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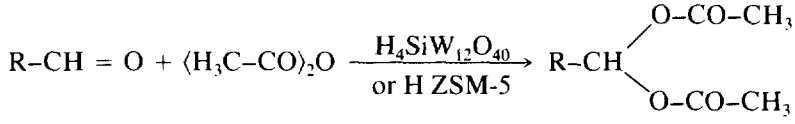
NOTES

Facile Conversion of Aldehydes to 1,1-Diacetates Catalysed by H ZSM-5 and Tungstosilicic Acid

The preparation of 1,1-diacetates from the aldehydes is a very useful synthetic reaction (*1*). Several synthetic methods have been reported for the preparation of 1,1-diacetates from aldehydes using protic acids such as sulfuric acid, phosphoric acid, or methane sulphonic acid (*2*). In addition, there are also reports of Lewis acids such as ferric chloride (*3*) and zinc chloride (*4*) as catalysts for the reaction. Among the Lewis-acid catalysts only $FeCl_3$ gives good yields (up to 93% for aromatic aldehydes). However, the yields fall for aliphatic aldehydes. Olah and Mehrotra (*5*) reported a solid superacid catalyst Nafion H for the formation of 1,1-diacetates. The reaction times are, however, very long (varies from 1–18 hr).

We now report an elegant and convenient method to prepare 1,1-diacetates from aldehydes and acetic anhydride using H ZSM-5 and tungsto-silicic acids as shown below:



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The present work is an extension of our earlier papers on the synthetic applications of H ZSM-5 and heteropolyacids (*6*, *7*). Our method has the following significant advantages over the previously reported methods:

(i) the reaction times are very short (15 min for the heteropolyacid);

(ii) very high yields even with deactivated aromatic aldehydes, and

(iii) the small quantities of the catalyst used facilitates very easy work.

Yet another interesting aspect of this work is that H ZSM-5 catalyst exhibits substantial difference in reaction rates for the *ortho* and *para* isomers of the aromatic aldehydes. Tungstosilicic acid, however, did not exhibit such an effect.

The aldehydes were all procured either from Fluka (Switzerland) or Aldrich Chemical Co. Ltd. (U.K.) and were of 99.5% purity. Tungstosilicic acid, acetic anhydride and the solvents were procured from British Drug House, India. H ZSM-5 (Si/Al = 90) was kindly supplied by Dr P Ratnasamy of National Chemical Laboratory, Pune, India. The BET surface area of the sample is 415 m^2/g and the adsorption capacity for water was found to be 8% by weight of the zeolite. The tungstosilicic acid ($H_4SiWO_{40} \cdot XH_2O$) was used as obtained for the reaction. H ZSM-5 was calcined at 400°C for 4 hr in air and cooled to room temperature before using for the reactions.

0.01 mol of the aldehyde was taken in a round bottom flask and 0.015 mol of freshly distilled acetic anhydride was added. Then tungstosilicic acid (10% by weight of the aldehyde) was added. The reaction mixture was stirred for 15 min. Progress of the reaction was monitored by GC fitted with a 30-m-long capillary column with an i.d. of 1.2 μm (RSL 300; OV-17). At the end of the

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TABLE 1

Yields of Aldehyde Diacetates Prepared Using Heteropolyacid (Tungstosilicic Acid)

Entry no.	Substrate	Reaction[a] time (h)	Yield[b] (%)
1	Benzaldehyde	0.25	98
2	4-Methylbenzaldehyde	0.25	91
3	4-Chlorobenzaldehyde	0.25	82
4	Hexahydrobenzaldehyde	0.25	99
5	*n*-Dodecanal	0.25	95
6	4-Nitrobenzaldehyde	0.25	94
7	2-Nitrobenzaldehyde	0.25	93
8	2,4-Dichlorobenzaldehyde	0.25	85

[a] All reactions are carried out at room temperature (26°C).
[b] Yield refers to isolated yield; unreacted aldehyde constitutes the balance.

reaction, the product was crystallized from a solvent mixture consisting of chloroform and petroleum ether in the ratio 3 : 2. In the case of H ZSM-5 catalysed reaction, 0.005 mol of the aldehyde was mixed with 0.007 mol of acetic anhydride and 40 mg of the catalyst was added and stirred. For aliphatic aldehydes, the amount of catalyst was increased to 100 mg. At the end of the reaction, the catalyst was filtered off and the product crystallized out in the same manner as mentioned above. The isolated solids in all cases were characterized by IR and NMR. With the zeolite catalyst, reactions were also carried out with and without stirring on the magnetic stirrer. The initial rates, in both cases, were comparable which implies that external mass transport does not significantly compete with the measured rates.

Table 1 gives the results of diacetate formation on tungstosilicic acid. It may be seen that high yields are obtained even for deactivated aromatic aldehydes and aliphatic aldehydes. (See, for example, entries 3, 6, 7). Time taken is also very short (15 min for completion of reaction). Indeed, the reactions are too fast to estimate initial rates.

Table 2 assembles the data for H ZSM-5 catalyst. This catalyst also gives high yields (>90%) for the deactivated aromatic aldehydes as well as for aliphatic aldehydes.

TABLE 2

Initial Rate and Yield Data for Aldehyde Diacetate Formation on H ZSM-5

Substrate	Initial rate[a] (mol mg^{-1} min^{-1})	Yield[b] (%)	Time required for final yield
1. Benzaldehyde	2.6×10^{-6}	98.4	1.5 hr
2. 2-Methylbenzaldehyde	1.5×10^{-7}	43.0	24 hr
3. 4-Methylbenzaldehyde	5×10^{-7}	90.5	24 hr
4. 4-Nitrobenzaldehyde	1.2×10^{-6}	98.0	5.5 hr
5. 2-Nitrobenzaldehyde	6.0×10^{-8}	4.0	24 hr
6. Hexanal	—	84.4	24 hr
7. 2-Ethyl hexanal	—	64.4	24 hr

[a] All reactions are carried out at room temperature (26°C).
[b] Yield refers to isolated yield; unreacted aldehyde constitutes the balance.

However, the time of reaction is very long for the aliphatic aldehydes.

It may be seen that the reactions are clean with 100% selectivity for H ZSM-5 as well as tungstosilicic acid. However, the reaction rates are far higher on the tungstosilicic acid in comparison to the zeolite. (Initial rates could not be computed on tungstosilicic acid since the reaction was very fast and reaches equilibrium in 15 min).

Interestingly it has been found that the *ortho*- and *para*-substituted benzaldehydes differ in reaction rates as well as final yields of the diacetates on the zeolite. For instance the initial rates in mol mg^{-1} min^{-1} for 2-nitrobenzaldehyde and 4-nitrobenzaldehyde are 6.0×10^{-8} and 1.2×10^{-6}, respectively, and the yield of the corresponding diacetates are 4.0 and 98.0%, respectively (see entries 4 and 5). Similar observations are made for the reactions of methyl benzaldehydes (entries 2 and 3). On the other hand, the tungstosilicic acid does not show any difference either in the reaction rates or in the final yields of products from the ortho and para isomers of the aldehydes. (Compare entries 6 and 7 in Table 1.) A similar result was obtained on tungstosilicic acid with the *ortho* and *para* isomers of chlorobenzaldehyde as well as methyl benzaldehyde, respectively.

Although, it is tempting to invoke shape sepectivity to explain the above result on H ZSM-5, it is important to consider other possible effects like steric and/or neighbouring group effects.

Attempts were made to separate *ortho* and *para* isomers of nitrobenzaldehyde and chlorobenzaldehyde by carrying out competitive diacetate formation. It was, however, found that due to coadsorption of the ortho isomer, the difference in reaction rates were not substantial enough to separate the isomers.

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