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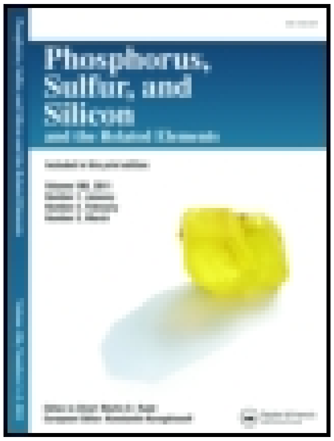

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CARO'S ACID SUPPORTED ON SILICA GEL, PART VIII: AN EFFICIENT AND SELECTIVE REAGENT FOR CONVERSION OF PHENYLHYDRAZONES AND SEMICARBAZONES TO THE CORRESPONDING CARBONYL COMPOUNDS

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CARO'S ACID SUPPORTED ON SILICA GEL, PART VIII: AN EFFICIENT AND SELECTIVE REAGENT FOR CONVERSION OF PHENYLHYDRAZONES AND SEMICARBAZONES TO THE CORRESPONDING CARBONYL COMPOUNDS

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Deprotection of phenylhydrazones and semicarbazones to their parent aldehydes and ketones in high yields has been carried out using caro's acid supported on silica gel as a selective oxidant under mild conditions.

Keywords: 2,4-Di-nitrophenylhydrazones; Caro's acid; deprotection; phenylhydrazones; semicarbazones

INTRODUCTION

Derivatives of carbonyl compounds such as phenylhyrazones and semicarbazones not only are used for the characterization and purification of carbonyl compounds but also play an important role in the protection of carbonyl compounds, as they are highly crystalline and stable compounds. Thus, the regeneration of carbonyl compounds from their derivatives under mild condition is an important process in organic synthetic chemistry.

The classical method for the cleavage of phenylhyrazones and semicarbazones to aldehydes and ketones includes acid hydrolysis, which is not suitable for acid-sensitive compounds.[1]

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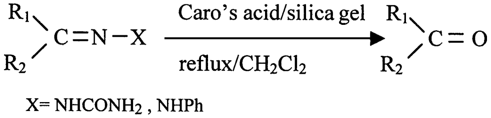
Several oxidative deprotection methods have been developed that have some advantages over the classical hydrolysis methods.[2–13] Little attention has been paid to the oxidative cleavage of phenylhyrazones and semicarbazones, and only a few reports are available dealing with the conversion of these derivatives to their corresponding carbonyl compounds.[14–18]

RESULTS AND DISCUSSION

We have previously reported that Caro's acid supported on silica gel is an efficient reagent for oxidation of organic compounds.[19,20]

We now report a mild and convenient method for oxidative deprotection of semicarbazones and phenylhydrazones in high yields using Caro's acid/silica gel (Scheme 1).

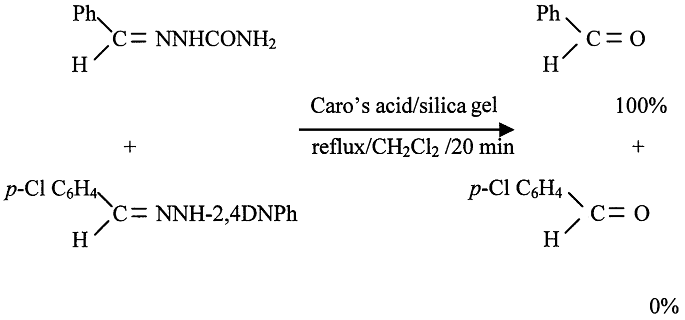


SCHEME 1

Our experiments show that semicarbazones and phenylhydrazones are converted to their corresponding aldehydes and ketones in refluxing dichloromethane. Further oxidation of aldehydes to their carboxylic acid is not observed. This reagent has wide applicability for regeneration of carbonyl compounds from aliphatic and aromatic semicarbazones and phenyl hydrazones (Table I).

It is noteworthy that the 2,4-dinitrophenylhydrazones are not deprotected by this reagent in appropriate yield. These results suggest that this procedure will show considerable selectivity between semicarbazones and phenylhydrazones with 2,4-dinitrophenylhydrazones. This was established by an experiment in which a mixture of an equal amount of the derivatives, semicarbazone of benzaldehyde and 2,4-dinitrophenylhydrazone of *p*-chlorobenzaldehyde, was treated with Caro's acid on silica gel in CH_2Cl_2 at reflux temperature for 20 min. Working up the reaction mixture showed that only the semicarbazone was selectively oxidized to banzaldehyde, and the 2,4-dinitrophenylhydrazone of *p*-chlorobenzaldehyde remained unchanged (Scheme 2).

Similar competitive reaction between phenylhydrazone of benzaldehyde and 2,4-dinitrophenyl-hydrazone of *p*-chlorobenzaldehyde



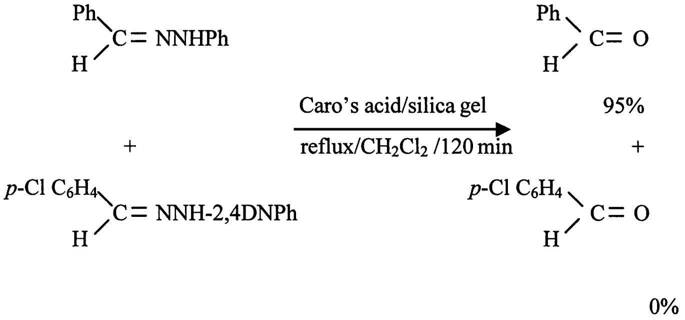
SCHEME 2

resulted only in the oxidation phenylhydrazone of benzaldehyde (Scheme 3).

When we treated α, β-unsaturated semicarbazone, only the C=N bond was selectively oxidized to the corresponding carbonyl compound, and the reagent was ineffective in oxidizing C=C double bond (Table I, Entry 8).

In order to show the efficiency of this method we have compared some of the results with relevant ones reported in the literature[14–18] (Table II). As indicated in Table II, when compared to other reagents Caro's acid on silica gel performs this transformation in higher yield, shorter reaction times, and milder conditions.

In conclusion the methodology described here for the regeneration of carbonyl compounds from their corresponding semicarbazones and phenylhydrazones with Caro's acid on silica gel is manipulatively simple, mild, highly selective, cheap, and it avoids disadvantages of other methods.



SCHEME 3

TABLE I Regeneration of Carbonyl Compounds from Semicarbazones and Phenylhydrazones with Caro's Acid/Silica Gel in Refluxing CH_2Cl_2

Entry	R1	R2	X	Time (min)	Yield[a,b] (%)
1	C_6H_5	H	$NHCONH_2$	20	100
2	*p*-MeO C_6H_4	H	$NHCONH_2$	35	100
3	*o*,*p*-$(MeO)_2$ C_6H_3	H	$NHCONH_2$	5	100
4	*p*-ClC_6H_4	H	$NHCONH_2$	8	100
5	*p*-BrC_6H_4	H	$NHCONH_2$	5	100
6	*p*-$NO_2C_6H_4$	H	$NHCONH_2$	50	90
7	*m*-NO2C_6H_4	H	$NHCONH_2$	80	90
8	$C_6H_5CH{=}CH$	H	$NHCONH_2$	39	100
9	C_6H_5	CH_3	$NHCONH_2$	5	100
10	C_6H_5	C_2H_5	$NHCONH_2$	7	100
11	CH_3	CH_3	$NHCONH_2$	4	100
12	C_2H_5	CH_3	$NHCONH_2$	10	100
13	—$(CH_2)_4$—		$NHCONH_2$	45	90
14	—$CH_2CH_2CH(C_6H_5)CH_2CH_2$—		$NHCONH_2$	25	100
15	Camphor		$NHCONH_2$	15	100
16	C_6H_5	H	NHC_6H_5	120	95
17	*p*-Me C_6H_4	H	NHC_6H_5	60	90
18	*o*-OHC_6H_4	H	NHC_6H_5	50	90
19	*o*-ClC_6H_4	H	NHC_6H_5	75	90
20	*m*-ClC_6H_4	H	NHC_6H_5	105	95
21	*p*-BrC_6H_4	H	NHC_6H_5	85	95
22	*p*-$NO_2C_6H_4$	H	NHC_6H_5	90	90
23	*o*-OHC_6H_4	CH_3	NHC_6H_5	150	90
24	C_6H_5	C_6H_5	NHC_6H_5	125	90

[a] Products were characterized by their physical constants, spectral characteristics (IR, ^1H NMR) and comparison with authentic samples.

[b] Yields are of pure isolated products.

EXPERIMENTAL

Products were isolated, and their physical data were compared with those of known samples. Solvent was freshly distilled. Phenylhyrazones, 2,4-dinitrophenylhydrazones, and semicarbazones were prepared according to the described procedures.[21]

General Procedure for Deprotection of Semicarbazones and Phenylhydrazones

In a round-bottomed flask (50 ml) equipped with a condensor and a magnetic stirrer, a mixture of the substrate (1 mmol) in CH_2Cl_2 (5 ml) and Caro's acid on silica gel (3 mmol) was placed. The reaction mixture was stirred at reflux temperature for the specified time (Table I). The

TABLE II Comparison of Some of the Results Obtained by the Desemicarbanozation with Caro's Acid Supported on Silica Gel with Some of Those Obtained by BTPPMS,[a,17] Dowex-50,[16] ACC/alumina,[b,14] $CuCl_2.2H_2O$,[15] and QDC[c,18]

Entry	Reagent	Substrate	Time (min)	Yield (%)	Reaction condition
1	Caro's acid/ Silica gel	Acetophenone semicarbazone	5	100	CH_2Cl_2, Reflux
		Benzaldehyde semicardazone	20	100	
2	BTPPMS	Acetophenone semicarbazone	60	95	MeCN, Reflux
3	Dowex-50	Acetophenone semicarbazone	60	90	H_2O, Reflux
		Benzaldehyde semicardazone	300	32	
4	ACC/alumina	Acetophenone semicarbazone	360	59	CH_2Cl_2, Reflux
		Benzaldehyde semicardazone	240	72	
5	$CuCl_2.2H_2O$	Acetophenone semicarbazone	30	81	MeCN, Reflux
		Benzaldehyde semicardazone	90	51	
6	QDC	Acetophenone semicarbazone	132	77	MeCN, Reflux
		Benzaldehyde semicardazone	135	85	

[a] BTPPMS, Benzyltriphenylphosphonium peroxymonosulfate.
[b] Ammonium chlorochromate.
[c] Quinolinium dichromate.

progress of the reaction was monitored by thin layer chromatography (TLC) or gas chromatography (GC). After completion of the reaction the solid material was filtered and washed with CH_2Cl_2, and dried by Na_2SO_4. The combined filtrates were evaporated on a rotary evaporator. The resulting crude material was purified on a silica gel plate (eluent: hexane/ethyl acetate, 5:1) to afford the pure carbonyl compound, yield 90–100% (Table I).

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