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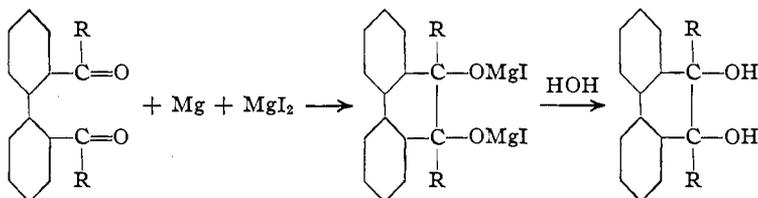
THE REARRANGEMENT OF 9,10-DIARYLDIHYDROPHENANTHRENE DIOLS

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In continuing the study of the pinacol-pinacol rearrangement,¹ we have investigated the rearrangement of a number of 9,10-diaryldihydrophenanthrenediols. These glycols correspond to pinacols and it appeared that they would be formed by the reduction of 2,2'-diacylbiphenyls by a mixture of magnesium and magnesium iodide in the same manner that ketones are reduced to pinacols.²



It was found that 2,2'-dibenzoylbiphenyl ($R = C_6H_5$) reacts with the binary mixture and is reduced to a mixture of stereoisomeric 9,10-diphenyldihydrophenanthrenediols. The product formed in the largest proportion is a pinacol which melts at 179–180°; a small amount of a pinacol melting at 202° is produced. Our products were found to be identical with the two stereoisomeric forms of diphenyldihydrophenanthrenediol that had been obtained by Werner and Grob³ and by Acree⁴ by other methods. These investigators prepared the low-melting pinacol by the action of phenylmagnesium bromide on phenanthrenequinone; the high-melting isomer was obtained by the reduction of dibenzoylbiphenyl by zinc and potassium hydroxide. On repeating the latter reaction we actually obtained a mixture of the two isomers and not a single compound.

Werner and Grob reported that the two isomeric diphenyldihydrophenanthrenediols when treated with a mixture of sulfuric acid and hydrochloric acid at 200° gave the same pinacol, 10,10-diphenylphenanthrene (9). We have repeated the rearrangement reaction using acetyl chloride at a lower temperature and also acetic acid containing a small amount of iodine² in order to be certain that the product was not the result of a secondary action⁵ but was the initial product of rearrangement.

¹ Bachmann and Moser, *THIS JOURNAL*, **54**, 1124 (1932).

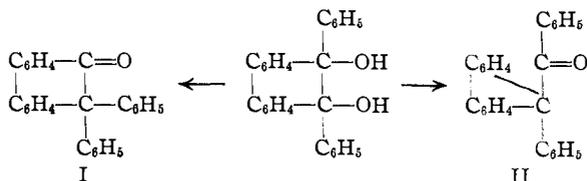
² Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

³ Werner and Grob, *Ber.*, **37**, 2887 (1904).

⁴ Acree, *Am. Chem. J.*, **33**, 186 (1905).

⁵ "Annual Reports," 1930, Vol. 27, p. 120; also Bergmann and Schuchardt, *Ann.*

Under these conditions each pinacol gave diphenylphenanthrone, showing that of the two possible rearrangements, I and II, only the mechanism I, involving the migration of the phenyl group, takes place.



Since in symmetrical mixed pinacols the relative migration aptitudes of the *p*-tolyl and the anisyl groups were found to be greater than that of the phenyl group, it was predicted¹ that in the rearrangement of di-*p*-tolyl-dihydrophenanthrenediol and of dianisyl-dihydrophenanthrenediol the *p*-tolyl group and the anisyl group, respectively, would migrate practically exclusively. These new pinacols were synthesized and subjected to rearrangement. It is found that the predictions are confirmed. Rearrangement of di-*p*-tolyl-dihydrophenanthrenediol gives 10,10-di-*p*-tolylphenanthrone(9); dianisyl-dihydrophenanthrenediol gives 10,10-dianisylphenanthrone(9).

It was possible to prepare two stereoisomeric di-*p*-tolyl-dihydrophenanthrenediols and two stereoisomeric dianisyl-dihydrophenanthrenediols. A high-melting compound was obtained by reduction of the corresponding 2,2'-diacylbiphenyl by magnesium and magnesium iodide or by zinc and potassium hydroxide; a low-melting isomer resulted from the action of a Grignard reagent on phenanthrenequinone. The two stereoisomeric di-*p*-tolyl-dihydrophenanthrenediols were rearranged to the same pinacolin; in like manner the pair of dianisyl-dihydrophenanthrenediols gave the same compound on rearrangement. All of the pinacols are oxidized by chromic acid to the corresponding 2,2'-diacylbiphenyls.

The investigation of the rearrangement of substituted dihydrophenanthrenediols is being continued.

Experimental

Reduction of 2,2'-Dibenzoylbiphenyl by Mg + MgI₂.—Two grams of 2,2'-dibenzoylbiphenyl was added to a mixture of magnesium and magnesium iodide prepared from 2 g. of iodine and 1 g. of magnesium powder in 15 cc. of ether and 30 cc. of benzene; an insoluble oily complex of ketone and magnesium iodide precipitated. The mixture was refluxed until the oily complex had disappeared. The pinacol which was obtained on hydrolysis of the filtered solution was recrystallized from *n*-propyl alcohol. In this way there was obtained 1.1 g. of needle-like crystals of 9,10-diphenyldihydrophenanthrenediol melting at 202°; from the alcoholic filtrate 0.65 g. of the low-melting pinacol was isolated. When this latter product was recrystallized from acetic acid, it was obtained in the form of prisms melting at 179–180°. These prisms were found to be identical with the pinacol which was prepared by the action of phenylmagnesium bromide on phenanthrenequinone according to the directions of Acree.⁴ Acree ob-

tained 25 g. of product from 20 g. of phenanthrenequinone. Recently, Schlenk and Bergmann⁶ reported that they obtained only one-half of this yield. We obtained, in agreement with Acree, a yield of 26 g. of recrystallized pinacol from 20 g. of phenanthrenequinone.

When dibenzoylbiphenyl was treated with zinc and potassium hydroxide according to the directions of Werner and Grob, there was obtained a 76% yield of the high-melting pinacol and a 13% yield of the low-melting compound. Reduction of dibenzoylbiphenyl by zinc and acetic acid at room temperature gave the high-melting pinacol as the principal product; when the reaction was carried out in a warm solution the product was not pinacol but the pinacolin, diphenylphenanthrone.

Rearrangement of 9,10-Diphenyldihydrophenanthrenediol.—The product obtained by heating 1 g. of pinacol of m. p. 179–180° with a mixture of 10 cc. of acetyl chloride, 5 cc. of acetic acid and 20 cc. of benzene was practically pure 10,10-diphenylphenanthrone-(9). The same compound was obtained by rearrangement under the same conditions of the pinacol melting at 202°; from 0.5 g. of pinacol there was obtained 0.44 g. (92%) of pure diphenylphenanthrone.

2,2'-Di-*p*-toluylbiphenyl, $\text{CH}_3\text{C}_6\text{H}_4\text{COC}_6\text{H}_4\text{C}_6\text{H}_4\text{COC}_6\text{H}_4\text{CH}_3$.—This compound was prepared from 2-bromo-4'-methylbenzophenone by the Ullmann reaction. The substituted benzophenone was obtained by the action of the Grignard reagent from 17 g. of *p*-bromotoluene in 35 cc. of ether on 12 g. of *o*-bromocyanobenzene in 35 cc. of benzene. After twelve hours of refluxing, the reaction mixture was treated with water and the ketone-imine was hydrolyzed in the usual manner. The ketone was recrystallized from alcohol; yield, 15 g. (83%). Heidenreich⁷ obtained this ketone from *o*-bromobenzoyl chloride and toluene. Our method of synthesis proves that it was the *p*-methyl derivative that was formed in the Friedel and Crafts reaction carried out by him.

A mixture of 2 g. of 2-bromo-4'-methylbenzophenone and 5 g. of copper powder was heated with stirring at 200° for one-half hour. The mass was cooled and extracted with acetone. Evaporation of the acetone gave 2,2'-di-*p*-toluylbiphenyl. Recrystallization from acetic acid gave needle-like prisms melting at 137°; yield, 0.95 g. (68%).

Anal. Calcd. for $\text{C}_{28}\text{H}_{22}\text{O}_2$: C, 86.1; H, 5.7. Found: C, 85.9; H, 5.6.

Reduction of 2,2'-Di-*p*-toluylbiphenyl. (a) **By Mg + MgI₂.**—Two grams of 2,2'-di-*p*-toluylbiphenyl was added to a mixture of magnesium and magnesium iodide prepared from 2 g. of iodine and 1 g. of magnesium powder in 15 cc. of ether and 30 cc. of benzene. The mixture was refluxed until the insoluble oily complex of ketone and magnesium iodide had disappeared. The pinacol which was obtained by hydrolysis of the filtered solution was recrystallized from a mixture of benzene and alcohol. The product (1.8 g.) appeared to be a mixture of pinacols. When it was recrystallized from *n*-propyl alcohol, there was obtained 1.0 g. of di-*p*-tolylidihydrophenanthrenediol in the form of transparent prisms; m. p. 213°.

Anal. Calcd. for $\text{C}_{28}\text{H}_{24}\text{O}_2$: C, 85.7; H, 6.2. Found: C, 85.9; H, 6.2.

(b) **By Zn + KOH.**—One gram of 2,2'-di-*p*-toluylbiphenyl was dissolved in 40 cc. of 95% alcohol, several grams of zinc dust and 5 cc. of 40% potassium hydroxide solution were added and the resulting mixture was refluxed for eight hours. The solution was filtered and the filtrate was poured into water. The solid which precipitated was filtered off and recrystallized from *n*-propyl alcohol; m. p. 213°; yield, 0.6 g. (60%). This compound was identical with the product obtained by means of magnesium and magnesium iodide. From the filtrate 0.1 g. of pinacol melting at 136° was isolated.

⁶ Schlenk and Bergmann, *Ann.*, **463**, 209 (1928).

⁷ Heidenreich, *Ber.*, **27**, 1452 (1894).

9,10-Di-*p*-tolylidihydrophenanthrenediol (Low-melting Isomer).—To the Grignard reagent which had been prepared from 42 g. of *p*-bromotoluene in 80 cc. of ether was added 50 cc. of benzene and then 17 g. of phenanthrenequinone in portions. The mixture was refluxed for five hours, cooled and hydrolyzed. The crude ditolylidihydrophenanthrenediol which was obtained by evaporation of the ether-benzene solution was digested with cold alcohol in order to remove oily impurities and it was then recrystallized from a mixture of benzene and alcohol; m. p. 103°; yield, 18 g. (57%). When the product was recrystallized again from *n*-propyl alcohol the melting point remained unchanged. When, however, a small amount was recrystallized from ethyl alcohol, the melting point was changed to 136°. This represents a second modification of the compounds, for both behaved alike on oxidation and rearrangement. The low-melting form is very soluble in hot organic solvents; it crystallizes from acetic acid in needle-like prisms containing solvent of crystallization which melt at 84°. The 136° modification is not very soluble in cold or in hot alcohol but is readily soluble in hot acetone; it crystallizes from acetic acid without solvent.

Anal. Calcd. for C₂₈H₂₄O₂: C, 85.7; H, 6.2. Found: C, 85.3; H, 6.1.

Oxidation of 9,10-Di-*p*-tolylidihydrophenanthrenediol.—Eight grams of pinacol (m. p. 103°) was added to a solution of 1.6 g. of chromic anhydride in 4 cc. of water and 100 cc. of acetic acid. The mixture was warmed on a steam-bath for one-half hour and was then poured into water. The colorless solid which precipitated was filtered off and was recrystallized from acetic acid; yield of 2,2'-di-*p*-toluylbiphenyl, 6 g. (75%); m. p. 137°. The product was identical with 2,2'-di-*p*-toluylbiphenyl which was synthesized from 2-bromo-4'-methylbenzophenone by the Ullmann reaction.

In another run, oxidation of 1 g. of pinacol gave needles melting at 125.5–126.0°. This product proved to be a second form of di-*p*-toluylbiphenyl. This low-melting form can be converted to the modification melting at 137° by inoculation of an acetic acid solution of the low-melting form or of the melted compound with a crystal of the high-melting form.

Oxidation of 1 g. of pinacol of m. p. 136° gave 0.80 g. (80%) of 2,2'-di-*p*-toluylbiphenyl. In like manner oxidation of the pinacol of m. p. 213° gave an 80% yield of the diketone.

Rearrangement of 9,10-Di-*p*-tolylidihydrophenanthrenediol.—One-half gram of pinacol (m. p. 213°) was heated for five minutes with 3 cc. of acetic acid to which a crystal of iodine² had been added. Two cc. of alcohol saturated with sulfur dioxide was added in order to remove the iodine. On cooling, 0.41 g. of 10,10-di-*p*-tolylphenanthrone (9) melting at 159° crystallized out. From the filtrate an additional 0.04 g. of the same product was isolated, making a total yield of 95% of that theoretically possible. Bergmann and Schuchardt⁸ report 158° for the melting point of di-*p*-tolylphenanthrone which they obtained by rearrangement of di-*p*-tolylbiphenylene ethylene glycol.

One-half gram of the pinacol of m. p. 103° was heated with acetic acid and iodine in the same manner; again the product was ditolylphenanthrone. Rearrangement by means of acetyl chloride gave the same product. Finally, the same compound resulted on rearrangement of the second modification (m. p. 136°) of this stereoisomeric pinacol.

2,2'-Dianisoylbiphenyl, CH₃OC₆H₄COC₆H₄C₆H₄COC₆H₄OCH₃.—The ketone, 2-bromo-4'-methoxybenzophenone,⁷ was prepared by the action of anisylmagnesium bromide from 19 g. of *p*-bromoanisole on 12 g. of *o*-bromocyanobenzene; yield, 13 g. (69%). A mixture of 4.4 g. of this ketone and 10 g. of copper powder was heated at 200° for thirty minutes. Extraction of the cooled mass with acetone gave 2,2'-di-

⁸ Bergmann and Schuchardt, *Ann.*, **487**, 225 (1931).

anisoylbiphenyl. The compound was recrystallized from acetic acid and was obtained in the form of needle-like prisms; yield, 1.6 g. (50%). The compound melted at 147°, then solidified and melted at 152–153°. The low-melting modification can be changed to the high-melting form by inoculation of a solution of the former with a crystal of the latter.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.6; H, 5.2. Found: C, 80.0; H, 5.4.

Reduction of 2,2'-Dianisoylbiphenyl.—Reduction of 1 g. of 2,2-dianisoylbiphenyl by a mixture of magnesium and magnesium iodide gave 0.62 g. of 9,10-dianisylldihydrophenanthrenediol. After two recrystallizations from *n*-propyl alcohol it was obtained in the form of prisms (0.43 g.); m. p. 188–190°. The pinacol is not very soluble in cold or in hot alcohol; it is somewhat more soluble in hot propyl alcohol.

Anal. Calcd. for $C_{28}H_{24}O_4$: C, 79.2; H, 5.7. Found: C, 79.3; H, 5.7.

By refluxing a mixture of 2.5 g. of 2,2'-dianisoylbiphenyl, 10 g. of zinc dust, 100 cc. of alcohol and 10 cc. of 40% potassium hydroxide for six hours, there was obtained 9,10-dianisylldihydrophenanthrenediol. From hot *n*-propyl alcohol there crystallized 1.3 g. of pinacol of m. p. 188–190°; from the filtrate a 10% yield of the stereoisomer melting at 154–155° was isolated.

Oxidation of the dianisylldihydrophenanthrenediol (m. p. 188–190°) by a solution of chromic anhydride in acetic acid gave an 80% yield of 2,2'-dianisoylbiphenyl; m. p. 152–153°.

9,10-Dianisylldihydrophenanthrenediol (Low-melting Isomer).—Seventeen grams of phenanthrenequinone was added in portions to the Grignard reagent which had been prepared from 46 g. of *p*-bromoanisole in 80 cc. of ether and 50 cc. of benzene. After being refluxed for six hours, the mixture was hydrolyzed. A viscous oil was obtained which partly crystallized after three weeks. The mass was digested with a cold mixture of benzene and alcohol; this dissolved the oil but not the crystals. By recrystallization from *n*-propyl alcohol the dianisylldihydrophenanthrenediol was obtained as heavy diamond-shaped plates; m. p. 154–155°; yield, 8 g.

Anal. Calcd. for $C_{28}H_{24}O_4$: C, 79.2; H, 5.7. Found: C, 78.9; H, 5.7.

Oxidation of 3.0 g. of this pinacol by a solution of 0.6 g. of chromic anhydride in 36 cc. of acetic acid and 2 cc. of water at 100° gave 2.52 g. (83%) of 2,2'-dianisoylbiphenyl.

Rearrangement of 9,10-Dianisylldihydrophenanthrenediol.—By heating 0.5 g. of dianisylldihydrophenanthrenediol (m. p. 154–155°) with 3 cc. of acetic acid containing a small amount of iodine, there was obtained 0.46 g. (95%) of 10,10-dianisylphenanthrone(9) melting at 151–152°. This product was found to be identical with dianisylphenanthrone which was synthesized in a yield of 80% by the action of dimethyl sulfate on bis-(*p*-hydroxyphenyl)-phenanthrone.⁹

The dianisylldihydrophenanthrenediol of m. p. 188–190° gave a quantitative yield of dianisylphenanthrone when it was treated with acetic acid and iodine.

Summary

The binary system $Mg + MgI_2$ reduces 2,2'-dibenzoylbiphenyl to a mixture of stereoisomeric diphenyldihydrophenanthrenediols. 2,2'-Di-*p*-toluylbiphenyl and 2,2'-dianisoylbiphenyl are reduced in the same manner to the corresponding substituted diaryldihydrophenanthrenediols.

The three pairs of stereoisomeric diaryldihydrophenanthrenediols readily undergo the pinacol-pinacolin rearrangement; in these rearrangements

⁹ Goldschmidt, Vogel and Bredig, *Ann.*, **445**, 123 (1925).

migration of the phenyl, *p*-tolyl and anisyl groups occurs practically exclusively.

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THE INTERACTION OF AMIDES WITH ANILINE

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Very little information is to be found in the literature regarding the interaction of amides with aniline. To study this question, two methods were chosen: (1) to leave the amides in contact with aniline for varying periods at several temperatures, and (2) to conduct the amide vapors through a hot tube, discharging them into cold aniline.

Except for a catalytic transformation of acetamide into methylamine (or $\text{HCN} + \text{H}_2$) and carbon monoxide using nickel¹ at 400° , the only recorded course of pyrolysis of acetamide is the one into acetonitrile² and water. In our high temperature experiments there was the possibility of deammonation into ketene. With acetamide the equation would be $\text{CH}_3\text{CONH}_2 \rightarrow \text{CH}_2\text{CO} + \text{NH}_3$. If so, the acetanilide might originate either from acetamide or ketene.

Actually, aniline was found to be quite non-reactive at 100° with such amides as acetamide, propionamide or isobutyramide. In fact, a mixture of the amide and aniline could be distilled (to 240°) without giving rise to anilide in the residue. Continued refluxing, however, was found to generate small yields of anilide, the best yields coming from propionamide. It was found that isobutyramide was exceedingly sluggish.

When the amides were passed through a tube which was maintained at $500\text{--}700^\circ$, some pyrolysis undoubtedly occurred because of nitrile formation. By passing the hot, effluent gases directly into cold aniline, fairly good yields of propionanilide or acetanilide, but no isobutyranilide, were obtained. The data for a few representative runs out of seventy-five which were performed are collected in Table I. The percentage yield of anilide is based on the amide which was not recovered. Examination of the data shows the best yields of acetanilide and propionanilide at tube temperatures of about 500° and contact times of but a few seconds. As high as 45–49% yields of propionanilide resulted, as compared with a 28% yield of acetanilide and no yield of isobutyranilide. Somewhat higher yields of acetanilide were obtained on a few occasions, but the selected runs seem more characteristic.

¹ Mailhe, *Mat. grasses*, 15, 6488, 6531 (1923); *Bull. soc. chim.*, 37, 1394 (1925).

² Boehner and Andrews, *THIS JOURNAL*, 38, 2503 (1916); Boehner and Ward, *ibid.*, p. 2505.