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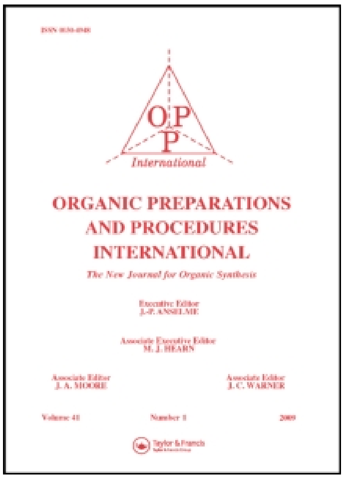

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TRIMETHYLAMMONIUM CHLOROCHROMATE (TMACC) ADSORBED ON ALUMINA FOR CLEAVAGE OF CARBON-NITROGEN DOUBLE BONDS UNDER NON-AQUEOUS CONDITIONS

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the mp. of the hydrochloride, since a sample prepared by the method outlined in this reference had mp., mmp, IR and NMR identical to the samples prepared by us. Its dihydrochloride was also indistinguishable from the dihydrochloride mentioned in this publication.

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TRIMETHYLAMMONIUM CHLOROCHROMATE (TMACC) ADSORBED ON ALUMINA FOR CLEAVAGE OF CARBON-NITROGEN DOUBLE BONDS UNDER NON-AQUEOUS CONDITIONS

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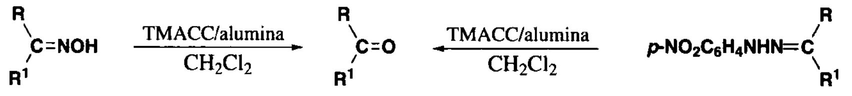
Oximes and *p*-nitrophenylhydrazones not only are used for the characterization and purification of carbonyl compounds but also for the protection of carbonyl compounds, as they are generally highly crystalline and stable compounds. The regeneration of carbonyl compounds from their derivatives under mild conditions is an important process in synthetic organic chemistry. The classical methods for the cleavage of oximes to aldehydes and ketones include acid hydrolysis, which is not suitable for acid sensitive compounds.[1] Several oxidative deoximation methods have been developed which have some advantages over the classical hydrolysis method.[2-15] Little attention has been paid to the oxidative cleavage of *p*-nitrophenylhydrazones, and only a few reports are available dealing with the conversion of these derivatives to their corresponding carbonyl compounds.[3a] However, many of these methods do not describe the deoximation of aldoximes[2] or often give low yields[3] or the liberated aldehydes are overoxidized to the carboxylic acid.[4] Moreover, the reagents used are often hazardous or very toxic[3b,4c,5] and expensive.[2b,2c,3b,3h,6] In some case the reagents need to be freshly prepared[2b,2c,3e,3f,7] or the reactions require anaerobic conditions[5b,6a,8] and long reaction times.[3b,4a,4c] We now report that trimethylammonium chlorochromate (Me_3NHCrO_3Cl, TMACC) adsorbed on alumina (TMACC/alumina) is a convenient, non-hazardous and efficient reagent for the oxidative cleavage of carbon-nitrogen double bonds to their parent carbonyl compounds. This reagent is stable and easily prepared by the addition of a weighed amount of alumina to a solution of trimethylammonium chlorochromate in water and rotary evaporation to dryness.

The reaction is performed by stirring of a mixture of the oxidant and oxime or *p*-nitrophenylhydrazone in dichloromethane at a suitable temperature. Our experiments show that oximes are converted to their corresponding aldehydes and ketones in good yields. Further oxidation of aldehydes to carboxylic acids was not observed. *p*-Nitrophenylhydrazones are also transformed to their carbonyl compounds in dichloromethane in high yields. 2,4-Dinitrophenylhydrazones are inert under the same conditions. The results obtained from the oxidation of nine oximes and eight *p*-nitrophenylhydrazones are reported in Table 1. The oxidation of other functional groups with this reagent is under investigation.



1 **2**

a) R^1 = Ph, R^2 = CH_3 b) R^1, R^2 = -$(CH_2)_5$- c) R^1, R^2 = -$(CH_2)_4$- d) R^1 = *p*-NO_2Ph, R^2 = CH_3
e) R^1 = p-CH_3OPh, R^2 = H f) R^1 = Ph, R^2 = H g) R^1 = *p*-BrPh, R^2 = H h) R^1 = PhCH=CH, R^2 = H
i) R^1 = 3-CH_3O-4-OH-Ph , R^2 = H j) R^1, R^2 = Ph k) R^1 = Ph, R^2 = CH_3 l) R^1, R^2 = -$(CH_2)_5$-
m) R^1, R^2 = -$(CH_2)_4$- n) R^1 = *p*-NO_2Ph, R^2 = CH_3 o) R^1, R^2 = CH_3CH_2 p) R^1 = *p*-CH_3OPh, R^2 = H
q) R^1 = Ph, R^2 = H

TABLE 1. Oxidative Cleavage of Carbon-Nitrogen Double Bonds with TMACC/alumina

Substrate (**1** or **3**)	Temp. (°)	Ratio of oxidant/**1** or **3**	Time (h)	Yield[a] (%)	mp. of 2,4-DNP of **2** Found(°)	Lit.[16](°)
1a	38	1.5	7	83	236-237	237
1b	38	1.5	7	78	159-160.5	160
1c	38	1.5	7	73	144-147	145.5-146.5
1d	38	1.5	7	70	258-260	—[b]
1e	38	1.5	5.5	75	252-255	254
1f	38	1.5	4.7	79	235-236.5	237
1g	38	1.5	6	66	188-191	—[c]
1h	38	1.5	4	58	210-212	200.5-201.5
1i	38	1.5	6	63	265-267	267-268
3j	38	1.5	9.2	80	237-239	238
3k	38	1.5	3.2	90	236-237	237
3l	38	1.5	9.5	88	159-160.5	160
3m	38	1.5	8.5	78	144-147	145.5-146.5
3n	38	1.5	6.7	75	258-260	—[b]
3o	38	1.5	6	68	153-156	156
3p	38	1.5	5.7	93	252-255	254
3q	38	1.5	8.6	77	235-236.5	237

a) Yields were based on 2,4-dinitrophenylhydrazone derivatives identified by comparison of mps and spectra characteristics with those of the corresponding authentic samples, prepared independently. b) Calcd for $C_{14}H_{11}N_5O_6$: C 47.86, H 4.88, N 19.94; Found C 47.91, H 4.87, N 20.01. c) Calcd for $C_{13}H_9N_4O_4Br$: C 42.76, H 2.48, N 15.34; Found C 42.81, H 2.50, N 15.41.

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EXPERIMENTAL SECTION

Mps were determined on a micro-melting point apparatus and are uncorrected. IR spectra were measured on a Nicolet FT-IR spectrometer. The ^{1}H NMR spectra were obtained on a Varian EM-360 A (60MHz) spectrometer in $CDCl_3$ with TMS as the internal standard. The elemental analyses were measured on a Perkin-Elmer 2400 spectrometer. To the best of our knowledge, TMACC is not explosive.

Preparation of TMACC /Alumina.- To a solution of chromium trioxide (20g, 0.2mol) in water (50mL) was added trimethylamine hydrochloride (16.8g, 0.2mol) over 15min at 40°. The mixture was then cooled until a yellow-orange solid formed and reheated to 40° to give a solution. Neutral alumina (120g, 100-200 mesh) in one portion was then added to the solution with stirring at 40°. After evaporation on a rotary evaporator at 65°, the orange solid was dried in vacuum at 50° for 1 h. The reagent may be kept for several months in air at room temperature without losing its activity.

General Procedure for the Oxidation of Oximes or *p*-Nitrophenylhydrazones with TMACC/Alumina.- To a three-necked flask fitted with a condenser and mechanical stirrer, was added one mmol of substrate (**1** or **3**) and 15 mL of CH_2Cl_2. The flask was heated in a water bath (38°). To the solution was then added the suitable amount of TMACC/alumina in batches with stirring. The mixture was stirred for additional 3~10h. The progress of the reaction was followed by TLC (silica gel GF-254, 7:1 cyclohexane-ether). The reaction mixture was filtered by suction and the solid material was washed with ether several times. Evaporation of the combined filtrates furnished the product which was isolated as its 2,4-dinitrophenylhydrazone.

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A FACILE SYNTHESIS OF NEW 2-PHOSPHONOBENZYLOXY-1,3,2-BENZOXAZA(DIOXA OR DIAZA)PHOSPHOLES

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Phosphorus-containing heterocyclic compounds have received much attention due to their biological importance.[1-3] Previously, we reported the synthesis of some thio (seleno) phosphate-phosphonate derivatives and their significant herbicidal, antiviral and fungicidal activities.[4] In continuation of our work of elaborating phosphate-phosphonates into a variety of heterocyclic systems of biological