56. *The Mechanism of the Conversion of Δ^{γ}-Butenol into Δ^{β}-Butenyl Bromide.*

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LINSTEAD and RYDON (J., 1934, 1995) found that Δ^{γ}-butenol (I; $X = OH$), on treatment with a hot mixture of sulphuric and hydrobromic acids, afforded a mixture of Δ^{β}-butenyl bromide (II; $X = Br$) and Δ^{γ}-butenyl bromide (I; $X = Br$), and pointed out that this apparent tautomeric change was unusual in that the propene system is separated from the only polar atom by a methylene group. Other work (Boorman, Linstead, and Rydon, J., 1933, 568; Linstead and Rydon, *ibid.*, p. 580) indicates that such activation through an intervening methylene group is improbable; for this reason it was decided to investigate the reaction more closely.

(I.) $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2X$ $\qquad$ $CH_3{\cdot}CH{:}CH{\cdot}CH_2X$ (II.)

For the quantitative investigation it was necessary to develop methods for the analysis of mixtures of Δ^{β}- and Δ^{γ}-butenols and of the corresponding bromides. A suitable reaction for the two alcohols was their esterification by means of hydrobromic acid (*d* 1·48) at room temperature, Δ^{β}-butenol reacting readily, and Δ^{γ}-butenol not at all. For the analysis of mixtures of the bromides the reverse reaction was employed, Δ^{β}-butenyl bromide being hydrolysed, and the Δ^{γ}-isomeride unattacked, at room temperature in aqueous acetone.

The alcohols are unchanged after 100 hours' boiling. Prévost (*Ann. Chim.*, 1928, **10**, 147) has shown that Δ^{β}-butenyl acetate is hydrolysed by alkali without isomerisation; we have confirmed this and also shown that the same is true for Δ^{γ}-butenyl acetate. Moreover, the alcohols are recovered practically unchanged after being heated for 48 hours with 30% potassium hydroxide solution at 100°. It is thus evident that the isomeric change is not readily brought about by the alkaline reagents generally employed for effecting such reactions.

Since the isomerisation was first observed in the presence of acids, a number of acid catalysts were tried, but without success, the alcohols being recovered almost unchanged after boiling with acetic anhydride and with acetic acid, followed by the hydrolysis of the acetates produced. The slight changes observed are attributed either to the presence of impurities, since the purification of small amounts of the alcohols was a matter of some difficulty, or to the operation of the mechanism advanced below; it is evident, however, that there is no question of the setting up of a reversible equilibrium, since the small apparent change is not increased by prolonged treatment. Attention was next directed to the bromides; once again the action of heat alone, of hot 50% sulphuric acid, and of hot hydrobromic acid (*d* 1·48) brought about no detectable migration of the double bond.

When, however, Δ^{γ}-butenol was distilled from a mixture of hydrobromic and sulphuric acids under the conditions used in the original observation (Linstead and Rydon, *loc. cit.*), the bromide formed was found to be a mixture containing 74% of the Δ^{β}-isomeride. Under the same conditions, Δ^{β}-butenol afforded no Δ^{γ}-butenyl bromide.

This suggested that a preliminary dehydration of Δ^{γ}-butenol to butadiene occurred, followed by 1 : 4-addition of hydrogen bromide :

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH \xrightarrow{-H_2O} CH_2{:}CH{\cdot}CH{:}CH_2 \xrightarrow{+HBr} CH_3{\cdot}CH{:}CH{\cdot}CH_2Br$$

Strong evidence in favour of this hypothesis was obtained in two ways. (1) When Δ^{γ}-butenol was treated with sulphuric acid under approximately the same conditions as those obtaining in the conversion into the bromide, butadiene was formed (identified as its tetrabromide). (2) Passage of butadiene through a hot mixture of sulphuric and hydrobromic acids of the same concentration as that used in the preparation of the bromide afforded a product, the lower-boiling portion of which (the monobromo-compound) was a mixture of 89% of Δ^{β}-butenyl bromide with 11% of the Δ^{γ}-isomeride. The higher proportion of the Δ^{γ}-butenyl bromide in the product from Δ^{γ}-butenol is probably due to a certain amount of direct esterification.

The simple analytical methods developed in this work were applied in a study of the isomerisation of α-methylallyl alcohol to Δ^{β}-butenol. Although the result was unsuccessful, it is desirable, in view of Young and Winstein's work (*J. Amer. Chem. Soc.*, 1935, **57**, 2013), to draw attention to some of the results so obtained. α-Methylallyl alcohol and the derived bromide were found to react, under the standard conditions, to the same extent as the corresponding Δ^{β}-butenyl compounds. Although not surprising, in view of the rapidity with which the equilibrium $CH_2{:}CH{\cdot}CHMeX \rightleftharpoons CH_3{\cdot}CH{:}CH{\cdot}CH_2X$ is set up (cf., *inter alia*, Baudrenghien, *Bull. Soc. chim. Belg.*, 1922, **31**, 160; Bouis, *Ann. Chim.*, 1928, **9**, 410; Young and Winstein, *loc. cit.*), this result shows that, whatever the proportion of α-methylallyl derivatives in our Δ^{β}-butenyl compounds, the whole would react on analysis as if it were the pure Δ^{β}-butenyl derivative; this possible variable factor is, therefore, without influence on our results.

EXPERIMENTAL.

Δ^{γ}-Butenol was prepared by the method of Linstead and Rydon (*loc. cit.*) and finally purified by repeated distillation over quicklime; the pure alcohol had b. p. 114°, $d_{4^\circ}^{20^\circ}$ 0·8531, $n_D^{20^\circ}$ 1·4109, $[R_L]_D$ 20·90 (calc., 21·70). It was characterised as its 3 : 5-*dinitrobenzoate*, m. p. 59° (Found : N, 10·7. $C_{11}H_{10}O_6N_2$ requires N, 10·5%); the *p*-nitrobenzoate and the phenylurethane are oils.

Δ^{γ}-Butenol was converted into the bromide by means of phosphorus tribromide and pyridine (Linstead and Rydon, *loc. cit.*); Δ^{γ}-butenyl bromide had b. p. 98—102°, $d_{4^\circ}^{20^\circ}$ 1·3280, $n_D^{20^\circ}$ 1·4627, $[R_L]_D$ 27·83 (calc., 27·97) (Found : Br, 58·8. Calc. : Br, 59·2%). When it was refluxed with silver 3 : 5-dinitrobenzoate in dry ether for 2 hours, Δ^{γ}-butenyl 3 : 5-dinitrobenzoate was produced, m. p. and mixed m. p. 59°.

Preparation of Δ^{β}-Butenol (*Crotyl Alcohol*).—The methods described in the literature give only poor yields; the following is an improvement of the procedure of Charon (*Ann. Chim. Phys.*, 1899, **17**, 215) : A suspension of 400 g. of crotonaldehyde in 4 l. of water was added to zinc–copper couple prepared from 400 g. of zinc foil, 635 c.c. of glacial acetic acid were added, and the mixture was kept at room temperature until the odour of crotonaldehyde was no longer perceptible (about 3 days). The liquid was filtered, made alkaline with sodium hydroxide, and distilled in steam. From the distillate, saturated with potassium carbonate, ether extracted a product, which was dried with potassium carbonate and fractionated. The fraction, b. p. 117—122°, on repeated distillation over quicklime, gave Δ^{β}-butenol (40—60 g.), b. p. 119°, $d_{4^\circ}^{20^\circ}$ 0·8496, $n_D^{20^\circ}$ 1·4222, $[R_L]_D$ 21·54 (calc., 21·70). The alcohol was characterised as its p-*nitrobenzoate*, m. p. 44° (Found: N, 6·6. $C_{11}H_{11}O_4N$ requires N, 6·3%), 3 : 5-dinitrobenzoate, m. p. 51°, mixed m. p. with Δ^{γ}-butenyl 3 : 5-dinitrobenzoate, 47—48° (Found: N, 10·5. Calc. for $C_{11}H_{10}O_6N_2$: N, 10·5%), and *phenylurethane*, m. p. 65° (Found: N, 7·7. $C_{11}H_{13}O_2N$ requires N, 7·7%).

Δ^{β}-Butenyl Bromide.—A mixture of Δ^{β}-butenol (45 g.) and pyridine (14 g.) was added during 3 hours with mechanical stirring to phosphorus tribromide (67 g.) at 0°. The mixture was then distilled until frothing, accompanied by nauseous fumes, occurred. The distillate was washed with alkali and water, dried over calcium chloride, and redistilled. Yield, 42 g. (50%); b. p. 101—104°, $d_{4°}^{20°}$ 1·3280, $n_D^{20°}$ 1·4616, $[R_L]_D$ 27·96 (calc., 27·97) (Found: Br, 59·4. Calc.: Br, 59·2%). The 3 : 5-dinitrobenzoate prepared from it had m. p. and mixed m. p. 51°.

Analytical Methods.—(i) *Mixtures of Δ^{β}- and Δ^{γ}-butenol.* The mixture was weighed (0·5 g.) into a 100 c.c. measuring flask, treated with 2 c.c. of hydrobromic acid (*d* 1·48; previously standardised against *N*/20-sodium carbonate), and kept at room temperature for 2 hours. The mixture was then made up to 100 c.c. with water and 10 c.c. portions were titrated against *N*/20-sodium carbonate. The composition of the mixture was read off from a reference curve plotted from the following data, obtained with artificial mixtures and 8·83*N*-hydrobromic acid:

Δ^{β}-Butenol, %	0	22·7	45·2	59·0	100
Reaction, %	0	13·9	30·9	38·2	62·7

(ii) *Mixtures of Δ^{β}- and Δ^{γ}-butenyl bromide.* The mixture was weighed (0·5 g.) into a 100 c.c. measuring flask, dissolved in 50 c.c. of purified acetone, made up to 100 c.c. with water, and kept at room temperature for 24 hours; aliquot portions were then titrated with *N*/20-sodium carbonate, and the percentage hydrolysis calculated. The composition of the mixture was read off from a reference curve plotted from the following results, obtained with synthetic mixtures:

Δ^{β}-Butenyl bromide, %	0	16·0	43·0	85·0	100
Hydrolysis, %	0	9·8	29·3	62·7	70·4

Attempted Isomerisation of the Alcohols.—(i) *Action of heat.* (a) Δ^{β}-Butenol was boiled under reflux. Analysis showed the product to contain 100% of Δ^{β}-butenol after 24 hours, and 98% after 72 hours.

(b) Δ^{γ}-Butenol, treated similarly, was unchanged after 100 hours.

(ii) *Action of potassium hydroxide.* (a) 3 G. of Δ^{β}-butenol were heated at 100° in a sealed tube with 8 c.c. of 30% aqueous potassium hydroxide. The product contained 98·5% of Δ^{β}-butenol.

(b) An exactly similar experiment with Δ^{γ}-butenol gave a product containing 96% of Δ^{γ}-butenol.

(iii) *Action of acetic acid.* (a) A mixture of 5 g. of Δ^{β}-butenol and 10 g. of acetic acid was heated under reflux at 110—115° for 6 hours and poured into 80 c.c. of 10% sodium carbonate solution. The acetate was extracted with ether, dried, and distilled. The product, b. p. 120—128°, was hydrolysed with hot 30% aqueous sodium hydroxide and then distilled in steam. The alcohol, isolated from the distillate in the usual way, had b. p. 117—119° and contained 96% of Δ^{β}-butenol (3 : 5-dinitrobenzoate, m. p. 51°; mixed m. p. with authentic Δ^{β}-butenyl 3 : 5-dinitrobenzoate, 50—51°).

(b) A similar experiment with Δ^{γ}-butenol yielded a product, b. p. 112—114°, containing 93% of Δ^{γ}-butenol.

(iv) *Action of acetic anhydride.* (a) A similar experiment (6 hours' heating) with Δ^{β}-butenol, acetic anhydride being used in place of acetic acid, gave a product, b. p. 117—119°, consisting of pure Δ^{β}-butenol (3 : 5-dinitrobenzoate, m. p. and mixed m. p. 51°). A similar experiment in which the time of heating was 24 hours also gave pure Δ^{β}-butenol.

(b) A similar experiment (6 hours' heating) with Δ^{γ}-butenol yielded a product, b. p. 112—114°, containing 91% of Δ^{γ}-butenol (3 : 5-dinitrobenzoate, m. p. 59°; mixed m. p. with authentic Δ^{γ}-butenyl 3 : 5-dinitrobenzoate, 57°). A similar experiment in which the time of heating was 24 hours gave a product containing 94% of Δ^{γ}-butenol.

Attempted Isomerisation of the Bromides.—(i) *Action of heat.* Δ^{β}- and Δ^{γ}-Butenyl bromide were each heated for 24 hours in sealed tubes at 100°; the products were found on analysis to be the unchanged bromides.

(ii) *Action of sulphuric acid or hydrobromic acid.* Either bromide was heated at 100° in a sealed tube with an equal volume of 50% (by vol.) sulphuric acid or with one-quarter of its volume of hydrobromic acid (*d* 1·48) for 24 hours. The product was shown by analysis to be unchanged bromide in every case.

Action of a Mixture of Hydrobromic and Sulphuric Acids on the Alcohols.—10 G. of the alcohol were added to a mixture of hydrobromic and sulphuric acids (prepared by reduction with sulphur dioxide of 14·3 g. of bromine and 18·5 g. of ice); to the hot stirred solution, 9 c.c. of concentrated sulphuric acid were added drop by drop, the distillate being collected until nothing further passed over. The product was washed with dilute sodium hydroxide solution and with water, dried, and distilled, the fraction, b. p. 97—106°, being collected. The product from Δ^{β}-butenol was found, on analysis, to consist of pure Δ^{β}-butenyl bromide. The product from Δ^{γ}-butenol was hydrolysed under the standard conditions to the extent of 55%; it was, therefore, a mixture of 74% of Δ^{β}-butenyl bromide with 26% of the Δ^{γ}-isomeride.

Butenyl Bromide from Butadiene.—Butadiene (generated from the tetrabromide) was passed into a hot mixture of hydrobromic and sulphuric acids of the composition used in the last experiment. The distillate was collected and worked up. The lower-boiling fraction, b. p. 98—105° (Found: Br, 58·9. Calc. for C_4H_7Br: Br, 59·2%), was hydrolysed to the extent of 65% under the standard conditions; it therefore contained 89% of Δ^{β}-butenyl bromide and 11% of the Δ^{γ}-compound. When it was refluxed for 2 hours in dry ether with silver 3 : 5-dinitrobenzoate, Δ^{β}-butenyl 3 : 5-dinitrobenzoate was obtained, m. p. and mixed m. p. 49—50°.

Butadiene from Δ^{γ}-Butenol.—10 G. of Δ^{γ}-butenol were added drop by drop to 25 c.c. of 50% (by vol.) sulphuric acid at 120°. The vapours were passed through a condenser to remove liquid products, and the uncondensed gas led into an ice-cooled mixture of bromine and water. The excess of bromine was destroyed with sulphur dioxide, and the solid twice crystallised from light petroleum, yielding butadiene tetrabromide, m. p. 116° (mixed m. p. 115—116° with an authentic specimen).

Experiments with α-Methylallyl Alcohol.—The alcohol was prepared from methylmagnesium iodide and acraldehyde (Delaby, *Bull. Soc. chim.*, 1923, **33**, 603; Bouis, *Ann. Chim.*, 1928, **9**, 402) and had b. p. 96—98°. On treatment with hydrobromic acid under the standard conditions (p. 263) the percentage reaction was 21·8 after 15 minutes and 58 after 1 hour (the corresponding figures for Δ^{β}-butenol were 29·4 and 60·2).

α-Methylallyl bromide was prepared from the alcohol by the phosphorus tribromide–pyridine method (cf. p. 263) and had b. p. 95—105°. Under the standard conditions it was hydrolysed to the extent of 69%, which is almost identical with the corresponding result for Δ^{β}-butenyl bromide.

An attempt to apply the bromometric method of Linstead (J., 1927, 355) was unsuccessful, since the amount of addition was small and the rate of addition to α-methylallyl alcohol only slightly greater than to Δ^{β}-butenol. Methods based on the hydrogenation of the alcohols were also unsuccessful.

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