph		NBS HMTAB	2 2	86 79

a) Yields are of isolated products b) Known products[9] were characterized by their physical constants, IR, ^{1}H NMR or comparison with authentic samples.

EXPERIMENTAL SECTION

HMTAB was prepared according to the reported procedure.[7] NBS, aldehydes and ketones were obtained from Lancaster, U. K. IR and ^{1}H NMR spectra were recorded on Bomem MB-104 FT IR and JEOL FX 90 Q (90 MHz) instruments respectively. Elemental analyses were obtained on a Perkin Elmer Model 240C instrument (North Maharashtra University, Jalgaon).

General Procedure.- An oxime (1 mmol) was mixed with NBS (1.1 mmol) or HMTAB (2 mmol) in the presence of few drops of water at room temperature. A spontaneous reaction took place with evolution of brown fumes. After completion of the reaction, the yellow- brown color of the mixture disappeared. Then the product was extracted with pentane (2 x 10 mL) and after drying (Na_2SO_4) the pentane was evaporated under reduced pressure to give the product.

IR and 1H NMR data of some new compounds are given below.

2o, IR: 1190, 1505, 1600, 1705, 3350, 3500 cm-1; ^{1}H NMR (90 MHz, D_2O): $\delta = 5.6$ (s, 1 H, = CH), 7.4 (m, 8 H, Ar-H).

Anal. Calcd. for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.56; N, 5.81. Found: C, 69.72; H, 4.82; N, 5.88

2p, IR: 1200, 1510, 1610, 1700, 3300, 3400 cm-1; ^{1}H NMR (90 MHz, D2O): $\delta = 0.1$ (s, 6 H, 2 x Si-CH_3), 0.9 (s, 9 H, Si-$C(CH_3)_3$), 5.4 (s, 1 H, = CH), 7.5 (m, 8 H, Ar-H).

Anal. Calcd. for $C_{20}H_{25}NO_3Si$: C, 67.60; H, 7.04; N, 3.94. Found: C, 67.58; H, 7.05; N, 4.02

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A CONVENIENT AND EFFECTIVE METHOD FOR THE SYNTHESIS OF TETRAOXAQUATERENES

Submitted by (04/25/00)

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There is a great interest in the synthesis of new types of ionophores; among others calixarenes[1,2] and cyclodextrins[3-5] are well known. Recent papers dealing with the synthesis of tetraoxaquaterenes show that this may be a very interesting scaffold in supramolecular chemistry. Among all quaterenes, the synthesis of octamethyltetraoxaquaterene (**3**) is documented very well. One of the best methods, already published by Chastrette *et al.*,[6,7] based on the one-pot reaction of furan (**1**) with acetone (**2**), carried out in the presence of hydrochloric acid and lithium perchlorate, afforded the desired product **3** in 25% yield. Several attempts at modification of the reaction conditions were unsuccessful.[8,9]