[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

PYROLYSIS OF AN α-HYDROXY KETAL[1]

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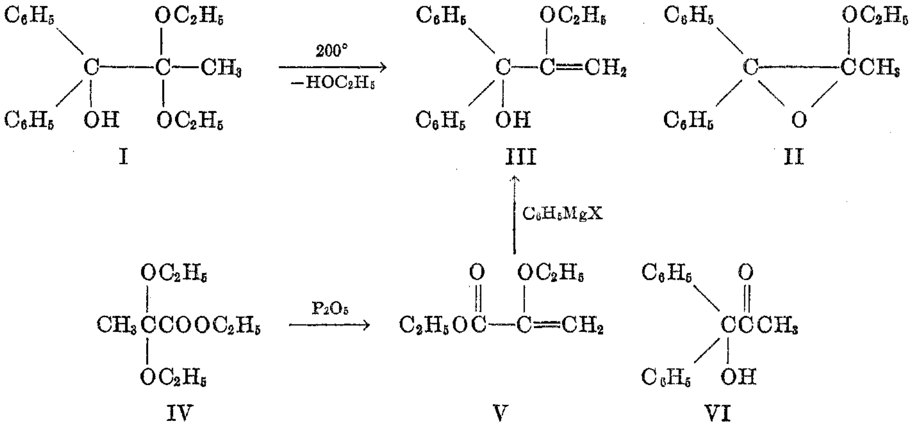
The object of the present investigation was to determine whether an α-hydroxy ketal (I) would undergo intramolecular alcohol interchange to give an epoxy ether (II) or would lose the elements of alcohol to give a vinyl ether (III) when subjected to pyrolysis conditions. The epoxy ether (II) could not be prepared in the conventional manner (1) since treatment of the halo ketone with sodium alkoxide has been shown to give a Favorski-type rearrangement (2). The results indicate that in the example investigated the sole product is the vinyl ether (III). Further, the corresponding α-chloro ketal (VII) also lost alcohol easily to give the chloro vinyl ether (VIII).

Parham (3) has recently investigated the intramolecular alcohol interchange of δ-hydroxyacetals and found that *tert*-alcohols undergo intra- but not intermolecular alcohol interchange with acetals.

The α-hydroxy ketal chosen was 2,2-diethoxy-1,1-diphenyl-1-propanol (I) which had been prepared recently (2). When this α-hydroxy ketal was heated to 200° ethyl alcohol was evolved smoothly and 92% of a product could be obtained which had the correct carbon, hydrogen, and ethoxyl analysis for the vinyl ether (III) or the epoxy ether (II). The infrared spectrum (Fig. 1) indicated a hydroxyl group and the structure of the product was proven to be the vinyl ether (III) by the following independent synthesis IV → V → III.



Ethyl α-ethoxyacrylate (V) was prepared in 85% yield from the ketal ester IV by the method of Claisen (4). Two equivalents of phenylmagnesium bromide reacted smoothly with the acrylate ester (V) to give the vinyl ether III in 48% yield. Seifert, *et al.* (5) recently reported that ethyl α-methoxycrotonate and methylmagnesium bromide gave 3-methoxy-4-methyl-2-pentanone in 59% yield,

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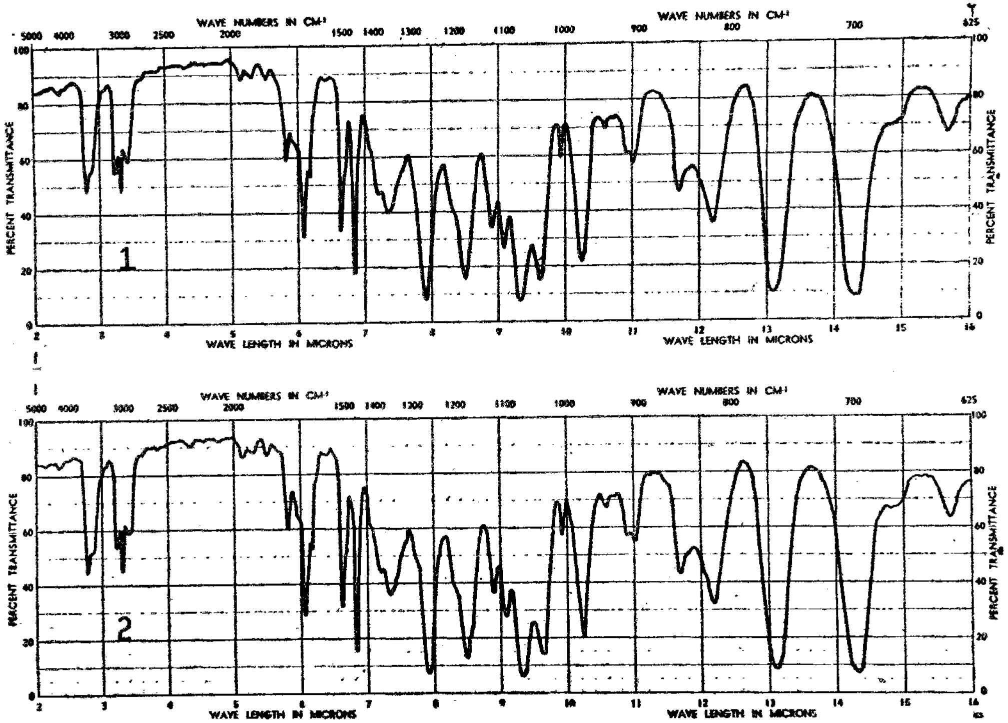
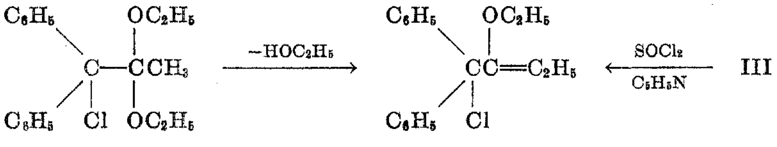


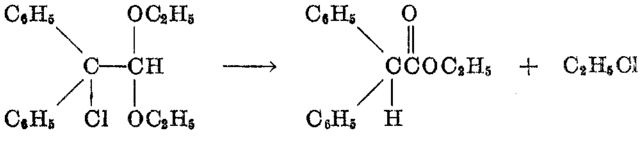
Fig. 1. Infrared Absorption Spectra of 1,1-Diphenyl-2-ethoxy-2-propen-1-ol (III) from Pyrolysis (Curve 2) and from Independent synthesis (Curve 1). Both spectra were taken with the pure liquids in a 0.013-mm. cell. (Courtesy of Dr. L. E. Kuentzel and Miss D. Orlowski, Wyandotte Chemicals Corp., Wyandotte, Michigan.)

by first addition of the Grignard reagent in a 1,4 manner to the α,β-unsaturated ester followed by further reaction with only one equivalent of Grignard reagent to form a ketone from the ester. Hydrolysis of III to the hydroxy ketone (VI) was accomplished in 63% yield and proved that the Grignard reagent did not add to the α,β-unsaturated ester in a 1,4 manner in the present example. The structure of VI recently has been proven in this laboratory. The vinyl ether (III) prepared above was identical with the compound isolated from the pyrolysis as shown by a comparison of physical properties and infrared spectra (Fig. 1).

The chloro ketal (VII), which previously had been prepared and identified in this laboratory (2) proved to be unstable at room temperature and over a period of months also lost the elements of ethyl alcohol to give the chloro vinyl ether (VIII) in 85% yield. The structure of this vinyl ether was proven by synthesis from the vinyl alcohol (III). VIII could be isolated in 70% yield from the reaction of III with thionyl chloride in the presence of pyridine and proved to be identical with the decomposition product of VII by mixture melting point determination.



VII VIII



IX X

It is interesting to compare the decomposition of the chloro ketal (VII) with a similar chloro acetal (IX) which recently has been reported (6) to decompose on standing to give a 55% yield of the ester (X) and ethyl chloride. From the present example it appears that the elimination of an alkyl halide, which transforms an α-haloacetal to an ester (IX → X), does not occur with an α-halo ketal which can preferentially lose the elements of alcohol.

EXPERIMENTAL

Pyrolysis of 2,2-diethoxy-1,1-diphenyl-1-propanol (I). Into a 25-ml. distilling flask, which had been washed with acid solution and then dried, was placed 10 g. of crystalline hydroxy ketal (I), m.p. 73–74° (2). The flask was heated to 180°, at which temperature ethyl alcohol began to distill. After one-half hour at 200–210°, the distillation of alcohol had ceased and the contents of the flask had turned from a colorless to a light brown liquid. The alcohol was identified by b.p. 76–78°, n_D^{25} 1.3595, and the preparation of a 3,5-dinitrobenzoate derivative whose melting point was not depressed when mixed with an authentic sample, m.p. 92–93°.

The liquid remaining in the flask was distilled to give 7.8 g. (92%) of 1,1-diphenyl-2-ethoxy-2-propen-1-ol (III), b.p. 129–132° (0.3 mm.); n_D^{25} 1.5687.

Anal. Calc'd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13; OC_2H_5, 17.72.

Found: C, 80.52; H, 7.09; OC_2H_5, 18.01.

Ethyl α-ethoxyacrylate (V). In a 100-ml. round-bottomed flask fitted with a Claisen head was placed 19 g. (0.1 mole) of the ketal-ester (IV) dissolved in 8 g. (0.1 mole) of pyridine. To this solution was added 7.0 g. (0.05 mole) of phosphorus pentoxide. The mixture was refluxed two hours and then distilled at atmospheric pressure to give 12.2 g. (85%) of the ethyl α-ethoxyacrylate (4), b.p. 172–179°; n_D^{25} 1.4329.

Preparation of 1,1-diphenyl-2-ethoxy-2-propen-1-ol (III). In a 300-ml. three-necked flask equipped with a reflux condenser, dropping-funnel, and stirrer was placed 4 g. (0.17 mole) of magnesium in 50 ml. of anhydrous ether. To the mixture was added with stirring 28 g. (0.18 mole) of bromobenzene in 30 ml. of dry ether. The solution, which turned brown during the addition, was refluxed for one hour. The solution was then cooled and 12 g. (0.083 mole) of ethyl α-ethoxyacrylate dissolved in 30 ml. of anhydrous ether was added slowly. After refluxing for one hour, the reaction mixture was cooled and hydrolyzed with 100 ml. of ammonium chloride solution. The layers were separated and the water layer washed several times with ether. The ether layers were combined and dried over sodium sulfate, after which the ether was evaporated under reduced pressure. Distillation of the residual liquid gave 2.5 g. of forerun, b.p. 100–148°, and 10.2 g. (48%) of 1,1-diphenyl-2-ethoxy-2-propen-1-ol (III), b.p. 150–154° (2 mm.); n_D^{25} 1.5688.

Anal. Calc'd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13; OC_2H_5, 17.72.
Found: C, 79.81; H, 7.37; OC_2H_5, 17.60.

Hydrolysis of 1,1-diphenyl-2-ethoxy-2-propen-1-ol (III). The hydroxy vinyl ether (III) (0.5 g.) was dissolved in a mixture of 10 ml. of ethyl alcohol, 5 ml. of concentrated hydrochloric acid, and 5 ml. of water. After three hours at the reflux temperature, a solid was obtained by distillation of the alcohol, water, and acid under reduced pressure. The solid, when recrystallized from acetone cooled in Dry Ice, gave 0.28 g. (63%) of white crystals, m.p. 65–66°. Mixture melting point with authentic α-hydroxy-α,α-diphenylacetone (2) was not depressed. In addition, an *oxime* was prepared, m.p. 160–161°, which did not depress the melting point of an authentic oxime (2).

Decomposition of 1-chloro-1,1-diphenyl-2-propanone diethyl ketal (VII). A 10-g. sample of the crystalline chloro ketal (VII), m.p. 71–72°, was placed in a stoppered test tube and allowed to stand for four months. After this time the contents had partially liquefied and had turned brown. The material was dissolved in acetone and on cooling the solution in a Dry Ice bath, 7.3 g. (85%) of 3-chloro-3,3-diphenyl-2-ethoxy-1-propene (VIII) was obtained, m.p. 72–74°. The melting point of a mixture of this product with the starting chloro ketal (VII) was greatly depressed. An analytical sample was obtained by further recrystallization from acetone, m.p. 73–74°.

Anal. Calc'd for $C_{17}H_{17}ClO$: C, 74.86; H, 6.24; Cl, 13.01; OC_2H_5, 16.51.
Found: C, 74.96; H, 6.29; Cl, 13.03; OC_2H_5, 16.14.

Independent synthesis of 3-chloro-3,3-diphenyl-2-ethoxy-1-propene (VIII). In the usual apparatus was placed 2 g. (7.9 millimoles) of hydroxy-ene compound (III) and 0.62 g. (7.9 millimoles) of anhydrous pyridine. These were dissolved in 10 ml. of benzene and the solution was cooled in ice. Then 0.92 g. (7.9 millimoles) of thionyl chloride (in 25 ml. of benzene) was added through the dropping-funnel. After the addition, the flask was kept at 50–60° for three hours, and then the benzene layer was washed twice with 25-ml. portions of water, sodium bicarbonate, hydrochloric acid (1%), and water. After the benzene layer was dried over sodium sulfate, the benzene was evaporated at reduced pressure leaving a yellow viscous liquid which solidified. This solid was recrystallized from acetone (cooled in Dry Ice) to give 1.5 g. (70%) of 3-chloro-3,3-diphenyl-2-ethoxy-1-propene, m.p. 73–74°. The mixture m.p. with a compound obtained from decomposition of the chloro ketal (VII) showed no depression.

SUMMARY

An α-hydroxy ketal (I) was shown on pyrolysis to lose the elements of alcohol to give a hydroxy vinyl ether (II) and not an epoxy ether (III). The corresponding α-chloro ketal (VII) also lost alcohol to give the chloro vinyl ether (VIII).

DETROIT 1, MICHIGAN

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