pressure (bath 50°). The residue was triturated for several hours with absolute acetone. The resulting white solid, which was very hygroscopic, was carefully dried in a vacuum desiccator over phosphorus pentoxide (weight 8.0 g., 63%). A 0.900-g. sample was weighed rapidly, dissolved in water, and the solution diluted to 10 ml. The rotation of the solution in a 1-dcm. tube was found to be +1.48°; $[\alpha]_D$ +16.4°. The only value given in the literature is the one reported by Senderens,[13] who found $[\alpha]_D$ +12.2° for the monohydrate of lactitol. He reported the m. p. to be 78°. Our product melted to a milky liquid at 79–80° and increased in volume about five-fold; at 130–140° the mass turned to a yellow glass-like solid which decomposed at 190–200°. Neuberg and Marx[14] reported that anhydrous lactitol decomposed at 200°.

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[13] Senderens, *Compt. rend.*, **170**, 47 (1920).

[14] Neuberg and Marx, *Biochem. Z.*, **3**, 539 (1907).

## Summary

1. A method of catalytic hydrogenation has been developed whereby the delta lactones of aldonic acids are reduced in good yield to the corresponding sugars. The gamma lactones are also reduced, but they usually give lower yields of the sugars owing to the further reduction of the sugars to the corresponding sugar alcohols.

2. The method has been adapted to the reduction of the sugars to the corresponding sugar alcohols. It is possible to obtain practically complete reduction and to isolate the sugar alcohols in 63–80% yields.

Chicago, Illinois Received August 29, 1935

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[Contribution from the Chemical Laboratory of the University of Illinois]

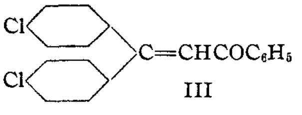
# The Reversibility of the Friedel–Crafts Condensation. Hydrogenation Phenomena

By L. L. Alexander, A. L. Jacoby and Reynold C. Fuson

It was to be predicted that the reversible addition of aromatic hydrocarbons to $\alpha,\beta$-unsaturated carbonyl compounds[1] would be prevented by the presence of suitable substituents on the *beta* carbon atom. Several examples of conjugated systems have now been found which do not yield addition products but instead undergo hydrogenation. Thus, 1,1-diaryl-2-acylethylenes do not condense with benzene in the presence of aluminum chloride, but, instead, *are hydrogenated to the corresponding saturated diaryl ketones.*

$$\underset{\text{I}}{(Ar)_2C{=}CHCOR} \xrightarrow[AlCl_3]{C_6H_6} \underset{\text{II}}{(Ar)_2CHCH_2COR}$$

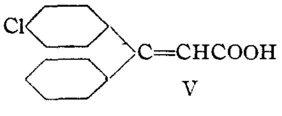
For example, 1,1-di-(*p*-chlorophenyl)-2-benzoylethylene (III) is converted to $\alpha$-benzohydrylacetophenone (IV).



III

$(C_6H_5)_2CHCH_2COC_6H_5$

IV



V

$(C_6H_5)_2CHCH_2COOH$

VI

$(C_6H_5)_2C{=}CHCOC_6H_5$

VII

$(C_6H_5)_2C{=}CHCOC(CH_3)_3$

VIII

Similarly, $\beta$-(*p*-chlorophenyl)-cinnamic acid (V) gives $\beta,\beta$-diphenylpropionic acid (VI). In both of these examples replacement as well as hydrogenation is involved. However, the chlorine-free analog of III—1,1-diphenyl-2-benzoylethylene (VII)—appears to undergo only the latter change; it gives IV. In a similar fashion, 1,1-diphenyl-2-trimethylacetylethylene (VIII) is transformed into its hydrogenation product, $\alpha$-benzohydrylpinacolone.

However, it seemed possible that this type of transformation might not be dependent on the presence of a hetero conjugated system, but might be simply a property of stilbenes. In order to clear up this point stilbene, *p*-bromostilbene and *p,p'*-dichlorostilbene were each subjected to treatment with benzene in the presence of anhydrous aluminum chloride. *In each case the product was dibenzyl.* The generalized form of the equation is $XC_6H_4CH{=}CHC_6H_4X + 2C_6H_6 + 2H = C_6H_5CH_2CH_2C_6H_5 + 2C_6H_5X$. It is seen that this process involves replacement of aryl groups as well as hydrogenation at the double bond.

The various mechanisms which suggest themselves for these processes raise the question as to whether the addition of benzene, the elimination of the substituted phenyl group and the hydrogenation are related processes and, if so, in what sequence they occur. The work is being continued from this point of view.

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[1] For references to earlier papers of this series, see Woodward, Borcherdt and Fuson, This Journal, **56**, 2103 (1934).

## Experimental Part

### α-Benzohydrylacetophenone (IV)

**A. From 1,1-Di-(*p*-chlorophenyl)-2-benzoylethylene (III).**—A mixture of 0.75 g. of the dichloro ketone, 1.5 g. of aluminum chloride and 20 cc. of dry benzene was saturated with dry hydrogen chloride and allowed to stand at room temperature for twelve hours. The product melted at 91.5–92°, and was shown by the method of mixed melting points to be α-benzohydrylacetophenone.

**B. From 1,1-Diphenyl-2-benzoylethylene (VII).**—α-Benzohydrylacetophenone was also obtained by applying the foregoing procedure to 1,1-diphenyl-2-benzoylethylene.

**α-Benzohydrylpinacolone.**—In a like manner, the interaction of 5 g. of 1,1-diphenyl-2-trimethylacetylethylene (VIII), 10 g. of aluminum chloride, 100 cc. of dry benzene, and dry hydrogen chloride gave 3.6 g. of α-benzohydrylpinacolone. The product melted at 83–84.5°, and the melting point was not depressed when this sample was mixed with an authentic specimen of the ketone.

**Ethyl β-Phenyl-β-(*p*-chlorophenyl)-β-hydroxypropionate.**—A mixture of 54.1 g. of *p*-chlorobenzophenone, 50 g. of ethyl bromoacetate and 225 cc. of dry benzene was treated with 19.6 g. of granulated zinc. The mixture was warmed and stirred for an hour and then decomposed with dilute acid in the usual manner. The product (from alcohol) melted at 79–80.5°; yield, 79%.

*Anal.* Calcd. for $C_{17}H_{17}O_2Cl$: C, 67.0; H, 5.6. Found: C, 67.3; H, 5.7.

**β-Phenyl-β-(*p*-chlorophenyl)-β-hydroxypropionic acid** was obtained by saponification of the ester. It crystallized from dilute alcohol in light yellow needles melting at 188.5–189°, with decomposition.

*Anal.* Calcd. for $C_{15}H_{13}O_3Cl$: C, 65.1; H, 4.7. Found: C, 64.9, 65.2; H, 4.9, 4.7.

**β-(*p*-Chlorophenyl)-cinnamic Acid** (V).—A mixture of 44.2 g. of β-phenyl-β-(*p*-chlorophenyl)-β-hydroxypropionic acid, 24.6 g. of acetic anhydride and 10.9 g. of freshly fused sodium acetate was heated for four hours under reflux. The solution was then poured into water and the mixture allowed to stand at room temperature for two weeks. The cinnamic acid was recrystallized from alcohol; m. p. 168°.

*Anal.* Calcd. for $C_{15}H_{11}O_2Cl$: C, 69.6; H, 4.3; neut. equiv., 258.5. Found: C, 69.6; H, 4.4; neut. equiv., 260.8.

**β,β-Diphenylpropionic Acid** (VI).—The chloro acid was shaken with a mixture of benzene, aluminum chloride, and hydrogen chloride over a period of twenty hours. The product (from an ether–petroleum ether mixture) melted at 151–152°, and was shown by the mixed melting point method to be β,β-diphenylpropionic acid.

### Dibenzyl

**A. From *p,p'*-Dichlorostilbene.**—One and a half grams of powdered aluminum chloride was added to a mixture of 1 g. of *p,p'*-dichlorostilbene and 20 cc. of dry benzene. The mixture became dark red in color. Dry hydrogen chloride was bubbled through the mixture for thirty minutes. The reaction mixture was then stirred at room temperature for sixteen hours and poured on a mixture of ice and hydrochloric acid. The product melted at 51.5° and when mixed with *dibenzyl* did not depress the melting point; yield, 70%.

**B. From Stilbene.**—By a similar procedure involving stilbene and in which the reaction time was fifty-four hours, a 20% yield of dibenzyl was obtained.

**C. From *p*-Bromostilbene.**—In this experiment, in which the reaction time was seventeen hours, 2.9 g. of dibenzyl was obtained from 5 g. of the bromostilbene. The color change from brown to red was again noticed.

## Summary

1. 1,1-Di-(*p*-chlorophenyl)-2-benzoylethylene and β-(*p*-chlorophenyl)-cinnamic acid react with benzene in the presence of aluminum chloride to give, respectively, α-benzohydrylacetophenone and β,β-diphenylpropionic acid.

2. Under the same conditions, 1,1-diphenyl-2-benzoylethylene and 1,1-diphenyl-2-trimethylacetylethylene undergo hydrogenation to α-benzohydrylacetophenone and α-benzohydrylpinacolone.

3. Similar treatment converts stilbene, *p*-bromostilbene and *p,p'*-dichlorostilbene into dibenzyl.

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