Tetrahedron Letters No. 34, pp 2981 - 2984, 1976. Pergamon Press. Printed in Great Britain.

THE REARRANGEMENT OF TERTIARY PROPARGYL ALCOHOLS TO α,β-UNSATURATED ALDEHYDES IN THE PRESENCE OF POLYMERIC ORGANOSILYL VANADATES.

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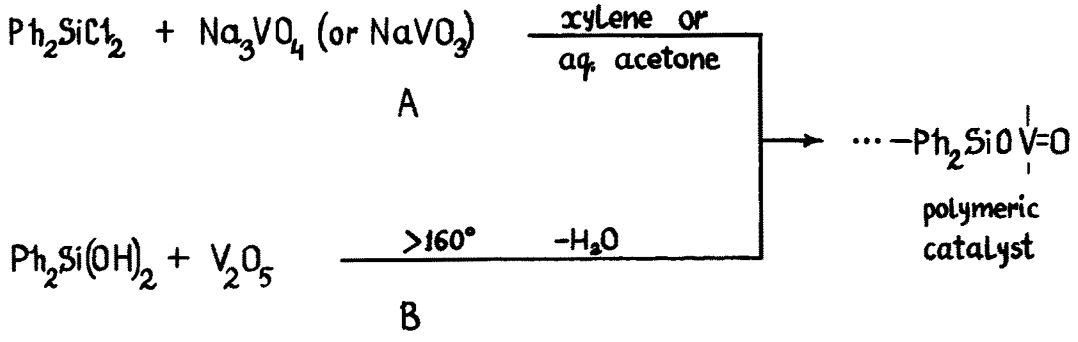
(Received in UK 25 June 1976; accepted for publication 5 July 1976)

Tertiary propargyl alcohols have been shown to rearrange to the corresponding α,β-unsaturated aldehydes when heated in the presence of organosilyl vanadates $(R_3SiO)_3VO$, but no details of this interesting subject have been reported[1]. The shortcoming of such catalysts lies in their inclination to hydrolysis; the rearrangement, therefore, must be carried out in dry medium. We found this rearrangement to proceed also in the presence of polymeric silyl vanadates which contained $-Ph_2SiO\overset{|}{\underset{|}{V}}=O$ groups. Such catalysts, unlike monomeric vanadic esters, are not easily hydrolyzed.

$$R_1R_2C(OH)C\equiv CH \xrightarrow{-Ph_2SiO\overset{|}{\underset{|}{V}}=O} R_1R_2C=CHCHO$$

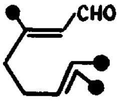
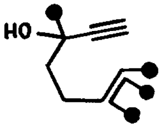
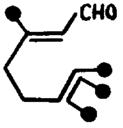
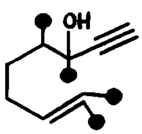
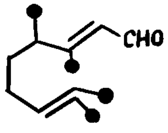
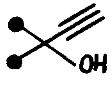
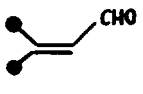
We developed also simple methods for preparation of the polymeric catalysts. The first method (A) is based on the reaction between diphenyldichlorosilane and sodium vanadate in aqueous acetone or in xylene. The reaction in aqueous acetone affords catalysts which are soluble in organic solvents, one in xylene gives insoluble polymers. The second method (B) consists in heating diphenylsilanediol with vanadium pentoxide, the water being removed as it is formed.



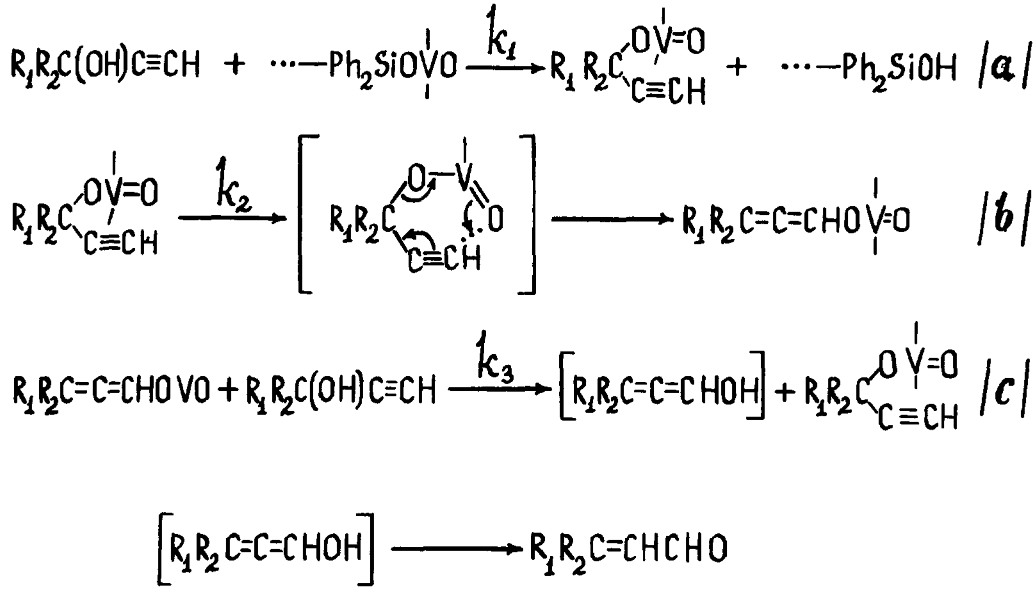
The composition of catalysts obtained by the method A in aqueous acetone depends on the initial ratio of diphenyldichlorosilane and sodium vanadate. Product with highest vanadium content is formed when molar ratio Na_3VO_4/Ph_2SiCl_2 0.33 is used. A representative procedure for polymeric catalyst synthesis follows. Solution of diphenyldichlorosilane (40.5 g) in acetone (130 ml) was added rapidly to a stirred solution of sodium vanadate (10.1 g) in water (152 ml). After 7 min. stirring cold water (350 ml) was added. The precipitate was filtered off, washed with water and dried in vacuo to give 38.8 g of polymeric catalyst (Found %: Si 12.5, V 6.9). IR spectra of polymeric catalysts contain absorption band at 1015 cm^{-1} which is taken as corresponding to the V=O stretching frequency[2,3]. Week broad band in the 600 cm^{-1} region is attributed to the V-O vibration[2]. Absorption in the 930--910 cm^{-1} region indicates the presence of V-O-Si fragment[4,5], strong sharp band at 1130 cm^{-1} is due to Ph-Si group[6].

The two above methods (A and B) afford active polymeric catalysts for the rearrangement of propargyl alcohols to unsaturated aldehydes. The polymeric catalysts may be exposed to air for a long time without loss of activity. The rearrangement may proceed both in solvents and without them. Good yields of aldehydes are available when the rearrangement is carried out in hydrocarbons at temperature>110°C. The unsaturated aldehydes are isolated from the reaction mixtures by vacuum-distillation. Reaction conditions and yields of aldehydes are listed in Table 1.

Table 1.

Starting propargyl alcohol	Rearrangement product	Reaction conditions (temperature °C, solvent)	Conversion of propargyl alcohol, %	Yield of unsaturated aldehyde, % (g.l.c.)
		149, undecane or o-xylene	85	83
		149, undecane	89	84
		149, undecane	86	71
		140, diethylene glycol dimethyl ether	45	91

The rearrangement of dehydrolinalool in undecane was chosen by us as the subject of a kinetic study. Kinetic experiments were run under N_2 in thermostatted cell equipped with a stirrer. Concentrations of reagents and products were determined by g.l.c. The rearrangement was found to be of zero order in dehydrolinalool and pseudo-first order in polymeric catalyst, and appeared to proceed according to the following mechanism:



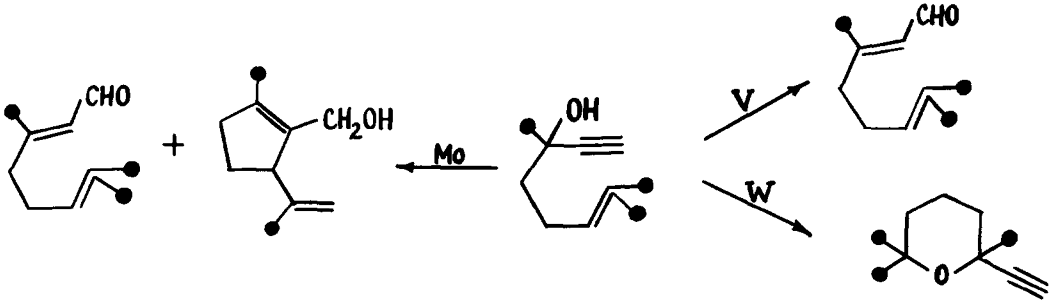
The rate-limiting step occurs in the isomerisation of intermediate propargyl vanadate[7] to allenic vanadate (reaction (b)) probably involving six-membered cyclic transition state; the reaction (c) running much faster ($k_3 \gg k_2$). According to this mechanism, the rearrangement should be described by the equation $d[D]/dt = -k_2[Cat]_0$ which is in agreement with kinetic results ($[D]$ - dehydrolinalool concentration, $[Cat]_0$ -initial concentration of catalyst). Using the temperature dependence of k_2, the values of activation energy and entropy were calculated to be 22.2 $kcal.mol^{-1}$ and -15.5 $cal.mol^{-1}.K^{-1}$ respectively. The negativity of activation entropy confirms the suggestion that the rearrangement proceeds via cyclic transition state. The rate of rearrangement depends on the type of solvent used. Being highest in hydrocarbons, the rate decreases in polar solvents. In alcohols and dimethyl formamide no reaction is observed at all (Table 2).

It was of interest to prepare polymeric catalysts containing chromium, molybdenum and tungsten instead of vanadium. We succeeded in obtaining such polymers by reacting diphenyldichlorosilane and sodium chromate, molybdate or tungstate respectively. Polymers obtained exhibited catalytic properties

Table 2.

Solvent	undecane	o-xylene	methylheptylketone	N,N-dimethylaniline	dibutyl ether	n-heptyl alcohol	dimethyl formamide
Relative rate of rearrangement	1.0	1.0	0.6	0.6	0.3	0.0	0.0

different from those of polymeric silyl vanadates. Thus, tungsten-containing catalyst isomerized dehydrolinalool mainly to 2,6,6-trimethyl-2-ethynyltetrahydropyran (47% yield). Heating dehydrolinalool (170°, 14 hrs) in the presence of molybdenum-containing polymer under N_2 affords a mixture of citral (28% yield) and 2-hydroxymethyl-1-methyl-3-isopropenylcyclopent-1-ene (12% yield): b.p. 76-78° (1 mm), n_D^{20} 1.4922; PMR (100 MHz, CCl_4, TMS) : 1.60 (3H), 1.73 (3H, s), 3.30-3.50 (1H, m), 3.83-4.05 (2H, AB, J_{AB} = 12Hz), 4.56-4.74 (2H, m). (Found: C 78.88, H 10.66. $C_{10}H_{16}O$ requires: C 78.94, H 10.52%). On heating dehydrolinalool in the presence of chromium-containing polymer no reaction occured.



References and Notes

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7. The intermediate formation of propargyl vanadate was confirmed by appearance of acetylenic proton peak (δ 2.48) besides acetylenic proton peak due to starting dehydrolinalool (δ 2.30) in PMR-spectrum of a mixture (1:1) of dehydrolinalool and $(Et_3SiO)_3VO$.