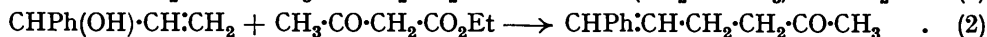
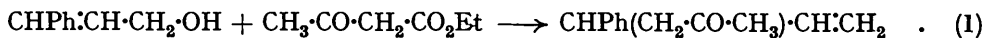


236. *Addition of $\beta\gamma$ -Unsaturated Alcohols to the Active Methylene Group. Part II. The Action of Ethyl Acetoacetate on Cinnamyl Alcohol and Phenylvinylcarbinol.*

By M. F. CARROLL.

Cinnamyl alcohol reacts with ethyl acetoacetate in the presence of a catalyst at 180—220° to give γ -phenyl- Δ^{α} -hexen- ϵ -one, and phenylvinylcarbinol under the same conditions gives cinnamylacetone.

THE action of ethyl acetoacetate on linalool and geraniol gives the same product (this vol., p. 704). Cinnamyl alcohol and phenylvinylcarbinol give two different compounds:



The reactions were carried out as previously described; in (1) cinnamyl acetoacetate was obtained as an intermediate product.

The ketone obtained in (2) was identified by comparison with cinnamylacetone prepared from ethyl acetoacetate and cinnamyl chloride (Bergmann and Corte, J., 1935, 1363), and by the melting point of a mixture of the 2:4-dinitrophenylhydrazones.

The ketone obtained in (1) was fractionated: the first and the last fraction gave the same derivatives in good yields, thus showing that no other isomeric ketone was present. The constitution was proved by oxidation to α -phenyl-lævulic acid, which was also prepared from ethyl α -bromophenylacetate and ethyl acetoacetate.

To examine the by-products formed in the reaction, the ketone was converted into the oxime, which was easily removed by fractional distillation. The residue consisted of cinnamyl alcohol and acetate.

The results show that each alcohol produces the corresponding ketone only, and that no transposition takes place.

EXPERIMENTAL.

Cinnamyl chloride was conveniently prepared in large quantities as follows: 100 g. of cinnamyl alcohol (m. p. 32.5°) and 100 c.c. of concentrated hydrochloric acid were shaken in the cold and left for 1 day. The spent acid was removed, and a further 100 c.c. of concentrated acid added to the oil; the process was repeated. (The acid from the second and the third treatment was added to fresh 100 g. portions of cinnamyl alcohol.) On washing and distillation, 80 g. of cinnamyl chloride were obtained (71% of the theoretical), d_4^{20} 1.092, n_D^{20} 1.5830.

Cinnamylacetone was prepared from the chloride in the usual way, except that potassium carbonate and acetone were used in place of sodium ethoxide. The ethyl cinnamylacetoacetate

obtained, b. p. 165—170°/2.5 mm., gave, on hydrolysis with dilute sodium hydroxide solution, the ketone, b. p. 128—130°/5 mm., n_D^{20} 1.5483 (oxime, m. p. 89—90°; 2:4-dinitrophenylhydrazone, m. p. 144—146°).

Phenylvinylcarbinol (compare Meisenheimer and Beutter, *Annalen*, 1933, 508, 58).—Cinnamyl chloride (1 mol.), acetic acid (2.5 mols.), and potassium acetate (1.5 mols.) were heated at 90—100° for 3 hours. Water was added, and the oil washed and distilled. The acetates obtained (0.92 mol., containing about 0.3 mol. of phenylvinylcarbinyl acetate) were hydrolysed by the cautious addition of 40% sodium hydroxide solution to an alcoholic solution. The hydrolysis was followed titrimetrically, and when it was complete, water was added, and the oil washed and fractionally distilled. The phenylvinylcarbinol had b. p. 90—95°/2 mm., n_D^{20} 1.5431. The recovered cinnamyl alcohol was used for the preparation of more of the chloride.

α -Phenyl-lævulic Acid.—A mixture of ethyl α -bromophenylacetate (0.1 mol.), ethyl acetoacetate (0.15 mol.), potassium carbonate (0.15 mol.), and 50 c.c. of acetone was refluxed for 3 hours, the acetone distilled off, water added, and the oil separated, washed, and hydrolysed with alcoholic sodium hydroxide. On acidification 19 g. of the acid were obtained, m. p. 125—126° after crystallisation from benzene.

Reaction between Cinnamyl Alcohol and Ethyl Acetoacetate.—The experiments were carried out as described in a previous paper (*loc. cit.*). Cinnamyl alcohol (1 mol.), ethyl acetoacetate (1.05 mols.), and 1 g. of sodium acetate were heated to 165° during 3 hours, to 185° during 3 hours, and to 240° during 2 hours. Carbon dioxide began to be evolved at 170° when most of the ethyl alcohol formed had distilled off. The total distillate (51 g.) contained 6 g. of acetone, 2 g. of ethyl acetate, and 43 g. (0.93 mol.) of ethyl alcohol. The residue was washed and distilled, and three main fractions collected: (1) 81 g., b. p. 95—100°/1 mm., (2) 26 g., b. p. 100—115°/1.5 mm., (3) 30 g., b. p. 115—150°/2 mm., mainly cinnamyl acetoacetate. Fractions (1) and (2) contained 60% and 35%, respectively, of the ketone and variable amounts of cinnamyl alcohol and acetate.

The first fractions from several runs were systematically fractionated, but could be resolved only into two main fractions: (a) a mixture of the ketone (60%), cinnamyl acetate (25%), and cinnamyl alcohol (15%); (b) a mixture of the acetate (60%) and the alcohol (40%). The total distillate contained 0.33 mol. of the ketone, 0.16 mol. of the alcohol, 0.16 mol. of the acetate, and 0.14 mol. of cinnamyl acetoacetate.

To isolate the γ -phenyl- Δ^{α} -hexen- ϵ -one, fraction (a) was hydrolysed with aqueous alkali and 90 g. of the product were added to 100 c.c. of 10% sodium hydroxide solution and stirred mechanically while 800 c.c. of 3% permanganate solution were run in. On distillation a middle fraction (40 g., b. p. 99—103°/2 mm., n_D^{20} 1.5325) was obtained containing 96% of the ketone (2:4-dinitrophenylhydrazone, m. p. 101—102°). Only benzoic acid was identified in the aqueous layer.

The original distillate was tested for isomeric ketones as follows: Fraction (1) was fractionally redistilled; 2 g. of the first fraction, containing 60% of the ketone, gave 1.4 g. of the dinitrophenylhydrazone, m. p. 100—103°, and 3 g. of the last fraction, containing 34% of the ketone, gave 1.3 g., m. p. 100—102°. Mixed m. p. 100—102°.

The ketone was identified by oxidation to α -phenyl-lævulic acid. 12 G. of the purified ketone were emulsified in 50 c.c. of 5% sodium hydroxide solution with good agitation, and 200 c.c. of 3% permanganate solution added slowly. After extraction with chloroform, acidification of the aqueous solution gave 4 g. of an acid, m. p. 125—126.5° after crystallisation from benzene and mixed m. p. 125—126° with α -phenyl-lævulic acid (Found: *M*, by alkali titration, 193. Calc.: *M*, 192).

Cinnamyl acetoacetate was obtained from the end fractions of several runs, and was purified by distillation, b. p. 159°/1.5 mm. On hydrolysis with weak alkali, acetone, carbon dioxide, and cinnamyl alcohol were obtained in good yield. The pure ester was heated at 220—240° for 3 hours and gave 0.24 mol. of the ketone, 0.15 mol. of the alcohol, 0.15 mol. of the acetate, and 0.2 mol. of unchanged ester.

Reaction between Phenylvinylcarbinol and Ethyl Acetoacetate.—A mixture of 0.2 mol. of the carbinol, 0.27 mol. of ethyl acetoacetate, and 0.3 g. of potassium acetate was heated to 220° during 3 hours and maintained at this temperature for 3 hours. Evolution of carbon dioxide began at 180° and was practically complete at 220°; 15 c.c. of distillate were obtained containing 0.25 mol. of ethyl alcohol. The residue was washed and distilled and gave 10 g. of ethyl acetoacetate, 2 g. of an alcoholic fraction, and 26 g. (0.15 mol.) of cinnamylacetone, b. p. 125—130°/4 mm., n_D^{20} 1.5475. The oxime was obtained in good yield, m. p. 87.5—89°, mixed m. p.

with the oxime of cinnamylacetone 88—89°. The 2 : 4-dinitrophenylhydrazone (yield, almost quantitative) had m. p. 145—146.5° and mixed m. p. 145—146°.

The author is indebted to the Directors of A. Boake, Roberts and Co. for permission to publish this work.

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[*Received, June 17th, 1940.*]
