The Reaction between Diphenylalkanes and Maleic Anhydride by the Friedel and Crafts Method

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Introduction

It is a well-known fact that the Friedel and Crafts reaction between maleic anhydride and an aromatic compound results in the formation of a β-aroylacrylic acid. For example, benzene reacts with maleic anhydride to produce β-benzoylacrylic acid. In this case, an excess of maleic anhydride does not lead to the production of any detectable quantity of acids of the types, $C_6H_4(COCH=CHCOOH)_2$, $C_6H_3(COCH=CHCOOH)_3$, etc., nor can such products be obtained by the action of maleic anhydride on benzoylacrylic acid in any solvent with alminum chloride as catalyst[1]. This is also the case in the reaction between maleic anhydride and diphenyl[2]. This fact is illustrated as an E-effect of a carbonyl group by the electronic theory. Therefore, it is expected that the reaction between maleic anhydride and such a compound as one in which two benzene rings are separated by some methylene groups, e.g. diphenylmethane or bibenzyl, should result in substitution of each benzene ring by $-COCH=CHCOOH$ radicals. But some investigators[3] reported that the reaction between diphenylmethane and succinic anhydride, similarly to the reaction under consideration, gave only β-(*p*-benzyl) benzoyl propionic acid. On the other hand, there are some reports which support the first opinion. For instance, in addition to $C_6H_5-(CH_2)_n-C_6H_4COOH$ (n is 1 or 2), Liebermann[4], and Liebermann and Zsuffa[5] obtained $HOOCC_6H_4-(CH_2)_n-C_6H_4COOH$ (n is 1 or 2) by the reaction of diphenylmethane or bibenzyl and oxalyl chloride, and Duval[6] produced *p*-benzylacetophenone and *p*, *p*′-diacetyldiphenylmethane from diphenylmethane and acetyl chloride by the Friedel and Grafts reaction. But hitherto the reaction of diphenylalkanes and maleic anhydride has not been reported.

Now, in the present work the Friedel and Crafts reaction between diphenylmethane and bibenzyl, and maleic anhydride were studied, and diphenylmethane-4, 4′-di-γ-oxocrotonic acid and bibenzyl-4, 4′-di-γ-oxocrotonic acid were obtained respectively. The reduction of these compounds by zinc and acetic acid was examined and diphenylmethane-4, 4′-di-γ-oxobutyric acid and bibenzyl-4, 4′-di-γ-oxobutyric acid respectively were obtained. Furthermore these saturated ketoacids were reduced by a modified Clemmensen reduction method to diphenylmethane-4, 4′-dibutyric acid and bibenzyl-4, 4′-dibutyric acid, respectively.

Experimental Part

(1) Synthesis of Diphenylmethane and Bibenzyl.—a) Diphenylmethane was produced by the reaction between benzyl chloride and benzene in the presence of aluminium amalgam as catalyst according to the method of Hartman and Phillips[7]. The reaction product was purified by fractional distillation under reduced pressure and distillate boiling at 97–98°C/1.5 mmHg was collected. The yield was 49–54.6% of the theoretical amount.

b) Bibenzyl was produced by the reaction of 1, 2-dichloroethane with benzene in the presence of anhydrous aluminium chloride as catalyst according to the method described in "Organic Synthetic Chemistry"[8]. The reaction product was also purified by fractional distillation under reduced pressure and distillate boiling at 105–6°C/3 mmHg (m.p. 51–52°C) was collected. The yield was 66.2–74.6% of the theoretical amount.

(2) Diphenylmethane-4, 4′-di-γ-oxocrotonic acid.—The Friedel and Crafts condensation of maleic anhydride with various aromatic hydrocarbons was extensively studied by the use of such a solvent as carbon disulfide, nitrobenzene, and chlorinated hydrocarbons or aromatic hydrocarbon itself. It was found in the previous work[9] that 1, 2-dichloroethane gave the best result. So it was also used here as a solvent.

In a 1 l. four-necked, round-bottomed flask fitted with a mechanical stirrer, a reflux condenser, a dropping funnel, and a thermometer, were placed

1) M.T. Bogert and J.T. Ritter, *J. Am. Chem. Soc.*, **47**, 526 (1925).
2) H.G. Oddy, *J. Am. Chem. Soc.*, **45**, 2156 (1923).
3) J.W. Cook, A.M. Robinson and E.M. Roe, *J. Chem. Soc.*, 1939, 266; L.F. Fieser, et al., *J. Am. Chem. Soc.*, **70**, 3201, Table C (1948).
4) C. Liebermann, *Ber.*, **45**, 1186 (1912).
5) C. Liebermann and M. Zsuffa, *Ber.*, **45**, 852 (1911).
6) M.H. Duval, *Bull. chim. soc.*, [4], **7**, 789 (1913).
7) W.W. Hartman and R. Philips, "Organic Syntheses, Coll. Vol.", John Wiley & Sons, Inc., New York, N.Y. (1943), II, p. 232.
8) R. Oda, "Organic Synthetic Chemistry", Kyoritsu-sha, Tokyo (1949), p. 92.
9) W. Koga, *J. Chem. Soc. Japan (Pure Chem. Sect.)* **76**, 1053 (1955).

49 g. (0.5 mol.) of maleic anhydride and 200 g. of dichloroethane. With cooling 105 g. of powdered, anhydrous aluminium chloride was added and stirred for about ten minutes, during which period most of the solid matter went into solution. Forty two grams (0.25 mol.) of diphenylmethane was then added slowly through a dropping funnel with efficient cooling and stirring. During this period the reaction mixture had to be kept below 3°C. After the addition had been completed, stirring was continued for about two hours at 5–6°C; at the end of this period the reaction mixture became very viscous and finally could not be stirred. The reaction mass was poured onto ice and hydrochloric acid and the solvent was removed by steam distillation. After cooling, the solid mass was collected and was dissolved in soda solution. The insoluble mass was filtered and the filtrate was acidified to Congo red by hydrochloric acid. The precipitated diphenylmethane-4, 4′-di-γ-oxocrotonic acid was filtered and washed with water. After drying for a day in vacuum desiccator, it weighed 42–53 g. (46–58% of the theoretical amount). It was purified by recrystallization from ethanol.

The purified acid is straw-yellow needles and melts at 255–6°C (from temperature at 220°C it turns from yellow to brown). It is soluble in hot alcohol and acetic acid but slightly in cold. It is practically insoluble in any other organic solvents or water.

Neutralization equivalent. Found: 304, 303. Calcd.: 308.

Anal. Found: C, 69.29; H, 4.36. Calcd. for $C_{21}H_{16}O_6$: C, 69.23; H, 4.40%.

Oxidation of this acid with alkaline permanganate gave colorlese crystals, which did not melt up to 300°C. The esterification of this acid in methanol gave colorless crystals which melted at 224–5°C (recrystallized from methyl ethyl ketone). This melting point agrees with that of dimethyl ester of benzophenone dicarboxylic acid-4, 4′ reported by Limplicht[10] and Staudinger[11] and analytical data is also in accordance with the calculated value as shown below.

Anal. Found: C, 68.45; H, 4.89. Calcd. for $C_{17}H_{14}O_5$: C, 68.46; H, 4.70%.

Furthermore alkaline fusion of the colorless acid melting above 300°C gave benzoic acid, m.p. 120°C, and terephthalic acid, identified as the methyl ester, m.p. 140–41°C; mixed m.p. 141–42°C.

Dimethyl ester of diphenylmethane-4, 4′-di-γ-oxocrotonic acid was made under the usual variety of conditions. The purified ester is a straw-yellow needle and melts at 128–128.5°C (recrystallized from methyl ethyl ketone).

Anal. Found: C, 70.38; H, 5.03. Calcd. for $C_{23}H_{20}O_6$: C, 70.41; H, 5.10%.

This colored isomeric ester (*trans*) rearranges slowly to the *cis*-isomer when its methyl ethyl ketone solution is exposed to sunlight for a few days. The *cis*-isomer is a colorless needle melting at 84–84.5°C.

(3) Bibenzyl-4, 4′-di-γ-oxocrotonic acid.—Bibenzyl-4, 4′-di-γ-oxocrotonic acid was produced similarly to diphenylmethane-4, 4′-di-γ-oxocrotonic acid. The yield was 56–69 g. (57.8–70.3% of the theoretical amount.)

This acid is practically insoluble in most organic solvents and water. So the purification is carried out in such a way that it was disssolved in soda solution and filtered and the filtrate was acidified by hydrochloric acid, or by the hydrolysis of the purified dimethyl ester of the acid by mineral acid.

The purified acid is a straw-yellow crystal and does not melt up to 300°C.

Nentralization equivalent. Found: 296, 292. Calcd.: 297.

Anal. Found: C, 69.89; H, 4.73. Calcd. for $C_{22}H_{18}O_6$: C, 69.84; H, 4.76%.

Oxidation of this acid with alkaline permanganate gave terephthalic acid, identified as the methyl ester, m.p. 140–41°C, mixed m.p. 141–42°C.

Dimethyl ester is formed in the same way as above. The purified ester is a straw-yellow needle melting at 137–8°C (recrystallized from methyl ethyl ketone).

Anal. Found: C, 70.88; H, 5.38. Calcd. for $C_{24}H_{22}O_6$: C, 70.94; H, 5.42%.

This colored isomer (*trnas*) also rearranges to the *cis*-isomer when its methyl ethyl ketone solution is exposed to sunlight for a few days. The *cis*-isomer is a colorless needle melting at 175.5–6.5°C.

(4) Diphenylmethane-4, 4′-di-γ-oxobutyric acid.—Ten grams of diphenylmethane-4, 4′-di-γ-oxocrotonic acid was suspended in 80 g. of acetic acid and to this was added a small portion of 15 g. of zinc dust with stirring After threee to four hours the reaction mixture became colorless; then it was poured in 1 l. of soda solution and dissolved. The insoluble mass was filtered and the filtrate was acidified with hydrochloric acid. The precipitated diphenylmethane-4, 4′-di-γ-oxobutyric acid was filtered and washed with water. After drying, it was purified by recrystallization from ethanol. The yield was 6.2–7.5 g. (61.3–74.3% for theoretical amount). The purified acid is a colorless needle melting at 224–5°C.

Anal. Found: C, 68.45; H, 5.56. Calcd. for $C_{21}H_{20}O_6$: C, 68.48; H, 5.43%.

Dimethyl ester is formed by refluxing methanol solution of the acid in the presence of concentrated sulfuric acid as catalyst. The purified ester (recrystallized from methanol) is a colorless thin plate and melts at 95°C.

Anal. Found: C, 69.23, H, 6.11. Calcd. for $C_{23}H_{24}O_6$: C, 69.70; H, 6.06%.

(5) Bibenzyl-4, 4′-di-γ-oxobutyric acid.—The reduction of the diphenylethane-4, 4′-di-γ-oxocrotonic acid was carried out in the same way as above. The yield was 5.5–7.6 g. (54.4–75.2% for theoretical amount). The purified acid is a colorless needle (recrystallized from a large amount of ethanol) and melts at 259–60°C.

10) H. Limpricht, *Ann.*, **312**, 97 (1900).
11) H. Staudinger and G.A.R. Kon, *Ann.*, **384**, 98 (1911).

Anal. Found: C, 69.06; H, 5.58. Calcd. for $C_{24}H_{22}O_5$: C, 69.11; H, 5.76%.

Dimethyl ester is formed by refluxing suspension of the acid in methanol in the presence of a small amount of concentrated sulfuric acid as catalyst. The purified ester (recrystallized from methyl ethyl ketone) is a colorless needle melting at 114.5°C.

Anal. Found: C, 70.40; H, 6.36. Calcd. for $C_{24}H_{26}O_5$: C, 70.24; H, 6.34%.

(6) Diphenylmethane-4, 4′-dibutyric acid and Bibenzyl-4, 4′-dibutyric acid.—The reduction of the carbonyl group of the above saturated keto acids according to Clemmensen's method or modified Martin-Clemmensen's method was unsuccessful, for these acids were insoluble in water, hydrochloric acid, or toluene. So the reduction was carried out according to Koelsch[12] who used ethanol as a solvent.

To the mixture of 45 cc. of ethanol, 45 cc. of concentrated hydrochloric acid, and amalgamated zinc, which was prepared from 15 g. of zinc dust and 1.5 g. of murcuric chloride, 5 g. of the acid, which should be reduced, was added and then was refluxed for one hour. A second portion of 45 cc. of concentrated hydrochloric acid was then added and refluxing was continued for six hours. The mixture was cooled and the solid mass was collected and dissolved in boilling 500 cc. of 5% aqueous sodium hydroxide. After filtration and acidification of the filtrate, the reduced acid was separated. It was purified recrystallization from ethanol.

Diphenylmethane-4, 4′-dibutyric acid.—The yield was 2.5–2.7 g. (54.1–58.4% for theoretical amount). Colorless needles, m.p. 199.5–200°C.

12) C.F. Koelsch, *J. Am. Chem. Soc.*, 55, 3885 (1933).

Anal. Found: C, 73.76; H, 6.97. Calcd. for $C_{21}H_{24}O_4$: C, 74.12; H, 7.06%.

Bibenzyl-4, 4′-dibutyric acid.—The yield was 2.2–2.5 g. (54.1–58.4% for theoretical amount). Colorless needles, m.p. 182–3°.

Anal. Found: C, 74.86; H, 7.44. Calcd. for $C_{22}H_{26}O_4$: C, 74.58; H, 7.36%.

Summary

(1) By the reaction of diphenylmethane and diphenylethane with maleic anhydride in the presence of aluminium chloride, diphenylmethane-4, 4′-di-γ-oxocrotonic acid and bibenzyl-4, 4′-di-γ-oxocrotonic acid were produced, respectively. And *cis* and *trans* isomers of dimethyl esters of these acids were prepared.

(2) By the reduction of the above two acids by zinc and acetic acid, diphenylmethane-4, 4′-di-γ-oxobutyric acid and bibenzyl-4, 4′-di-γ-oxobutyric acid were prepared.

(3) These saturated keto acids were reduced by amalgamated zinc in the mixture of ethanol and hydrochloric acid to diphenylmethane-4, 4′-dibutyric acid and diphenylethane-4, 4′-dibutyric acid.

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