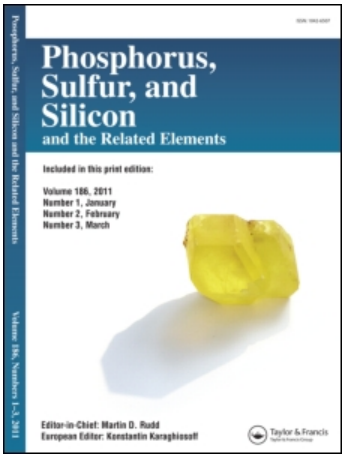

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CARO'S ACID SUPPORTED ON SILICA GEL. PART VI. A MILD REAGENT FOR REGENERATION OF CARBONYL COMPOUNDS FROM ACETALS, KETALS, AND 1,1-DIACETATES

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CARO'S ACID SUPPORTED ON SILICA GEL. PART VI. A MILD REAGENT FOR REGENERATION OF CARBONYL COMPOUNDS FROM ACETALS, KETALS, AND 1,1-DIACETATES

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Efficient conversion of acetals, ketals, and diacetates to carbonyl compounds is described using Caro's acid supported on silica gel. The deacetalization reactions are carried out in acetonitrile at room temperature. Reaction of diacetates is performed in refluxing dichloromethane, and their parent carbonyl compounds are obtained in good-to-excellent yields.

Keywords: 1,1-Diacetate; acetal and ketal; Caro's acid; regeneration of carbonyls

Acetals, ketals, and diacetates are frequently used to protect carbonyl compounds in the course of total synthesis. The shielding of carbonyls from nucleophilic attack is usual practice in multistep synthesis to exploit its electrophilic properties.[1] Therefore, deprotection to their parent carbonyl group is important in organic synthesis. The protection for carbonyls is often served as cyclic and acyclic acetals, which have proved to be more serviceable, and hence considerable efforts has been made for their introduction and removal.[2]

Most of the methods used for the cleavage of these protective groups employ aqueous or nonaqueous media acidified with mineral or organic acids.[3] However, this is very often incompatible with the presence of some other protected functional groups. To overcome the problem, a number of mild and nonaqueous cleaving methods have been reported. Some examples involve wet silica gel or $LiBF_4$ in acetonitrile,[4]

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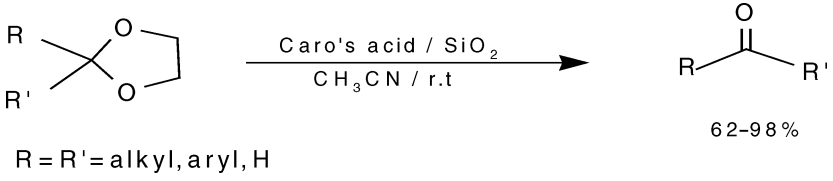
phosphorous triiodide and diphosphorus tetraiodide,[5] titanium (IV) chloride,[6] boron trifluoride-iodide ion,[7] and cerium(III) chloride.[8]

But many of these methods failed to deprotect the dioxalane moiety, and some procedures suffer from lack of selectivity; unsatisfactory yields; toxic, corrosive, and expensive reagents; elevated temperature or sever reaction condition; and formation of considerable amounts of side products. Hence, several milder methods that use neutral conditions and inorganic supported reagents have also been developed for deprotection of acetals and ketals.[9]

On the other hand, 1,1-diacetates have attracted considerable attention during recent years because these compounds are moderately stable, easily prepared, and can act as protecting groups for aldehydes. They are also important starting materials for the synthesis of dienes for Diels-Alder cycloaddition.[10] So far, various methods have been reported for the conversion of 1,1-diacetates to the corresponding aldehydes.[11–21] However, some of these methods have disadvantages such as high acidity, long reaction time, low yield of product, and the requirement of an additional microwave oven or inert atmosphere. The identification of a mild reagent for regeneration of aldehyes and ketones from acetals, ketals, and diacetates formed the basis of this investigation.

Recently, we have used Caro's acid supported on silica gel as an efficient oxidizing agent for some oxidative transformation in organic chemistry.[22] This reagent is easily prepared in situ from potassium persulfate and sulfuric acid.[23] We herein have examined Caro's acid supported on silica gel for deprotection of cyclic acetals, ketals, and diacetates. It was found that Caro's acid/SiO_2 can be used to deprotect acetals and ketals to the corresponding carbonyl compounds in acetonitrile at room temperature in good-to-excellent yields (Scheme 1).



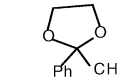
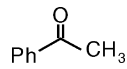
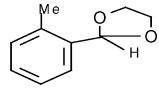
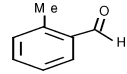
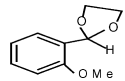
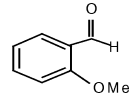
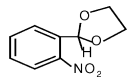
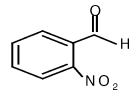
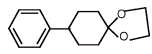
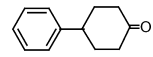
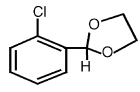
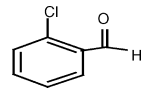
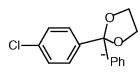
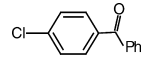
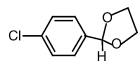
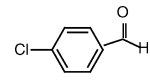
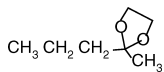
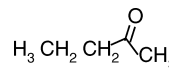
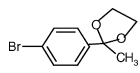
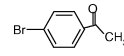
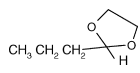
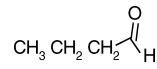
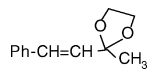
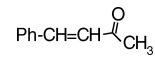
SCHEME 1

RESULTS AND DISCUSSION

The deprotection of acetals and ketals is studied in different solvents such as acetonitrile, tetrahydrofuran (THF), dichloromethane,

chloroform, dioxane, hexane, and cyclohexane. Acetonitrile turned out to be a suitable solvent for this transformation. Deprotection of acetals and ketals proceed at room temperature by stirring the acetals with equimolar quantity of the reagent in acetonitrile (Table I). Using

TABLE I Deprotection of Acetals and Ketals Using Caro's Acid Supported on Silica Gel

Entry	Substrate	Time (min)	Product	Yield (%)[a]
1		20		95[b]
2		20		95[b]
3		20		95[b]
4		75		80
5		50		90
6		60		84
7		60		93
8		45		78
9		25		86
10		40		95[b]
11		100		62
12		22		90

[a]Refers to isolated yield.

[b] Purity >98% (based on ^{1}H NMR), thus it was not purified further.

a catalytic or less than stiochiometric amounts were also tried. Fast completion and high yields were obtained in equimolar ratio. Surprisingly, in the case of acetals overoxidation of the parent aldehydes is not observed. As seen in Table I, a variety of cyclic acetals and ketals were treated with this reagent at room temperature. In this study we have found that acetals derived from aliphatic aldehydes and aromatic aldehydes bearing electron-withdrawing groups were deprotected slower than ketals, and deprotection of these compounds was not completed under above conditions, whereas ketals completely deprotected to their corresponding carbonyl compounds in good-to-excellent yields. The acid-sensitive tetrapyranyl ether group is unaffected under these conditions.[24] This method shows that Caro's acid that is impregnated onto silica gel support is efficient and has attained importance because of its good selectivity and ease of manipulation.

Finally, deprotection of 1,1-diacetates investigated using this reagent. As shown in Table II, different type of 1,1-diacetates, including those bearing electron-withdrawing substituents, are converted to the corresponding aldehydes in the presence of 0.5 molar ratio of Caro's acid

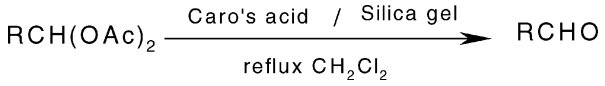
TABLE II Deprotection of 1, 1-diacetates in the Presence of Caro's Acid Supported on Silica Gel

Entry	R	Time (min)	Yield (%)[a,b]
1	C_6H_5	10	98
2	4-$MeOC_6H_4$	4	98
3	3,4-$(MeO)_2C_6H_3$	2	98
4	3,4-$(MeO)_2C_6H_3$	4	98
5	2-$MeOC_6H_4$	2	98
6	2-$NO_2C_6H_4$	120	80
7	3-$NO_2C_6H_4$	170	90
8	4-$NO_2C_6H_4$	200	50
9	5-Me-2-Furyl	2	100
10	5-NO_2-2-Furyl	5.5	100
11	$C_6H_5CH{=}CH$	7.5	90
12	4-BrC_6H_4	84	98
13	4-ClC_6H_4	45	80
14	1-Naphtyl	7	98
15	CH_3CH_2	300	90
16	$CH_3CH_2CH_2$	140	80
17	4-AcetoxyC_6H_4	7	90
18	$CH_3(CH_2)_4CH_2$	170	87
19	Ph CH_2CH_2	120	90
20	4-HOC_6H_4	20	95

[a]All products were identified by comparison of their physical data with those of authentic samples.

[b]Isolated yields.

supported on silica gel in dichloromethane. As shown in the Table II, caro's acid supported on silica gel can also deprotect the aliphatic diacetates to corresponding aldehydes in good yields (Scheme 2).



SCHEME 2

The carbon–carbon double bound and methoxy group remained intact in this method. It is important to note that aryl aldehyde diacetate is selectively deprotected in the presence of phenolic acetate function (Table II, entry 17). These selectivity is of value in organic synthesis.

In conclusion, we have developed a simple and efficient method for the selective deprotection of aryl diacetates. In addition, high yield of the products, short reaction time, ease of workup and nontoxicity of the reagent make this method a useful addition to the present methodologies.

EXPERIMENTAL SECTION

All yields refer to the isolated products and are characterized by ^{1}H NMR, IR, and comparison with authentic samples. ^{1}H NMR spectra were recorded with a EM 360 A (60 MHz) spectrometer. IR spectra were determined on a SP-1100, P-UV-Com instrument. Acetals and diacetates were prepared according to the reported methods.[25] Caro's acid/SiO_2 was prepared as detailed below.

Preparation of Caro's Acid

To ice cooled 98% sulfuric acid (4.7 g) is added in small portions potassium persulfate (4.5 g) with stirring. Crushed ice (13 g) and water (4 g) is added to this, and the temperature is kept below 15°C. Silica gel (5 g, thin layer chromatography (TLC) grade, kieselgel 60G, particle size 15 μm) is added in portions to the mixture and stirred for 4 h in an ice water bath. The mixture is then filtered under suction and dried in a desiccator to give a white free-flowing powder.

Deprotection of Acetals and Ketals: General Procedure

A suspension of acetals (1 mmol) and Caro's acid/silica gel (0.6 g, 1 mmol) in CH_3CN (4 ml) is prepared. The mixture is stirred

magnetically at room temperature for 20–100 min. After completion of the reaction, the reaction mixture is filtered and acetonitrile is evaporated, and then the residue is washed with dilute $NaHCO_3$ and extracted with dichloromethane (20 ml). Evaporation of the solvent gives the parent carbonyl compounds in good-to-excellent yields.

Deprotection of 1,1-Diacetate: General Procedure

To a solution of 1,1-diacetates (1 mmol) in dichloromethane (5 ml) was added Caro's acid/silica gel (0.5 mmol), and the mixture was stirred under reflux condition for the time indicated in the Table I. The reaction was followed by TLC. On completion of the reaction, the reaction mixture was filtered and washed with CH_2Cl_2. The combined filtrates were evaporated to give the crude products. Purification of the crude material on a silica-gel plate (eluent: n-C_6H_{14}/Et_2O: 4/1) afforded the pure aldehydes in 50–100% yields (Table II).

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