[Contribution from the Chemistry Department of the University of Illinois]

CHALCONES. II. DECOMPOSITION BY ALKALI

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Certain of the natural yellow and orange coloring matters are substituted benzalacetophenone derivatives called chalcones. The structure of these chalcones is usually determined by decomposing them with alkali and isolating and identifying the products. The degradation products however, depend on the condition used for splitting the chalcone.

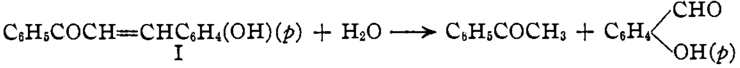
The chalcone from hyssopin was shown by synthesis to be 2,4,6-trihydroxystyryl-3,4-methylenedioxyphenyl ketone.[1] Oesterle[2] proposed the isomeric structure 2,4,6-trihydroxyphenyl-3,4-methylenedioxystyryl ketone because piperonal was produced by alkaline degradation, along with phloroglucinol and acetopiperone. Butein[3] gave resacetophenone and protocatechuic acid. On the other hand, eriodictyol,[4] homoeriodictyol[5] and hesperitin[6] yielded phloroglucinol and substituted cinnamic acids when subjected to alkaline degradation.

The purpose of the present work was to study the decomposition by alkali of two isomeric chalcones whose structure was known as a result of their synthesis. It was desired to determine the optimum conditions for splitting this type of molecule in order that a procedure might be available for the determination of the structure of naturally occurring chalcones.

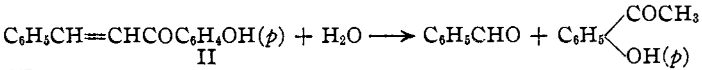
The chalcones studied were, 4-hydroxystyryl-phenyl ketone (I) and 4-hydroxyphenyl-styryl ketone (II). These were chosen because the decomposition products could be fairly easily separated and were well-known compounds which could be readily identified.

A series of experiments was carried out in which the chalcones were heated with various concentrations of aqueous potassium hydroxide ranging from 25 to 50% for different periods of time. The net results of a great number of experiments may be summarized as follows.

Aqueous potassium hydroxide caused the splitting of both of these chalcones at the double bond and the decomposition is merely the reverse of their mode of formation, as shown by the equations



$$\underset{\text{I}}{C_6H_5COCH{=}CHC_6H_4(OH)(p)} + H_2O \longrightarrow C_6H_5COCH_3 + C_6H_4\begin{matrix}\diagup CHO \\ \diagdown OH(p)\end{matrix}$$



$$\underset{\text{II}}{C_6H_5CH{=}CHCOC_6H_4OH(p)} + H_2O \longrightarrow C_6H_5CHO + C_6H_5\begin{matrix}\diagup COCH_3 \\ \diagdown OH(p)\end{matrix}$$

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[1] Shriner and Kleiderer, This Journal, **51**, 1267 (1929).

[2] Oesterle, *Schweiz. Apoth.-Ztg.*, **59**, 548 (1921).

[3] Auwers and Müller, *Ber.*, **41**, 4233 (1908).

[4] Will, *ibid.*, **18**, 1311 (1885).

[5] Power and Frank, *J. Chem. Soc.*, **91**, 887 (1907).

[6] Tiemann and Will, *Ber.*, **14**, 953 (1881).

It was found that chalcone (II) was decomposed by heating it with 33% potassium hydroxide for six hours. The isomeric chalcone (I) required the use of 50% potassium hydroxide and eight hours of refluxing. The yields of decomposition products were low (25 to 50% of the theoretical) due to secondary reactions of the products with the undecomposed benzalacetophenone derivative to give higher condensation products.[7] It is due to the formation of these products that no actual equilibrium concentrations could be determined for this reversible reaction. Sodium hydroxide cannot be used for these decompositions since the sodium salts of these chalcones are insoluble in the concentrated alkali solutions. In no case was cinnamic acid or *p*-hydroxycinnamic acid found among the decomposition products. The formation of the latter types of degradation products is evidently possible only in the case of highly substituted benzalacetophenones.

Experimental

4-Hydroxystyryl-phenyl Ketone.—Forty grams of acetophenone and 36 g. of *p*-hydroxybenzaldehyde were added to a solution of 24 g. of sodium hydroxide in 200 cc. of water and 100 cc. of alcohol. The mixture was warmed to 70° for two hours and then allowed to stand at room temperature for three days with occasional shaking. The dark red solution was then diluted with an equal volume of water and acidified. The precipitate, which consisted of 4-hydroxystyryl-phenyl ketone and some unreacted *p*-hydroxybenzaldehyde, was filtered, washed with 50% alcohol and then recrystallized twice from 95% alcohol. A yield of 25 g. of yellow needles was obtained which melted at 183–184°.

Anal. Subs., 0.2133: CO_2, 0.6235; H_2O, 0.1033. Calcd. for $C_{15}H_{12}O_2$: C, 80.32; H, 5.39. Found: C, 79.91; H, 5.41.

Decomposition of 4-Hydroxystyryl-phenyl Ketone by Alkali.—Ten grams of the above chalcone was refluxed with 200 cc. of 33% aqueous potassium hydroxide for a period of eight hours. The solution became dark red in color and an oil separated on top of the solution. The mixture was cooled and extracted with ether. The ether extract was dried and fractionally distilled. After distillation of the ether the only fraction obtained consisted of 2.5 g. of colorless oil which boiled at 197–202°. This was identified as acetophenone by conversion to the phenylhydrazone,[8] m. p. 105°. The alkaline solution was partly neutralized with hydrochloric acid and evaporated to a volume of about 50 cc. The precipitated potassium chloride was filtered off and the filtrate acidified and filtered again. This filtrate was treated with norite to remove some of the color and then extracted three times with ether. Evaporation of the ether and recrystallization of the residue from a small amount of 50% alcohol gave *p*-hydroxybenzaldehyde, m. p. 116°. It was identified by conversion to the phenylhydrazone, which melted at 181–182°. This agrees with the value given by Anselmino.[9]

4-Hydroxyphenyl-styryl Ketone.—Fifty-four grams of *p*-hydroxyacetophenone and 42 g. of benzaldehyde were condensed together by exactly the same procedure as described above for the isomeric chalcone; 57 g. of pale yellow crystals was obtained which melted at 173–174°. This agrees with the value given by Kostanecki and Tambor.[10]

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[7] Kostanecki and Rossbach, *Ber.*, **29**, 1488 (1896).

[8] Reisenegger, *ibid.*, **16**, 662 (1883).

[9] Anselmino, *ibid.*, **36**, 3974 (1903).

[10] Kostanecki and Tambor, *Ber.*, **32**, 1924 (1899).

Anal. Subs., 0.2069: CO_2, 0.6068; H_2O, 0.1016. Calcd. for $C_{15}H_{12}O_2$: C, 80.32; H, 5.39. Found: C, 79.99; H, 5.49.

Decomposition of 4-Hydroxyphenyl-styryl Ketone.—Ten grams of this chalcone was refluxed with 200 cc. of 50% aqueous potassium hydroxide for eight hours. Ether extraction of the alkaline solution yielded a small amount of benzaldehyde, b. p. 175–180°, which was identified by means of its phenylhydrazone;[11] m. p. 153–154°. A very small amount of benzyl alcohol was also obtained. This was undoubtedly produced by the Cannizzaro reaction. The alkaline solution produced a brown precipitate on acidification which was dissolved in dilute alkali. The solution was saturated with carbon dioxide which caused the separation of some unreacted chalcone along with some amorphous polymerization products. These were filtered and the filtrate was extracted three times with 100-cc. portions of ether. The ether was distilled and the residue recrystallized from a small amount of water. Crystals of *p*-hydroxyacetophenone melting at 107° were obtained. It was identified by means of a mixed melting point and conversion to the phenylhydrazone,[12] which melted at 135–136°.

Summary

Concentrated potassium hydroxide splits simple chalcones into the corresponding aldehyde and ketone. The best conditions for accomplishing this degradation and procedures for isolating the products are given.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

PREPARATION AND BACTERICIDAL PROPERTIES OF CERTAIN PENTADECANOIC, HEPTADECANOIC AND NONADECANOIC ACIDS. XIX[1]

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In two previous papers covering the preparation and properties of certain dialkyl acetic acids, it was demonstrated that the hexadecanoic acids were more effective bactericidally to *B. Leprae* than the octadecanoic acids, and far more effective than the dodecanoic, the tridecanoic or the tetradecanoic acids. Representatives of the missing series, pentadecanoic, heptadecanoic and nonadecanoic acids have now been prepared. The bacteriological results of the specific compounds produced are given in Table I.

It is obvious that the C_{15} and the C_{17} acids are not as effective as the C_{16}, and the C_{19} acids are less effective than the previously prepared C_{18} acids. From the tables containing the data for all of the acids from C_{12} to C_{19}, it may be concluded that the bactericidal action is zero for the C_{12} acids, and practically nil for the C_{13} acids. Beginning with the C_{14} acids the

[11] Biltz, *Ann.*, **305**, 171 (1899).

[12] Nencki, *Ber.*, **30**, 1770 (1897).

[1] The previous paper in this series is XVIII, Armendt and Adams, **52**, 1289 (1930).