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DEHYDRATION OF ALCOHOLS CATALYZED BY COPPER(II) SULFATE ADSORBED ON SILICA GEL

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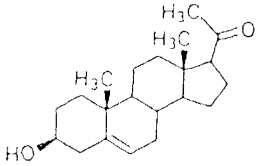
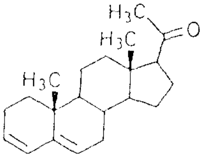
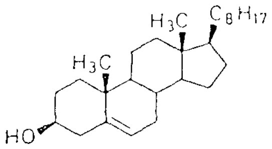
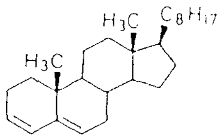
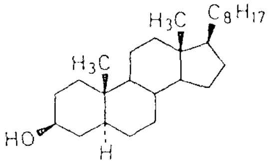
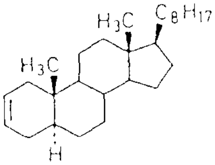
Abstract: Copper(II) sulfate adsorbed on silica gel efficiently dehydrated secondary and tertiary alcohols under mild conditions to give olefins. The rate of dehydration of tertiary alcohols is much faster than that of secondary alcohols.

Many organic reactions have been devised in which the reagents are deposited on various inorganic solid supports. They are often milder, more selective, and operationally simpler to perform than the corresponding homogeneous reactions, as is evident from reviews[1] and recent reports.[2,3] Anhydrous copper(II) sulfate has been reported to dehydrate alcohols under fairly drastic conditions.[4,5] We wish to report copper(II) sulfate adsorbed on silica gel dehydrates alcohols rapidly and selectively under mild conditions.

Some of the results are shown in Table 1. The catalyst was prepared by means of mixing chromatographic silica gel (230-400 mesh) with aqueous copper(II) sulfate and evaporating the water under reduced pressure (2 Torr) with heating. The catalytic activity of a definite amount of copper(II) sulfate continued to increase as the amount of silica gel increased until the weight ratio of silica gel to copper(II) sulfate got to about 4:1 (1.57 mmol $CuSO_4$/1 g silica gel). At higher ratios the activity was nearly constant regardless of the amount of silica gel. Also, the activity depended on drying temperature and drying time: there seems to be the most suitable degree of dryness. In the dehydration of cyclododecanol in refluxing carbon tetrachloride, the catalyst consisting of silica gel and copper(II) sulfate of equal weight (6.27 mmol $CuSO_4$/1 g silica gel) showed the highest activity when dried at 200 °C for 3 h or at 240 C for 1 h. The catalyst decreased its activity when dried further at 240 °C and showed no activity when dried at 300 °C for 1 h. The catalyst gradually lost its activity by being left in the air and recovered it by being dried again. The rate of the dehydration of alcohols was roughly proportional to the

Table 1. Dehydration of Alcohols Catalyzed by Copper(II) sulfate Adsorbed on Silica Gel.[a]

Alcohol	Time (min)	Product	Yield (%)
	60[b] 20[c]		86 57
	20 120[d]		95 95
	40		88
1-Methylcyclododecanol	30[e]	Methylenecyclododecane	52
		1-Methylcyclododecene	46
Cyclododecanol	15	Cyclododecene	98
	30[f]		0
2-Methylcyclohexanol (cis- and trans- mixture)	60	1-Methylcyclohexene 3- and 4-Methylcyclohexene	71 14
4-Methylcyclohexanol (cis- and trans- mixture)	50	3- and 4-Methylcyclohexene 1-Methylcyclohexene	88 2
1-Phenylethanol	50[e]	Styrene	83

a) Unless otherwise noted, the reactions were carried out under the standard reaction conditions described in the text. b) The refluxing solvent was toluene. c) The substrate and equimolar anhydrous copper(II) sulfate was heated at 190 °C without solvents. d) The refluxing solvent was cyclohexane e) The refluxing solvent was carbon tetrachloride. f) Anhydrous copper(II) sulfate was used instead of copper(II) sulfate on silica gel.

amount of the catalyst. Unless otherwise noted, the results mentioned in this paper were obtained by heating an alcohol (1.0 mmol) and the catalyst (0.91 g, 1.0 mmol $CuSO_4$) under reflux in tetrachloroethylene (10 ml) with stirring. This catalyst (1.33 mmol $CuSO_4$/1 g silica gel) was prepared from a mixture of one part of copper(II) sulfate pentahydrate and three parts of silica gel by being dried at 240 °C for 1 h. The reaction was monitored by TLC and NMR spectra of the supernatant solution of the reaction mixture. After the completion of the reaction, the olefins, isolated from the catalyst by filtration, were obtained uncontaminated with by-products. The amounts of olefins adsorbed on the catalyst were nearly negligible in most cases. In some cases, small additional amounts of the olefins were obtained by the elution from the catalyst with more polar solvents such as acetone, usually along with small quantities of recovered alcohols. Except for the reaction of the steroids, the yields of the products were evaluated by NMR and GC by the use of internal standards. The dehydration proceeded well in hydrocarbons and halogenated hydrocarbons such as cyclohexane, benzene, isooctane, toluene, carbon tetrachloride, tetrachloroethylene, and chlorobenzene. By being heated under reflux in acetonitrile, ethyl acetate, and 1,4-dioxane, cyclododecanol was not dehydrated. Melting points of all the steroidal products which were isolated and purified by recrystallization, were identical with the reported values.[2,6] Pregnenolone gave the $\Delta^{3,5}$-diene in the high yield by being heated under reflux with this catalyst in toluene. In the reaction between this steroid and anhydrous copper(II) sulfate without a solvent, the temperature had to be higher than 180 °C and the yield of the diene was not high because side reactions took place. In the reaction of this steroid with thionyl chloride or sulfuryl chloride in pyridine, the product obtained was not the diene but a chlorinated compound. Cyclododecanol also gave chlorocyclododecane instead of cyclododecene in the reaction with thionyl chloride in pyridine. The alcohol transformed completely into cyclododecene within 15 min by being heated under reflux in tetrachloroethylene with the supported reagent, while it was recovered after being heated under reflux with anhydrous copper(II) sulfate for 30 min. Tertiary alcohols were dehydrated much more rapidly than secondary alcohols. For example, when an equimolar mixture of 1-methylcyclododecanol and cyclododecanol was heated under reflux in carbon tetrachloride, the tertiery alcohol was consumed almost completely in 15 min while the secondary alcohol was scarcely. It was 3 h before cyclododecanol was entirely dehydrated. It has been reported that anhydrous copper(II) sulfate do not catalyze the isomerization of olefins even at 180 °C or higher.[4] However, in the reaction of 1-methylcyclododecanol and our supported reagent, the amount of 1-methylcyclododecene increased and that of methylenecyclododecane decreased by prolonged heating in tetrachloroethylene. It is presumed that the synergism of copper(II) sulfate and silica gel caused the isomerization, because no isomerization of methylenecyclododecane was observed when the olefin was heated under reflux with silica gel in tetrachloroethylene. 2-Phenylethanol and 1-dodecanol were recovered after being heated under reflux for 1 day in tetrachloroethylene.

The mechanism of this dehydration reaction is not clear yet, but the formation of an intermediate of carbonium cationic character is inferred because the dehydration rate of alcohols increased in the order of the groups of alcohols: primary $\ll$ secondary $<$ tertiary.

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6. The products obtained from pregnenolone, cholesterol, and cholestanol melted at 137 - 139 °C, 78 - 89 °C, and 66 - 69 °C, respectively. The melting points of the dehydrated compounds shown in Table 1 have been reported to be 138 -140 °C, 79 - 80 °C, and 68 - 70 °C, respectively.[2]

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