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Facile regeneration of carbonyl compounds from 2,4dinitrophenylhydrazones, oxime, hydrazones, and semicarbazones

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ABSTRACT

Derivatives of carbonyl compounds such as oximes, phenylhydrazones, semicarbazones and thiosemicarba-zones are used not only for the characterization and purification of carbonyl compounds[1,2] but also play an important role in the protection carbonyl compounds, as they are highly crystalline and stable compounds. Thus, the regeneration of carbonyl compounds from their derivatives under mild condition is important process in organic synthetic chemistry. We report classical method for the cleavage of oximes, phenylhydrazones, semicarbazones and thiosemicarbazones aldehydes and ketones.

KEYWORDS

Protection;
Aldehyde;
Ketone;
Hydrazine hydrochloride;
Sodium acetate.

INTRODUCTION

2,4-Dinitrophenylhydrazones and other derivatives of carbonyl compounds such oximes, phenylhydrazones[1,2], semicarbazones and thiosemicarbazones as are important Intermediates[3] in organic synthesis because of their use in the characterization and purification-of carbonyl compounds and plays an important role in the protection of these compounds[5-9]. Thus, the regeneration of carbonyl compounds from the Corresponding 2, 4-dinitrophenylhydrazones, oximes, phenylhydrazones, semicarbazone and thiosemicarbazones under mild conditions is an attractive process in organicsynthesis. Several such procedures for regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones have been reported, using sodium perborate and hydrogen peroxide carried out under mild conditions, some of methods of deprotection have a drawback of using expensive oxidant, strong oxidative conditions, need of freshly prepared reagents[6,7], tedious work-up, or they are often hazardous[3-6]. Although some of the known methods are carried out under mild reaction conditions,most of them require drastic conditions, high temperature, long reaction times, toxic or not- readily available reagents,they need to be freshly prepared, and have tedious work-up procedures. Little attention has been paid to the regeneration of carbonyl compounds from hydrazones, semicarbazones and azines[14-16]. Thus, there is a continuous need either to improve the existing protocols or to introduce new reagents to permit faster reaction, milder conditions, easier work-up and eco-friendly procedures.

EXPERIMENTAL

General M.P. determined on Buchi M.P. apparatus and were recorrected ^{1}H NMR spectra were ecorded on INM- PMX 60 NMR spectrometer (60MHz) in $CDCl_3$ using tetramethyl silane as internal

standard; and IR spectras in KBR disc on a hitachi were monitored by T.L.C.

PREPARATION OF DERIVATIVE OF ALDEHYDE AND KETONES

2,4-Dinitrophenylhydrazones, oxime samicarbazone, thiosamicarbazone hydrazone, etc were synthesized from corresponding carbonyl compounds according to the literature.25 allproducts were known and characterized by comparison of their MP or BP and IR spectra with those of authentic samples. Procedure of hydrazones, semicarbazone and 2, 4 DNP derivatives etc, Take 1gm. of hydrazine hydrochloride, semicarbazone and 2,4 DNP derivative in clean 100 ml. conical flask and to it 2gm. Of sodium acetate and added 100 ml. distilled water and become soluble completely, if not then slightly warm on water bath take 1gm. Aldehyde or ketones dissolve in 3 ml. alcohol (if methanol or ethanol) and then adds conical flask and heated in a water bath for required time for the completion of reactionA flaks is removed and cooled in crushed ice water to settle and developed crystal then separated of this crystal on filter we get hydrazones. Then product is dried and weigh and carry out melting point and tlc

DEPROTECTION OF HYDRZONE

1.2 mm of hydrazone, oxime,samicarbazone, thiosamicarbazone derivative of aldehyde or ketone add 15 ml of acetic acid, 1.1 mole of sodium per borate. Heat this mixture at 50^0 C for 5to10 minute then add 5 ml of 10% of H_2O_2 and continue heating cheack TLC. of reaction after 10-15 minut ($CHCl_3$+MeOH) after compleation of rection pour th e reaction in water (15ml) add diethyl ether wash ether layer.

RESULT

Sodium perborate and H_2O_2 are cheap and easily available easily sodium hypochlorite and both chemicals areb cheap and not more harmful Our approach to a clean and efficient regeneration of carbonyl compounds from 2,4-nitrophenylhydrazones.oxime, samicarbazone.,phenyl hydrazine, hydrazones, is mixed with sodium perborate and hydrogen peroxide, mix-

TABLE 1 : Deprotection of hydrazone

Sr No.	Hydrazones	Time for Deprotection in min.	Physical Constant after Deprotection (^{0}C)
1	Anisaldehyde	25	140
2	Cinnaldehyde	40	248
3	Benzaldehyde	30	180
4	2,4dimethoxybenzaldehyde	27	72
5	4-chlorobenzaldehyde	45	50
6	3- nitrobenzaldehyde	25	202
7	P-tolualdehyde	26	60
8	Salicylaldehyde	37	198
9	o-chlorobenzaldehyde	29	215
10	4-hydroxybenzaldehyde	19	119
11	Acetophenone	29	204

TABLE 2 : Result table for deprotection of phenyl hydrazone

Sr. No.	Hydrazones	Time for deprotection in min.	Physical Constant after deprotection (^{0}C)
1	Anisaldehyde	25	140
2	Cinnaldehyde	40	248
3	Benzaldehyde	30	180
4	2,4dimethoxybenzaldehyde	27	72
5	4-chlorobenzaldehyde	45	50
6	3- nitrobenzaldehyde	25	202
7	P-tolualdehyde	26	60
8	Salicylaldehyde	37	198
9	o-chlorobenzaldehyde	29	215
10	4-hydroxybenzaldehyde	19	119
11	Acetophenone	29	204

TABLE 3 : Deprotection of hydrazones

Sr. No.	Hydrazones	Time for deprotection in min.	Physical Constant after deprotection (^{0}C)
1	Anisaldehyde	26	140
2	Cinnaldehyde	42	248
3	Benzaldehyde	39	180
4	2,4dimethoxybenzaldehyde	28	72
5	4-chlorobenzaldehyde	34	50
6	3- nitrobenzaldehyde	28	202
7	P-tolualdehyde	27	60
8	Salicylaldehyde	34	198
9	o-chlorobenzaldehyde	23	215
10	4-hydroxybenzaldehyde	22	119
11	Acetophenone	30	204

ture placed water bath for 15-20 min for deprotection. It is noteworthy to mention that the above reaction remained incomplete under when oxidative power of sodium perborate increase in presence of hydrogen peroxide was used without hydrogen peroxide even with a higher ratio of reagent.

CONCLUSION

In conclusion, the present procedure for regeneration of carbonyl compounds from 2,4-dinitrophenylhydrazones, oximes, semicarbazone, hydrazones, phenyl hydrazones, etc. has all advantages of using sodium perborate hydrogen peroxide as eco-friendly and less toxic material, mild reaction conditions, easy work-up procedure, short reaction time, high to excellent yields.

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