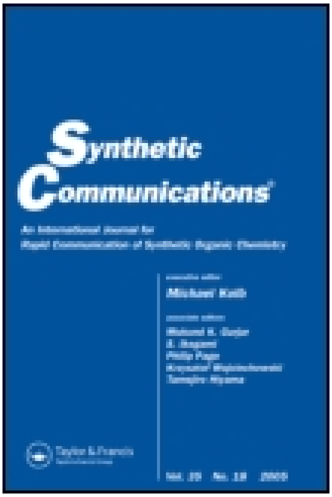

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Oxidative Deoximation to Their Parent Carbonyl Compounds with Ammonium Chlorochromate Adsorbed on Alumina

Gui-Sheng Zhang [a] , De-Hong Yang [a] , Mi-Feng Chen [a] & Kun Cai [a]
[a] Department of Chemistry , Henan Normal University , xinxiang, 453002, P.R. China

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OXIDATIVE DEOXIMATION TO THEIR PARENT CARBONYL COMPOUNDS WITH AMMONIUM CHLOROCHROMATE ADSORBED ON ALUMINA

Gui-Sheng Zhang,*De-Hong Yang, Mi-Feng Chen, Kun Cai
Department of Chemistry, Henan Normal University, xinxiang 453002, P.R.China

ABSTRACT: A convenient method for the oxidative cleavage of oximes to their parent aldehydes and ketones with ammonium chlorochromate adsorbed on alumina is described

Oximes are highly crystalline and very useful for the characterization and purification of carbonyl compounds. Besides, oxime was used to protect carbonyl group as one of stable protective groups. Regeneration of carbonyl compounds from their oxime derivatives under mild conditions is an important process in synthetic organic chemistry.

The classical methods for the cleavage of oximes to parent aldehydes and ketones include acid hydrolysis which is not suitable for acid sensitive compounds[1], Several oxidative deoximation methods have been developed which have found some advantages over the classical hydrolysis method[2~11].

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*To whom the correspondence should be addressed.

We have previously reported that ammonium chlorochromate adsorbed on alumina (ACC/alumina) is a convenient oxidant for hydroxy compounds to the corresponding compounds[12]. In the course of further exploration on the application of ACC/alumina in synthetic organic chemistry and because of the availability, convenience,and selectivity in oxidation by the reagent, it was investigated as a deoximative reagent with the results shown in the Table.

Our experiments showed that oximes were converted to their corresponding aldehydes and ketones in cyclohexane or the mixture solvent of cyclohexane and ether depending on the solubility. Further oxidation of aldehydes to their carboxylic acids were not observed. In contrast, deoximation using PCC suffers from long reaction time (12~94h) and low yields[2]. Hydrogen peroxide-PCC system is not suitable for aldoximes and overoxidation products are usually produced[3].

A summary of the results showed that ACC/alumina was a convenient reagent for selective oxidation of oximes, even with sensitive structure like salicylaldoxime and vanillic aldoxime, to their parent carbonyl compounds with the advantages of mild reaction condition, ease of work-up and better yields. But the oxidation of aromatic aldoximes containing electron-withdrawing group gave poor yields.The oxidation of p-bromobenzyl aldoxime gave a 45% yield and p-nitrobenzylaldoxime gave only 20%.

The reaction was simply performed by stirring excess oxidant with oximes in cyclohexane or a mixture solvent of cyclohexane and ether at suitable temperature, and was very profitable in the work-up, which became reduced to a mere filtration, followed by few washings of the solid by ether.

Scheme

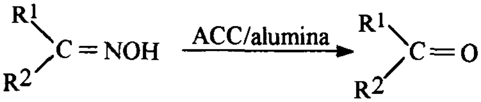
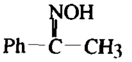
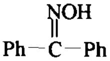
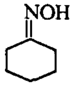
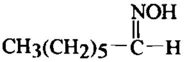
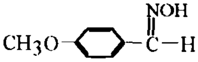
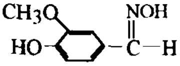
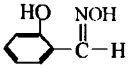
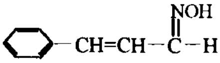
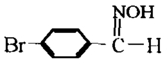
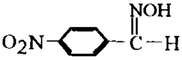


Table. Deoximation with ACC/alumina[a]

Substrate	Temp.(℃)	Time (h)	Yield (%)[b]	m.p.℃(lit.)[13] of 2,4-DNP
 $\mathrm{Ph-C(=NOH)-CH_3}$	60	5	85	238-240 (237)
 $\mathrm{Ph-C(=NOH)-Ph}$	60	6	77	236-238 (238)
	60	5	80	158-160 (160)
 $\mathrm{CH_3(CH_2)_5-C(=NOH)-H}$	35	1.5	72	105-107.5 (107)
	35	2	79	252-254.5 (254)
	35	2	75	266.5-267.5 (267-268)
	35	2	70	246-247.5 (248-250)
	35	2	73	200-202 (200.5-201.5)
	35	2.5	45	235-236 (237)
	35	2.5	20	318-319 (320)

a. The reaction was carried out with 1.5 equiv of ACC/alumina .

b. Yields were based on 2,4-dinitrophenylhydrazone derivative identified by melting point and the infrared spectra

Experimental Section

melting points were uncorrected. IR spectra were determined on a BIO-RAD FTS-40 instrument. ^{1}H NMR spectra were recorded with a HITACHI R-24B (60MHz) spectrometer. Solvent was freshly distilled. Salicylaldoxime was commercially available. Other oximes were prepared by reaction of parent ketones or aldehydes with hydroxyammonium chloride and identified by their melting point, IR and ^{1}H NMR. ACC/alumina was prepared according to literature[12].

General Procedure

In a round-bottomed three-necked flask (30ml) equipped with a condenser and a magnetic stirrer, placed a solution of the substrate (7mmol) in solvent (20ml). To the solution the oxidant (10g) was added in portion with stirring and the mixture was stirring for 1.5-6 h. The progress of the reaction was followed by GLC. The reaction mixture was filtered and the solid material was washed with ether several times. The combined filtrates was evaporated to furnished the product which was isolated as a 2,4-dinitrophenylhydrazone.

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