



Preparation of Acylals From Aldehydes Catalyzed By Au Nps/ Stilbite Zeolite

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Abstract:

In the present research article, Acylals and its derivatives synthesized by stirring aromatic aldehydes, acetic anhydride using gold nanoparticle deposited on stilbite zeolite. The reaction has many advantages over conventional methods such as short reaction time, easy work-up procedure, and reusable catalyst.

Key words: Gold nanoparticle, Stilbite zeolite, Acylals synthesis, Neat reaction.

Introduction

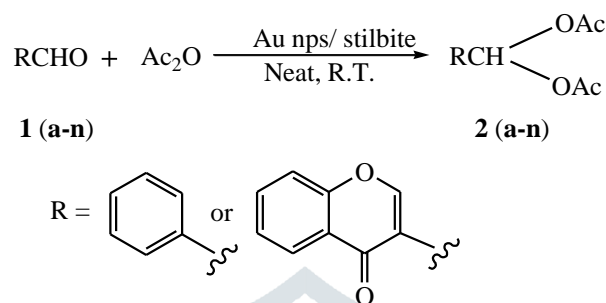
In recent years, heterogeneous catalysts have gained importance in several organic transformations due to their interesting reactivity, as well as for economic and environmental reasons but many heterogeneous catalysts are less active than the homogeneous catalyst because of the reaction rates are limited by the transport of the reactant to the active sites on the particle surfaces. The utility of the heterogeneous catalysts can be improved by using high surface area materials since the transport of the reactants to the active site on particle surface can be enhanced.

The protection of carbonyl groups plays an important role in organic synthesis as well as chemistry of drug design. Acylal formation is one of the most useful methods to protect carbonyl groups due to the stability of the resulting acylals. They are stable in neutral and basic media [1]. Acylals are synthetically important precursors for the preparation of 1-acetoxydienes for Diels–Alder reaction [2]. Chiral allylic esters have been obtained using palladium catalysts by an asymmetric allylic alkylation of gem-diesters [3]. The preparation of homoallyl acetates by allylation of acylal has also been reported [4].

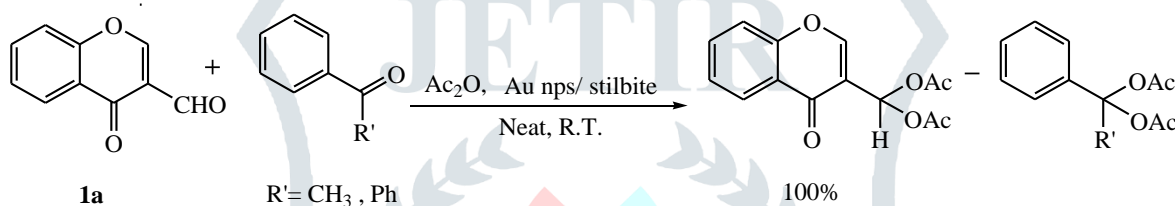
Generally, acylals have been prepared by the reaction of aldehydes with acetic anhydride catalyzed by (sulphuric, phosphoric and methanesulfonic acid) [5], I_2 [6], $InCl_3$ [7], $Cu(OTf)_3$ [8], $H_6P_2W_{18}O_{62} \cdot 24H_2O$ [9], $[Hmim]HSO_4$ [10], $SnCl_4/SiO_2$ [11], $GaCl_3$ [12] and CAN [13]. These are the reported methods for the synthesis of 1,1-diacetates from aldehydes. Although some of these methods have convenient protocols with good to high yields. The majority of these methods suffer at least from one of the following disadvantages: reaction under oxidizing conditions, prolonged reaction time, high temperature, use of moisture sensitive and expensive catalysts, use of

solvents, strong conditions, and difficulty in scaling up etc. therefore, development of catalysts working under mild reaction conditions is desirable

In recent years, solvent-free organic synthesis have offered more advantages as compared to their homogeneous counterparts due to the growing concern for the influence of organic solvent on the environment as well as on human body, economical demands and simplicity in the processes [14].



Scheme 1



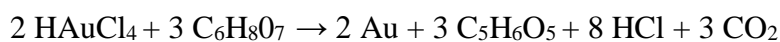
Scheme 2

Experimental

The uncorrected melting points of all compounds were taken in an open capillary in a paraffin bath. The progress of the reaction was monitored by TLC. IR spectra were recorded in KBr discs on a FTIR instrument. ¹H and ¹³C NMR spectra were recorded on 300 MHz and 75 MHz spectrometers, respectively, using CDCl₃ as a solvent and TMS as an internal standard.

Preparation of Au nps/ stilbite zeolite

Gold nanoparticles were prepared by the citrate-reduction procedure. A series of Au nanoparticles was synthesized using different solutions. The quantity of 200 µl, 300 µl, 400 µl and 500 µl were taken from 1% tetrachloroauric acid solution and diluted to 50 ml to make 10 mM, 15 mM, 20 mM and 25 mM aqueous solutions of tetrachloroauric acid respectively. This solution in beaker was boiled until the temperature reach 80°C on a hot plate with magnetic stirrer. To this boiling solution, 1.5% trisodium citrate was added in continuous mode quickly with simultaneous stirring. After addition of sodium citrate solution, stirring continued until solution turns brilliant red colored. The synthesis reaction summarized as given below.



The above gold nanoparticle prepared were mixed with 2 gm of stilbite zeolite separately stirred for 2 hrs, air dried and heated at 200 °C in muffle furnace, cooled and named as A, B, C, D. This samples are used as a catalyst in organic transformation. It was found that the sample C are act as a better catalyst.

General procedure for preparation of acylals

Aromatic aldehyde 1 (a-n) (1 mmol), acetic anhydride (2 mmol) and Au nps/stilbite (1 mol%) were taken in a round bottom flask and stirred at room temperature. The time required for each reaction is indicated in Table 1. The reaction was followed by TLC (*n*-Hexane: EtOAc, 9:1). After completion of the reaction, the mixture was diluted with ethyl acetate (15 mL). The organic layer was washed with 10% NaHCO₃ solution and water and then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to give pure 2 (a-n) in excellent yields.

Results and discussion

We would like to report a simple, mild, efficient and rapid method for the preparation of acylals from variety of aromatic and heteroaryl aldehydes with acetic anhydride in the presence of catalytic amount of Au nps/ stilbite zeolite at room temperature under solvent-free conditions (Scheme 1).

To optimize the reaction conditions, the reaction of benzaldehyde (1a) and acetic anhydride was selected as model reaction to investigate the effects of the catalyst at different amounts of catalyst on the yield. The best result was obtained by carrying out the reaction with 1:2 mol ratios of benzaldehyde: acetic anhydride and 1 mol% of Au nps/ stilbite zeolite at room temperature under solvent-free conditions and under this conditions 2a was obtained in 98% yield after 08 min (Table 1, compound 2a). To determine the role of Au nps/ stilbite, the model reaction was carried out in the absence of catalyst at room temperature under solvent-free conditions, the desired product was not obtained after 120 min. This result indicate that Au nps/ stilbite zeolite exhibit a high catalytic activity in this transformation.

The substrate, 4-oxo-(4*H*)-1-benzopyran-3-carbaldehyde has three active centers such as α , β -unsaturated carbonyl group, a C=C bond and a formyl group. Out of these three reactive centers, the reaction chemoselectively occurs at formyl group. Table 1 showed the aromatic and heteroaryl aldehydes having different substituents such as chloro, nitro, methoxy, methyl, bromo, fluoro, etc. were converted to the corresponding acylal derivatives with high yields. The acylals were prepared at room temperature and isolated by simple quenching in water and neutralization with NaHCO₃. All the reactions were completed within 07-20 min with excellent yields (91-98%). This methodology avoids the use of corrosive acids, solvents and requires only catalytic amount of the Au nps/ stilbite to promote the reaction. The identities of compounds 2 (a-n) were established by comparison of their physical and spectroscopic values with those earlier reported [11-13].


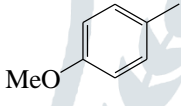
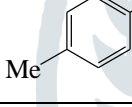
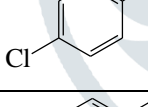
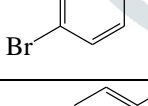
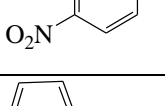
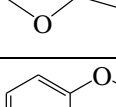
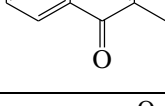
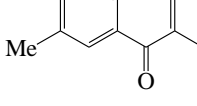
In order to show the high selectivity of the procedure, we investigated competitive reactions for the preparation of the acylals from 4-oxo-(4*H*)-1-benzopyran-3-carbaldehyde in the presence of acetophenone or benzophenone using a catalytic amount of Au nps/ stilbite zeolite at room temperature under solvent-free conditions. We found that ketones did not produce any acylals under the optimized reaction condition. This result suggested that chemoselective protection of aromatic and heteroaryl aldehydes in the presence of ketones could be achieved with this procedure (Scheme 2).

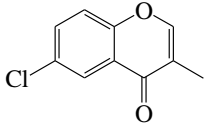
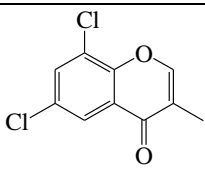
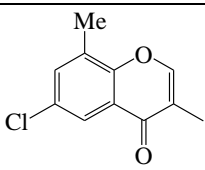
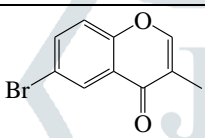
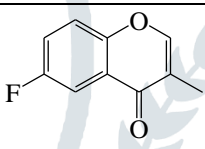
The data presented in this table 1. Show the promising features of this method in terms of molar ratio of the catalyst, reaction rate and yield of the product compared with those reported in the literature.

The reuse of the catalyst

One interesting property of the novel catalyst is its heterogeneous catalytic process. Thus, recovery of the catalyst is very convenient. After the reactions, the catalyst was recovered by filtration. It was washed with acetone and dried at 110 °C in oven. The recovered catalyst reused for further reaction. The activity of recovered catalyst was carefully investigated through the reaction of benzaldehyde and acetic anhydride. The yields and sample composition remained unchanged even after the catalyst had been recycled for a four time. The results are summarized in Table 2.

Table 1. Au nps/ stilbite zeolite catalysed preparation of acylals^a.

Compound	R	t/min	Yield % ^b	M.p.(°C) Found
2a		08	98	44-46
2b		12	98	65-66
2c		13	95	83-85
2d		07	97	81-82
2e		08	91	93-94
2f		11	94	123-124
2g		10	92	52-53
2h		14	95	130-131
2i		20	93	148-149

2j		15	93	170-172
2k		16	96	189-191
2l		19	93	162-164
2m		12	96	170-172
2n		09	95	154-156

^aReaction condition: aromatic and heteroaryl aldehydes (1 mmol), acetic anhydride (2 mmol), Au nps/ stilbite (1 mol%) at room temperature under solvent-free conditions.

^b Isolated yield based upon starting aldehyde.

Table 2. Reusability of the catalyst.

Entry	Cycle	Yield (%) ^{a,b}
1	Fresh	98
2	First	98
3	Second	97
4	Third	97

^aYield refers to isolated product.

^ball products are known.

Conclusion

In conclusion, we have describe a facile and efficient method for the preparation of acylals from a variety of aromatic and heteroaryl aldehydes with acetic anhydride in the presence of catalytic amount of Au/ stilbite at room temperature under solvent-free conditions. This method is highly selective for the synthesis of acylals from aromatic and heteroaryl aldehydes in the presence of ketones. The notable merits of the present method are short

reaction times, mild reaction conditions, excellent chemoselectivity, simple work-up procedure and excellent yield of products. Moreover, the catalyst used is mild, non-toxic and eco-friendly nature. It is thus a rapid, convenient and environmentally benign method for the preparation of compounds of type 2 (a-n).

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