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ACETYLATION BY KETENE OF ALCOHOLS SUPPORTED ON SOLID ADSORBENTS

Teiji CHIHARA,* Yuzuru TAKAGI, Shousuke TERATANI, and Haruo OGAWA†
The Institute of Physical and Chemical Research, Wako-shi, Saitama 351
†Department of Chemistry, Tokyo Gakugei University, Koganei-shi, Tokyo 184

Primary, secondary, and tertiary alcohols supported on solid adsorbents such as alumina, silica gel, celite, magnesium oxide, zinc oxide, titanium oxide, and charcoal were acetylated by ketene in good yields.

Solid adsorbents have been used as reaction media to control reactivity or selectivity. Either the reagent or the substrate is supported on the adsorbent. Many cases have been reported in which the reagent was supported,1) while a fewer examples are known on the second alternative. Examples are seen in the selective protection of carboxyl groups2) and carbonyl groups,3) and in the selective oxidation of primary amines and alkyl hydrogen succinates.4) Recently we have found that phenols supported on the solid adsorbents readily reacted with ketene (1) without heating.5) In this communication we wish to report the acetylation by 1 of alcohols supported on the solid adsorbents.

Methanol, ethanol, and propanol were easily acetylated by 1 without catalyst addition at room temperature. With the higher alcohols, however, the acetylated products hindered further reaction. 1-Butanol in a mixture of 75% butyl acetate is not further acetylated with 1.6) *t*-Butyl alcohol did not react with 1 in the absence of a catalyst. Various materials have been proposed as catalysts for the reaction of 1 with alcohols; sulfuric acid and *p*-toluenesulfonic acid are the most effective ones.7) Metal acetylacetonates,8) amides,9) ε-caprolactam,10) and potassium *t*-butoxide11) were also reported to catalyze the reaction. Our new method, however, does not require such catalysts. Various types of hexanols and benzyl alcohol were chosen as representatives of alcohols for the reaction.

One gram of 1-hexanol (2) was placed in a flask containing 10 g of silica gel powder and allowed to stand for 1 hour or more until the lumps disappeared. Then the silica gel powder was transferred to a glass fritted filter of 6.5 cm diameter equipped with a rubber stopper which had a small outlet column containing a small amount of alumina powder. The alumina powder was used to reduce evaporation loss of 2. The acetylation was conducted by introduction of 1 in a stream of nitrogen from the bottom of the glass filter. The end of the reaction was detected by g.l.c. analyses of the sample or by change in color of the alumina powder from white to yellow. Two ml of 1 kept in a dry ice trap were required to complete the reaction. Then the silica gel and alumina powder were washed with a solvent. After concentration of the eluate under reduced pressure, the product was purified by column

Table 1. Acetylation of Alcohols by Ketene[1]

substrate (1 g)	adsorbent (10 g)	amount of ketene / ml[2]	yield / g (%)
1-hexanol	SiO_2	4.5	1.18 (84)
	celite 545	2.2	1.14 (81)
	MgO	4.5	1.22 (86)
	ZnO	1.1	1.12 (79)
	Al_2O_3	3.9	1.09 (77)
3-hexanol	Al_2O_3	5.5	1.24 (88)
3-methyl-3-pentanol	Al_2O_3	6.2	0.99 (70)
cyclohexanol	Al_2O_3	4.9	1.08 (77)
benzyl alcohol	Al_2O_3	4.9	1.27 (91)

1) The reactions were conducted at room temperature.
2) Liquid state in a dry ice trap. This quantity depended on the experimental conditions especially on the shape of the reaction vessel.

chromatography to remove the polymerization products of 1. The yield was 1.18 g (84%).

The other results are summarized in Table 1. As can be seen from this table, alumina, magnesium oxide, zinc oxide, and celite were found to be effective adsorbents, and all of the alcohols tested were acetylated in good yields. Similarly polyhydric alcohols such as *trans*-1,4-cyclohexanediol, ethylene glycol, and glycerol were acetylated. Titanium oxide and charcoal were also effective adsorbents for the acetylation of 2.

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