[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ARIZONA]

REARRANGEMENT OF SOME β-ACETYLENIC ALCOHOLS TO UNSATURATED KETONES IN BASIC SOLUTION[1,2]

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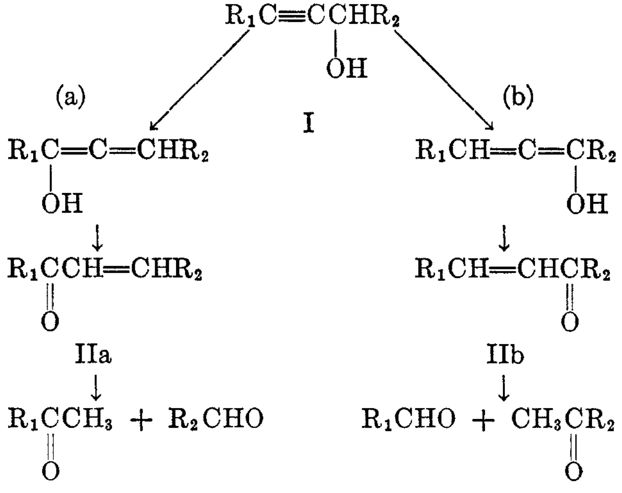
When 1,3-diphenyl-2-propyne-1-ol (I, $R_1 = R_2 =$ phenyl) was refluxed with an aqueous-alcoholic solution of potassium hydroxide a dark red solution was obtained which, on further heating, deposited a small amount of white solid, m.p. 256°, along with considerable tar. A similar reaction occurred when the alcohol was allowed to stand in the potassium hydroxide solution at room temperature for several days. Steam-distillation of the red solution gave a low yield of acetophenone and benzaldehyde. Such behaviour in alkaline solution is also characteristic of the isomeric unsaturated ketone, phenyl styryl ketone or chalcone (II, $R_1 = R_2 =$ phenyl). When heated in alkaline solution chalcone gives a dark red color and is cleaved to acetophenone and benzaldehyde (1) or converted to a higher condensation product, m.p. 256° (2) depending on the nature of the solvent. It seemed likely, therefore, that 1,3-diphenyl-2-propyne-1-ol had been rearranged to chalcone in the alkaline solution and that the observed products were then formed by the further reaction of the chalcone. Attempts to isolate chalcone from the reaction mixture were without success but in some runs a positive color test (3) for its presence in trace quantities was obtained.

Two different paths could give rise to chalcone from this β-acetylenic alcohol:

(a) 1,3-migration of the hydroxyl group followed by ketonization of the allenic alcohol formed.



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[1] The work described herein was carried out in part under a Frederick Gardner Cottrell special grant-in-aid from the Research Corporation.

[2] Presented before the Division of Organic Chemistry of the American Chemical Society, Chicago, Ill., September 4, 1950.

(b) 1,3-migration of a hydrogen atom (bond isomerization) followed by ketonization of the allenic alcohol formed.

Both types of rearrangement are known to give allenes from acetylenes, hydroxyl migration occurring when certain tertiary β-acetylenic alcohols are treated with acids (4) and bond isomerization when some acetylenic hydrocarbons are heated with alcoholic potassium hydroxide at high temperature (5). It will be seen above that, if R_1 and R_2 are different, the two paths will lead to different chalcones (IIa and IIb) and different cleavage products. It was found that when R_1 was phenyl and R_2 either *p*-bromophenyl or *p*-methoxyphenyl the cleavage products obtained were benzaldehyde and a substituted acetophenone establishing the path as bond isomerization (b). This appears to be the only reported instance of acetylene to allene bond isomerization in a compound other than a hydrocarbon.

Other β-acetylenic alcohols were investigated to determine the structural requirements for this reaction. Table I lists the alcohols which were rearranged and cleaved on refluxing with a 5% solution of potassium hydroxide in 50% aqueous ethanol. Only in the case of 1,3-diphenyl-2-propyne-1-ol was any solid higher condensation product obtained. In each case the aldehyde which corresponded to R_1 and the methyl ketone which corresponded to R_2 were obtained in low yield. Table II lists the alcohols which were recovered unchanged after refluxing in this alkaline solution. The rearrangement occurred only with secondary alcohols in which either R_1 or R_2 was an aromatic ring, undoubtedly due to the greater ease of ionization of the hydrogen in these alcohols. When potassium hydroxide in absolute ethanol or sodium ethoxide in absolute ethanol was used in place of the above solution a much larger amount of tar was formed and no other product could be isolated. Aniline, methylaniline, dimethylaniline, the three butylamines, and morpholine were without effect on any of the alcohols listed.

TABLE I

ALCOHOLS REARRANGED AND CLEAVED BY POTASSIUM HYDROXIDE

R_1	R_2	R_1CHO YIELD, %	R_2COCH$_3$ YIELD, %
Phenyl	Phenyl	15	12
Phenyl	*p*-Bromophenyl	11	9
Phenyl	*p*-Methoxyphenyl	7	7
Pentyl	Phenyl	4	8
Phenyl	Methyl	9	3

When pyridine or quinoline was substituted for the alkaline solution the alcohols in Table I, with the exception of 1-phenyl-1-butyne-3-ol (I, R_1 = phenyl, R_2 = methyl), showed no evidence of any reaction and could be recovered unchanged by removal of the organic base. The alcohols in Table II and 1-phenyl-1-butyne-3-ol, however, slowly developed marked color when dissolved in pyridine or quinoline, a very intense yellow-orange for those containing a phenyl group and a less intense yellow for the purely aliphatic ones. On the assumption that the color formation involved rearrangement of the β-acetylenic alcohol as the first step, the rearrangement products of γ-phenylpropargyl alcohol (I, R_1 = phenyl, R_2 = H) were investigated. Bond isomerization would yield cinnamic aldehyde (IIb, R_1 = phenyl, R_2 = H) while hydroxyl migration would yield phenyl vinyl ketone (IIa, R_1 = phenyl, R_2 = H). Cinnamic aldehyde gave no color when refluxed with pyridine for several days. However, phenyl vinyl ketone quite rapidly gave a color visually identical to that produced by γ-phenylpropargyl alcohol. Attempts to compare the two solutions spectrophotometrically were inconclusive as no maxima or minima occurred in the range of pyridine transparency although the two nearly linear curves were nearly identical in slope. When the alcohol was heated with various concentrations of pyridine in other solvents no color was produced. It is, as yet, impossible to decide whether the color formation actually involved 1,3-hydroxyl migration in a basic medium or whether both the alcohol and the ketone reacted with pyridine with the formation of a third compound responsible for the development of color. Some credence is given to the rearrangement hypothesis by the much greater speed with which the ketone gives the color. All attempts to recover any identifiable material from the pyridine solutions failed.

TABLE II

ALCOHOLS UNAFFECTED BY POTASSIUM HYDROXIDE SOLUTION

R_1	R_2
Phenyl	H
Pentyl	H
Pentyl	Methyl

TABLE III

ALCOHOLS GIVING COLOR WITH PYRIDINE AND QUINOLINE

R_1	R_2	COLOR
Phenyl	H	Orange, intense
Phenyl	Methyl	Orange, intense
Pentyl	H	Yellow, weak
Pentyl	Methyl	Yellow, weak

EXPERIMENTAL

The alcohols used in this work were prepared by the reaction of the appropriate aldehyde with the acetylenic Grignard reagent which was prepared by interaction of methylmagnesium bromide and the acetylenic hydrocarbon. The following are new compounds.

1,3-Diphenyl-2-propyne-1-ol was prepared in 75% yield by the reaction of benzaldehyde with phenylacetylenic Grignard reagent, b.p. 168° at 5 mm.

Anal. Calc'd for $C_{15}H_{12}O$: C, 86.6; H, 5.77.

Found: C, 86.4; H, 5.80.

1-(p-Bromophenyl)-3-phenyl-2-propyne-1-ol was prepared in 10% yield by the reaction of *p*-bromobenzaldehyde with phenylacetylenic Grignard reagent, m.p. 59–60° after recrystallization from petroleum ether.

Anal. Calc'd for $C_{15}H_{11}BrO$: C, 60.7; H, 3.71.

Found: C, 60.8; H, 3.75.

1-(p-Methoxyphenyl)-3-phenyl-2-propyne-1-ol was prepared in 72% yield by the reaction of anisaldehyde with phenylacetylenic Grignard reagent, m.p. 62–63° after recrystallization from petroleum ether.

Anal. Calc'd for $C_{16}H_{14}O_2$: C, 80.8; H, 5.88.

Found: C, 80.9; H, 5.86.

Reaction of β-acetylenic alcohols with potassium hydroxide solution. The alcohol (2 g.) was dissolved in 20 ml. of a 5% solution of potassium hydroxide in 50% aqueous ethanol. The solution, which turned red almost at once, was refluxed for 30 minutes after which it was decanted from the tarry deposit in the flask. The solid, if any, was removed. In the case of 1,3-diphenyl-2-propyne-1-ol about 200 mg. of solid, m.p. 256°, mixture m.p. with solid from chalcone (2) 256°, was formed. With the other alcohols no solid was isolated. The red solution was neutralized to *p*H 7 with dilute hydrochloric acid and was then steam-distilled until the distillate no longer gave a carbonyl reaction (3). In some runs the last portion of the steam-distillate gave a weak positive test for the presence of a chalcone (3). The distillate was divided into two equal portions from one of which the aldehydic product was isolated and identified as the methone derivative (6). The other portion was treated with either Fehling's solution or Tollens ammoniacal silver nitrate solution to oxidize the aldehyde after which the ketonic product was recovered and identified as the 2,4-dinitrophenylhydrazone. All identifications were made by mixture melting point with authentic specimens of the derivative in question. The non-steam-volatile residue was, in each case, an intractable tar. The yield of aldehyde and ketone varied from run to run but was in the range of 5–15%. No attempt was made to find conditions which would give an optimum yield.

TABLE IV

OPTICAL DENSITY OF PYRIDINE SOLUTIONS OF γ-PHENYLPROPARGYL ALCOHOL AND OF PHENYL VINYL KETONE[a]

λ, mμ	OBSERVED OPTICAL DENSITY	
	Alcohol	Ketone
315	1.15	1.27
320	1.05	1.14
325	0.94	1.01
330	.82	0.88
335	.71	.79
340	.58	.65
350	.46	.52
360	.32	.40
370	.20	.28
380	.11	.19
400	.05	.12
420	.02	.08

[a] Instrument adjusted to 100% transmission for pyridine blank.

The alcohols listed in Table II gave no color or other evidence of reaction when treated in this way and were recovered unchanged from the steam-distillate.

Color reaction with pyridine or quinoline. One gram of the β-acetylenic alcohol was dissolved in 5 ml. of pyridine or quinoline and the solution was either allowed to stand until no apparent further increase in color intensity was noted, usually three to seven days, or it was held at 75–85° for three hours. The colors developed were permanent showing no visual change after three months exposure to strong sunlight. The alcohols in Table I with the previously noted exception showed no color formation after several months in pyridine solution and the two solid alcohols studied could be recovered unchanged in melting point after refluxing with pyridine for many days.

Color development with phenyl vinyl ketone was carried out in exactly the same manner except that it was complete in about 30 minutes at room temperature or about five minutes at 75–85°.

Removal of the pyridine from the colored solutions by evaporation under a vacuum gave only a red-brown tar from which no pure substance could be obtained. Removal of the pyridine by pouring the solution into water or dilute acid gave a yellow-brown tar.

The absorption spectra of the pyridine solutions of γ-phenylpropargyl alcohol and phenyl vinyl ketone were run using a Beckman Model DU Spectrophotometer. Table IV contains the data for this determination. In each case the solutions were about 10^{-3} molar. Inasmuch as there were no maxima or minima the results were not converted to extinction coefficients but are reported merely as the observed optical density of the solution.

SUMMARY

Certain secondary aromatic β-acetylenic alcohols have been shown to undergo bond isomerization under relatively mild conditions in alkaline solution to yield an unsaturated ketone. This unsaturated ketone was not isolated but was cleaved by the alkaline solution to yield a simple aldehyde and ketone. Primary aromatic β-acetylenic alcohols as well as purely aliphatic secondary alcohols have been shown to be stable under these conditions.

Several such resistant alcohols have been found to give a color reaction with pyridine which may be indicative of a rearrangement involving the migration of a hydroxyl group. Evidence for assigning a definite mechanism is lacking.

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