

Studies on the Isomerization of Substituted Allyl Alcohols over Raney Nickel

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Substituted allyl alcohols, namely crotyl alcohol, 4-methylpent-3-en-2-ol, cinnamyl alcohol, 4-phenylbut-3-en-2-ol, 1,3-diphenylprop-2-en-1-ol, cyclopent-2-en-1-ol, and cyclohex-2-en-1-ol were found to isomerize to the corresponding carbonyl compounds in the presence of Raney nickel. The mechanism appears to involve the "half-hydrogenated state" followed by reversal as in the case of the well-known isomerization of olefins during hydrogenation. Tricyclo-[5.2.1.0^{2,6}]-dec-3-en-4-ols were also found to undergo isomerization to tricyclo-[5.2.1.0^{2,6}]-decan-3-one.

INTRODUCTION

This is a continuation of our earlier study on the isomerization of allyl alcohol over Raney nickel (1), substituted allyl alcohols were also studied. The isomerization of olefins bearing functional groups has been reviewed (2). Later on there were many reports on the isomerization of substituted allyl alcohols in the presence of *n*-butyllithium (3), ruthenium (4), rhodium (5, 6), and nickel (7) complexes under homogeneous conditions and over heterogeneous catalysts, e.g., aluminosilicates (8), palladium catalysts (9–11) Raney nickel (12), and also at heptane–water boundary using aqueous μ_3 -oxo-triruthenium acetate (13). Thermal isomerization of *trans*-1,3-diphenyl and *trans*-1,3-dimethylprop-2-en-1-ol was also reported (14).

EXPERIMENTAL

Proton nuclear magnetic resonance spectra were recorded on Varian XL 100 and Varian EM 390 instruments. Infrared and mass spectra were recorded using Perkin-Elmer 257 spectrophotometer and Varian MAT CH7 instruments, respectively. Gas-liquid chromatography (GLC) analyses

were done on Varian 1800 series and Varian 700 series chromatographs using hydrogen as carrier gas (thermal conductivity detector).

MATERIALS

Preparation of Raney nickel and deuterated Raney nickel has been described (1). 4-Methylpent-3-en-2-ol (15), 2-methylbut-3-en-2-ol (16), phenylbut-3-en-2-ol (15), 1,3-diphenylprop-2-en-1-ol (15), cyclopent-2-en-1-ol (17), cyclohex-2-en-1-ol (18), allylbenzene (19), tricyclo-[5.2.1.0^{2,6}]-dec-4-en-3-ols (20), allyl ether (21), allyl phenyl ether (22), allyl cyanide, vinyl acetic acid, and methyl vinyl acetate (23), were prepared according to the literature procedures.

PROCEDURES

Isomerization

(a) The methanol-washed Raney nickel (in the case of alkyl-substituted allyl alcohols) or xylene-washed Raney nickel (in the case of aryl-substituted allyl alcohols) (0.5 g) was added to the substituted allyl alcohol in the corresponding solvent (methanol in the case of alkyl-substituted alcohols and xylene in the case of aryl-substituted alco-

hols) and stirred for 12 h under reflux. The catalyst was filtered off and most of the solvent was evaporated and the residue was subjected to GC analysis.

(b) The reactant (5 g) and Raney nickel (1 g) were taken in methanol in a round-bottom flask which was connected to the hydrogenation apparatus. The system as flushed with hydrogen 3–4 times and the contents of the flask were kept under stirring in hydrogen atmosphere at atmospheric pressure. The samples were withdrawn with the help of a syringe at the required time intervals and subjected to GLC analysis.

(c) The reactant (5 g) and Raney nickel (1 g) were taken in isopropyl alcohol (50 ml) and were kept under reflux with stirring. Samples were withdrawn at the required time intervals and subjected to GLC analysis.

Analysis

The conversion was measured by GLC with 20% Carbowax 20M on varaport 30, 80–100 mesh, 6 ft. \times $\frac{1}{4}$ in. and 10 ft. \times $\frac{1}{4}$ in. and 20% SE-30 on Chromosorb-W, 60–80 mesh; 6 ft. \times $\frac{1}{4}$ -in. columns. The products were identified by comparing their retention times with those of the authentic samples or by isolation by preparative gas chromatography and spectroscopic identification. The reaction with allyl phenyl ether was followed by NMR.

RESULTS AND DISCUSSION

The isomerization of various substituted allyl alcohols over Raney nickel were studied and the results are shown in Table 1. The alkyl-substituted allyl alcohols underwent isomerization at the refluxing temperature of methanol (Table 1, Nos. 2 and 3)

TABLE I
Isomerization of Substituted Allyl Alcohols over Raney Nickel

S. No.	Substrate	Temperature (°C)	Products	% Yield
1.	Allyl alcohol	64	Propanal	62
			<i>n</i> -Propanol	3
2.	Crotyl alcohol	64	Butanal	25
			<i>n</i> -Butanol	5
3.	4-Methylpent-3-en-2-ol	64	4-Methylpentan-2-one	17
			4-Methylpentan-2-ol	4
4.	2-Methylbut-3-en-2-ol	64	Penten-2-one	—
			2-Methylbutan-2-ol	Traces
5.	Cinnamyl alcohol	135–140	β -Phenylpropionaldehyde	20
			Dihydrocinnamyl alcohol	5
6.	1,3-Diphenylprop-2-en-1-ol	135–140	(β -Phenyl)ethyl phenyl ketone	10
			1,3-Diphenylpropan-1-ol	4
7.	4-Phenylbut-3-en-2-ol	135–140	4-Phenylbutan-2-one	14
			4-Phenylbutan-2-ol	5
8.	Cyclopent-2-en-1-ol	135–140	Cyclopentanone	10
			Cyclopentanol	3
9.	Cyclohex-2-en-1-ol	135–140	Cyclohexanone	8
			Cyclohexanol	3
10.	Allylbenzene	135–140	<i>trans</i> - β -Methylstyrene	12
			<i>cis</i> - β -Methylstyrene	Traces
			<i>n</i> -Propyl benzene	2

Note. Catalyst-to-substrate ratio = 0.2. Weight of the substrate taken = 3 g. Reaction time = 12 h. Solvent: methanol for S. Nos. 1–4; xylene for S. Nos. 5–10.

and the aryl-substituted allyl alcohols at the refluxing temperature of xylene (Table 1, Nos. 5 to 7). Cyclic allyl alcohols also underwent isomerization at the refluxing temperature of xylene (Table 1, Nos. 8 and 9). The substituted allyl alcohols did not isomerize at room temperature unlike allyl alcohol.

The difficulty of isomerization of substituted allyl alcohols compared to allyl alcohol may be due to the steric hindrance in the adsorbed state. Other allyl derivatives such as allyl methyl ether, allyl phenyl ether, methyl vinyl acetate, allyl cyanide, and vinylacetic acid did not undergo ready isomerization at the refluxing temperature of methanol. Propargyl alcohol on stirring with Raney nickel at room temperature did not yield acrolein, but a highly viscous material, probably polymer, was obtained. This was not unexpected since acrolein itself underwent nearly complete polymerization, when it was stirred with Raney nickel at room temperature.

Isomerization of Substituted Allyl Alcohols in the Presence of Hydrogen/Isopropyl Alcohol

The reaction of substituted allyl alcohols yielded only small amounts of isomerized products in the presence of Raney nickel alone. However, they isomerized readily under hydrogenation conditions (using hydrogen gas or a hydrogen donor like isopropyl alcohol). Hence the latter conditions were employed for the study of isomerization of such compounds.

Cinnamyl alcohol was stirred with Raney nickel in hydrogen atmosphere at atmospheric pressure over Raney nickel using methanol as solvent. The samples were withdrawn at various time intervals and subjected to GLC analysis. Results are shown in Table 2. Similarly cinnamyl alcohol and isopropyl alcohol were taken (1:10 wt/wt ratio) and stirred over Raney nickel at the reflux temperature of isopropyl alcohol. The samples were withdrawn at vari-

TABLE 2
Isomerization of Cinnamyl Alcohol in the Presence of Hydrogen or Isopropyl Alcohol over Raney Nickel with Time

S. No.	Time (h)	Temperature (°C)	% Yield	
			β -Phenylpropionaldehyde	Dihydrocinnamyl alcohol
Procedure (b): in the presence of hydrogen				
1.	1.0	30	16	18
2.	2.5	30	20	25
3.	5.0	30	21	42
4.	9.0	30	—	98
Procedure (c): in the presence of isopropyl alcohol ^a				
5.	1.0	82	16	5
6.	2.5	82	19	11
7.	5.0	82	24	22
8.	9.0	82	20	37

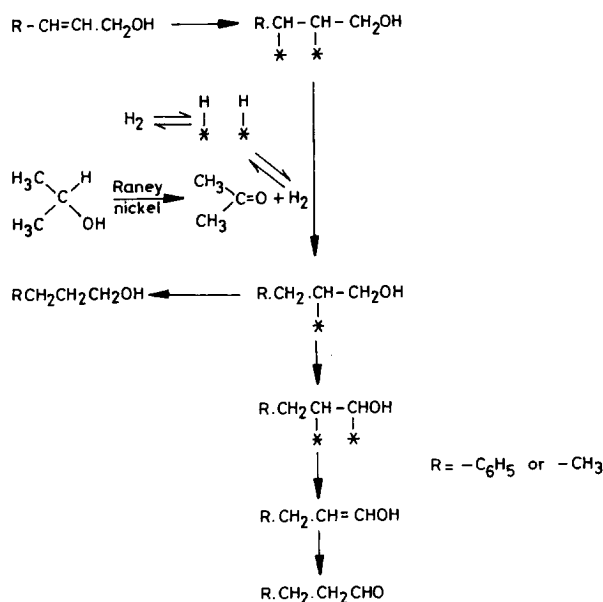
Note. Catalyst-to-substrate ratio = 0.2. Weight of cinnamyl alcohol taken = 5 g.

^a Cinnamyl alcohol-to-isopropyl alcohol ratio = 1:10 (wt/wt).

ous time intervals and the results are shown in Table 2.

In both the above cases, β -phenylpropionaldehyde was observed in addition to the usual hydrogenated product, dihydrocinnamyl alcohol. These were isolated by preparative GLC and characterized by ir and NMR. Results showed that at first there was an increase of the isomerized product, β -Phenylpropionaldehyde and later on it decreased and dihydrocinnamyl alcohol increased with time throughout the experiment. It showed that the initially formed β -phenylpropionaldehyde was getting reduced after its formation. Isomerization of cinnamyl alcohol to β -phenylpropionaldehyde in the absence of hydrogen or isopropyl alcohol was extremely slow. Hence a 1,3-sigmatropic shift of hydrogen as in the case of allyl alcohol was considered unlikely in this case. Formation of the isomerized product β -phenylpropionaldehyde can be viewed as proceeding through the "half-hydrogenated state" followed by its reversal as shown in Scheme 1, as proposed for the well-known isomerization of olefins during hydrogenation (25, 26).

It was already established that the hydrogen transfer over Raney nickel proceeded

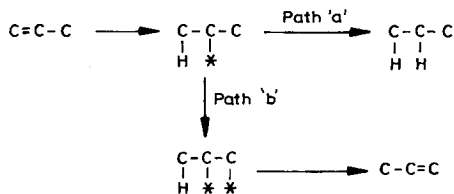


by a stepwise mechanism (27). Hence the above isomerization in the presence of isopropyl alcohol was also viewed as depicted in Scheme 2. Similar results were obtained with crotyl alcohol (Table 3) and allylbenzene (Table 4) also.

Since substituted allyl alcohols, namely, cinnamyl alcohol and crotyl alcohol underwent isomerization easily in presence of hydrogen and in view of the fact that Raney nickel contains 50–100 ml of hydrogen per gram (28) it was assumed that substituted allyl alcohols also underwent isomerization through "half-hydrogenated state."

Isomerization of α - and β -Tricyclo-[5.2.1.0^{2,6}]-dec-4-en-3-ols

Tricyclo-[5.2.1.0^{2,6}]-dec-4-en-3- β -ol (1) and tricyclo-[5.2.1.0^{2,6}]-dec-4-en-3- α -ol (2)



SCHEME 2

underwent isomerization to the corresponding saturated ketone, tricyclo-[5.2.1.0^{2,6}]-decan-3-one (3) on refluxing in xylene over Raney nickel for 24 h. Compound 2 was found to be more reactive (nearly three times) compared to compound 1.

If the isomerization proceeded through a 1,3-shift of hydrogen compound 1 should have isomerized at a faster rate than 2, assuming that the molecule will adsorb on the

TABLE 3
Isomerization of Crotyl Alcohol in the Presence of Hydrogen over Raney Nickel; Procedure (b)

S. No.	Time (h)	% Yield	
		Butanal	<i>n</i> -Butanol
1.	0.5	41	2
2.	1.0	38	4
3.	1.5	34	7
4.	2.5	30	20
5.	3.5	27	25

Note. Catalyst-to-substrate ratio = 0.2. Weight of crotyl alcohol taken = 5 g. Temperature = 30°C.

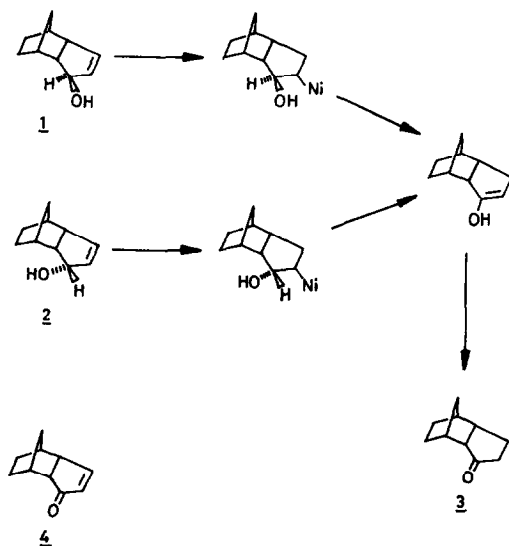
TABLE 4

Isomerization of Allylbenzene over Raney Nickel in Presence of Hydrogen/Isopropyl Alcohol with Time

S. No.	Time (h)	Temperature (°C)	% Yield	
			Propenylbenzene	Propylbenzene
Procedure (b): in the presence of hydrogen				
1.	0.5	30	Traces	21
2.	1.0	30	2	32
3.	2.0	30	12	56
4.	3.0	30	7	76
5.	4.0	30	4	93
6.	6.0	30	—	100
Procedure (c): in the presence of isopropyl alcohol				
7.	0.5	82	Traces	4
8.	1.0	82	3	7
9.	1.5	82	6	16
10.	2.0	82	10	22
11.	4.0	82	18	35

Note. Catalyst-to-substrate ratio = 0.2. Weight of the allylbenzene taken = 5 g.

catalyst surface preferentially on the exo-side and availability of an endo hydrogen is necessary for ready 1,3-sigmatropic migration without involving a hydrido-complex (24). The observed results were just the opposite. Since no unsaturated ketone, tri-



SCHEME 3

cyclo-[5.2.1.0^{2,6}-dec-4-en-3-one (4) was detected as intermediate, a stepwise mechanism involving dehydrogenation to the unsaturated ketone followed by hydrogenation of the double bond appears unlikely. The ready isomerization of compound 2 was in conformity with a mechanism involving a "half-hydrogenated state" (Scheme 3).

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