yield of 2,2-diphenylacenaphthenone-1, m.p. 172–173° (lit.[7] 171.3–172.4°). Both the acenaphthene and pyracene diphenyl ketones gave an orange color with concentrated sulfuric acid.

1,2-Pyracenediols. A. cis-1,2-Pyracenediol (Va). To a yellow-orange suspension of 1 g. of 1,2-diketopyracene (I) in 150 ml. of ethanol there was added in one portion 0.5 g. of sodium borohydride. This suspension was stirred for 2 hr. at room temperature during which time the orange solid dissolved to form a nearly colorless solution which showed a blue fluorescence. An additional 0.1 g. of sodium borohydride was added and stirring continued for 20 min. The reaction mixture was then decomposed by the drop-wise addition of excess 10% hydrochloric acid followed by 300 ml. of water. The white precipitate which slowly separated was collected on a filter. There was obtained 0.52 g. of crude Va, m.p. 240–250° dec. This product was crystallized from ethanol to form white needles, (40%), m.p. 264–265° dec.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.18; H, 5.75.

B. trans-1,2-Pyracenediol (Vb). The filtrate from the above preparation of the *cis* diol was saturated with salt and extracted exhaustively with ether. The ethereal solution was dried over anhydrous sodium sulfate and evaporated under reduced pressure leaving 0.5 g. of crude *trans*-1,2-pyracenediol (Vb), m.p. 130–138° which was crystallized from 400 ml. of water to yield white cubes, (35%), m.p. 188–189°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.19; H, 5.86.

The high melting diol Va (0.2 g.) was suspended in 5 ml. of the acetone–hydrochloric acid solution and anhydrous sodium sulfate (0.1 g.) was added. The white solid slowly dissolved over a period of 14 hr. at room temperature. The solution was filtered and the solvent evaporated. There was obtained 0.2 g. of 1,2-isopropylidenedioxypyracene, m.p. 120–135° dec. Crystallization from petroleum ether (b.p. 40–50°) yielded white needles, m.p. 164–165°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.78; H, 6.55.

The low melting diol Vb (0.2 g.) was subjected to the same reaction conditions as described above but was recovered unchanged.

When acenaphthenequinone was reduced with sodium borohydride as described for 1,2-diketopyracene (I), the reaction was instantaneous and quantitative. A 50–50 mixture of the known *cis* and *trans* acenaphthenediols[9] was obtained although separation proved more difficult.

Pyracenone-1 (VI). A mixture of the *cis* and *trans* 1,2-pyracenediols (Va and Vb) (0.2 g.) was subjected to the conditions of the pinacol rearrangement using glacial acetic acid and iodine.[7] The mixture was poured into aqueous sulfur dioxide. The precipitated gray solid (0.2 g.) melted at 140–165° and then formed a black residue which did not melt above 270°. Approximately one half of this gray product dissolved in hot ethanol. This solution was treated with decolorizing charcoal, filtered, and on cooling very light yellow crystals formed. There was obtained 0.08 g. (40%) of pyracenone-1 (VI), m.p. 180–181° (lit.[5b] m.p. 182–183°). The infrared spectrum showed absorption peaks at 1670 cm.$^{-1}$ and 1715 cm.$^{-1}$ Pyracenone-1 gave an orange-yellow color with concentrated sulfuric acid similar to that obtained with acenaphthenone-1.

A mixture of *cis* and *trans* acenaphthenediols was subjected to the same reaction conditions above but no acenaphthenone-1 was isolable.

BOULDER, COLO.

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(9) R. Criegee, L. Kraft, and B. Rank, *Ann.*, **507**, 159 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, A'IN SHAMS UNIVERSITY]

Studies of Quinoid Structures. IV.[1] Action of Grignard Reagents on Anthraquinone Monoanil

W. I. AWAD, A. K. FATEEN, AND M. A. ZAYED

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Grignard reagents add preferentially to the carbonyl group of anthraquinone monoanil under ordinary conditions. The constitution of the products is discussed.

It has been found[1–3] in these laboratories that Grignard reagents add preferentially to the carbonyl group of phenanthrenequinonimine, chrysenequinonimine, phenanthrenequinone monoxime, chrysenequinone monoxime, phenanthrene-quinone and chrysenequinone monosemicarbazones and benzil monosemicarbazone. This study is now extended to *p*-quinoid structures, *e.g.* anthraquinone monoanil (I). Grignard reagents add under normal conditions preferentially to the carbonyl group of I as shown in Scheme A.

The constitution of II is based on: (i) hydrolysis to give a nitrogen free keto compound (III), (ii) infrared spectrum showing the presence of C═N stretching frequency at 1639 cm^{-1}[4,5] and —OH stretching frequency at 3333 cm^{-1},[6] and (iii) elemental analysis. The ketone (III) showed clear carbonyl stretching frequency at 1680 cm^{-1},[7] but it did not show a free —OH stretching fre-

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(1) Studies of Quinoid Structures. III. Action of Grignard reagents on phenanthrenequinone monosemicarbazone, chrysenequinone monosemicarbazone and benzil monosemicarbazone. W. I. Awad, A. R. A. Raouf, and Miss A. M. Kamel (*J. Org. Chem.* in press).

(2) W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **22**, 881 (1957).

(3) W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **23**, 282 (1958).

(4) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Metheun, London, 1957, p. 223.

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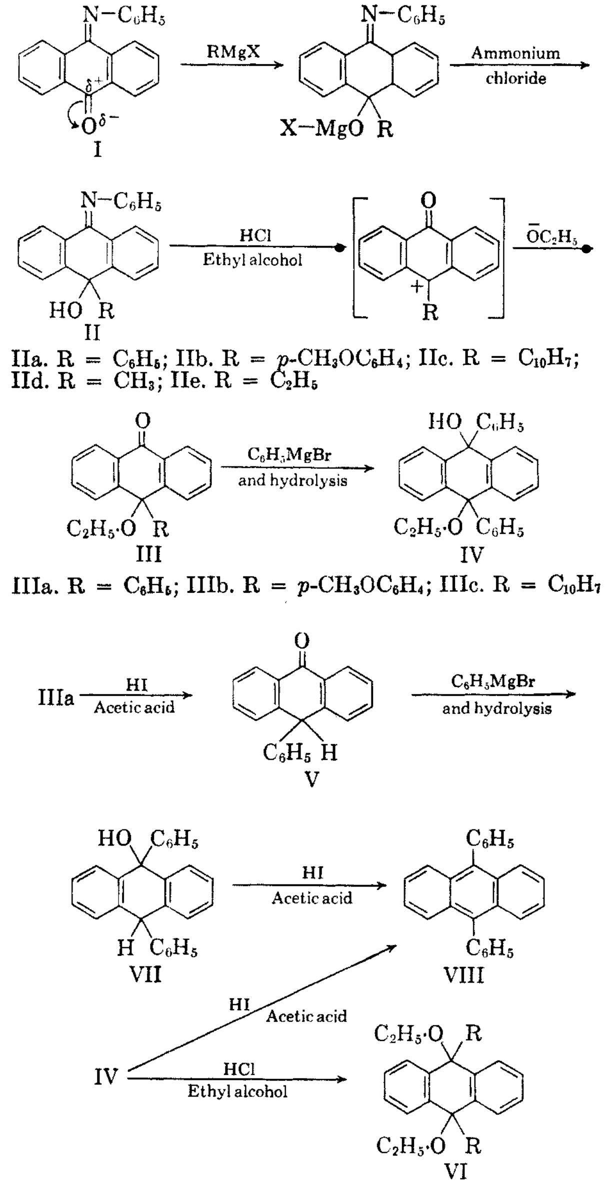
(6) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Metheun, London, 1957, p. 84.

(7) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Metheun, London, 1957, p. 176.



IIa. R = C_6H_5; IIb. R = p-$CH_3OC_6H_4$; IIc. R = $C_{10}H_7$; IId. R = CH_3; IIe. R = C_2H_5

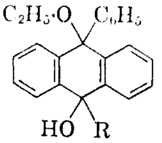
IIIa. R = C_6H_5; IIIb. R = p-$CH_3OC_6H_4$; IIIc. R = $C_{10}H_7$

VIa. R = C_6H_5; VIb, R = p-$CH_3OC_6H_4$

Scheme A

quency, and since the hydrolysis has been carried out in a hydrochloric acid–ethyl alcohol mixture, etherification of the free —OH has also taken place. This has been proved by the action of an ethyl alcohol–hydrochloric acid mixture on 9-hydroxy-9-phenyl anthrone (m.p. and mixture m.p. experiment). The melting point of IIIa was similar to that previously described by Liebermann and Lindenbaum.[8] When IIIa was treated with a hydroiodic acid–acetic acid mixture de-ethylation and reduction took place to give 10-phenylanthrone (V), (similar to the same reaction on 10-phenyl-10-methoxyanthrone by Schlenk and Bergmann[9]). Furthermore IIIa was treated by Grignard reagent to give IV which was de-ethylated and reduced with loss of water by the action of a hydriodic acetic acid mixture to give 9,10-diphenylanthracene (VIII). Ethylation of IV gave 9,10-diphenyl-9,10-diethoxyanthracene (VI). The action of a Grignard reagent on V gave VII[9] which was converted to VIII by heating with a hydriodic–acetic acid mixture. It is to be noted that the hydroxyl group in position 10 in II is not stable in acid medium compared with that in 10-hydroxy-10-phenyl-9-(10H)phenanthrone[2] under the same conditions. It seems that the hydroxyl in II is eliminated in the form of a water molecule by the proton of the medium. The carbonium ion formed (which is stabilized by the resonance with the benzene rings) is then attacked by the ethoxyl group of the alcohol to give the more stable ether (III). This was also confirmed by the fact that when IIIa was heated with a hydriodic–acetic acid mixture de-ethylation and reduction to V took place. The same applies to the de-ethylation of IV where it is followed by reduction and removal of water to give VIII.

10-Phenyl-10-ethoxy anthrone (IIIa) was allowed to react with anisyl- and α-naphthylmagnesium bromide to yield 9-hydroxy-9-anisyl-10-phenyl-10-ethoxy-9,10-dihydro-anthracene (IXa) and 9-hydroxy-9-naphthyl-10-phenyl-10-ethoxy-9,-10-dihydro-anthracene (IXb), respectively.



IX

IXa. R = p-$CH_3OC_6H_4$; IXb. R = $C_{10}H_7$

EXPERIMENTAL

Melting points are not corrected. Microanalyses were carried out by Alfred Bernhardt, im Max-Plank Institut, Mulheim (Ruhr) Germany. Infrared measurements were made on a Perkin-Elmer infracord Model 137 in nujol mulls or carbon tetrachloride solution.

(a) *Action of phenylmagnesium bromide on anthraquinone monoanil.*[10] A solution of anthraquinone anil (16.8 g.) in a hot mixture of dry benzene and dry ether (150 ml.) was added to an ethereal solution of phenylmagnesium bromide (from bromobenzene, 10.8 g., and magnesium, 1.44 g.) and the reaction mixture was heated at reflux for 2 hr. and left overnight. The product was hydrolyzed with a saturated solution of ammonium chloride, and the ether-benzene layer was separated, dried over anhydrous sodium sulfate, filtered and the solvent distilled. IIa was crystallized from petroleum ether (60–80°) to give 14.2 g. of yellow crystals, m.p. 158°.

Anal. Calcd. for $C_{26}H_{19}ON$: C, 86.42; H, 5.26; N, 3.87. Found: C, 86.18; H, 5.67; N, 3.51.

(b) *Hydrolysis of* IIa. IIa (2 g.) was heated at reflux for 2 hr. with a mixture of ethyl alcohol (25 ml.), and hydrochloric acid (25 ml.). On cooling, IIIa was filtered and crystallized from petroleum ether (60–80°) to give 1.4 g. of

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[8] C. Liebermann and S. Lindenbaum, *Ber.*, **38**, 799 (1905).

[9] von W. Schlenk and E. Bergmann, *Ann.* **463**, 98, 161, 174, 181 (1928).

[10] L. Sander, *Ber.*, **58**, 824 (1925).

yellow crystals, m.p. 157°. It was insoluble in sodium hydroxide solution.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.99; H, 5.46.

10-Phenyl-10-ethoxyanthrone was also prepared by the action of an ethyl alcohol–hydrochloric acid mixture on 10-phenyl-10-hydroxyanthrone[11] and mixture melting point gave no depression.

Preparation of 9,10-diphenyl-9-hydroxy-10-ethoxy-9,10-dihydroanthracene (IV). A solution of 10-phenyl-10-ethoxyanthrone (2.86 g.) in a mixture of dry benzene and dry ether (50 ml.) was added to an ethereal solution of phenylmagnesium bromide (from bromobenzene, 1.57 g., and magnesium, 0.24 g.) and the reaction mixture was treated as in (a). The product was crystallized from methyl alcohol to give 1.9 g. of colorless crystals, m.p. 224°. It gave an indigo color with concentrated sulfuric acid.

Anal. Calcd. for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.48; H, 5.92.

Action of a hydrochloric acid–ethyl alcohol mixture on IV. 9,10-Diphenyl-9-hydroxy-10-ethoxy-9,10-dihydroanthracene (2 g.) was treated as in (b). VI was crystallized from benzene to give 1.6 g. of pale yellow crystals, m.p. 275°.

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.68; H, 6.71. Found: C, 85.39; H, 6.59.

(c) *Action of a hydriodic acetic acid mixture on 10-phenyl-10-ethoxy anthrone* (III). Hydriodic acid (5 ml.) was added to a hot solution of III (1 g.) in acetic acid (3 ml.) and the reaction mixture was refluxed for 2 hr. The product was poured on cold water, and extracted with ether. The ethereal layer was washed with sodium bisulfite solution, then with sodium bicarbonate solution and water, then dried over anhydrous sodium sulfate. The ether was filtered and distilled, leaving a sticky product. It was triturated with petroleum ether (60–80°), then crystallized from petroleum ether (60–80°) to give 0.7 g. of V as yellow crystals, m.p. 146°.

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.88; H, 5.18. Found: C, 89.08: H, 5.22.

Action of a hydriodic-acetic acid mixture on 9,10-diphenyl-9-hydroxy-10-ethoxy-9,10-dihydro-anthracene. Hydriodic acid (1.7 sp. g.) (3 ml.) was added to a hot solution of 9,10-diphenyl-9-hydroxy-10-ethoxy-9,10-dihydro-anthracene (0.4 g.) in acetic acid (2 ml.) and the reaction mixture was treated as in (c). The product was crystallized from petroleum ether (60–80°) to give 0.25 g. of canary yellow crystals, m.p. 245–246° undepressed on admixture with an authentic sample of 9,10-diphenylanthracene.[12]

Anal. Calcd. for $C_{26}H_{18}$: C, 94.54; H, 5.45. Found: C, 94.37; H, 5.46.

Action of a hydriodic-acetic acid mixture on VII. Hydriodic acid (1.7 sp. g.) (2 ml.) was added to a hot solution of VII (0.2 g.) in acetic acid (2 ml.) and the reaction mixture was refluxed for 2 hr. The sticky product was triturated with petroleum ether (60–80°), then crystallized from acetic acid to give 0.1 g. of VIII as light yellow crystals, m.p. 245–246°, undepressed on admixture with an authentic specimen.

Action of anisylmagnesium bromide on I. A solution of anthraquinone anil (11.2 g.) in a hot mixture of dry benzene and dry ether (150 ml.) was added to an ethereal solution of anisylmagnesium bromide (from *p*-bromoanisole, 7.2 g., and magnesium, 0.96 g.) and the reaction mixture was completed as in (a). IIb was crystallized from petroleum ether (60–80°) to give 10.5 g. of yellow crystals, m.p. 147°.

Anal. Calcd. for $C_{27}H_{21}NO_2$: C, 82.86; H, 5.37; N, 3.58. Found: C, 83.01; H, 5.41; N, 3.52.

Hydrolysis of IIb. IIb (3.2 g.) was treated as in (b). IIIb was crystallized from petroleum ether (60–80°) to give 2 g. of yellow crystalline product, m.p. 181°.

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.18; H, 5.72.

Preparation of 9,10-dianisyl-9,10-diethoxy-9,10-dihydroanthracene. A solution of 10-anisyl-10-ethoxyanthrone (1.14 g.) in a mixture of dry benzene and dry ether (50 ml.) was added to an ethereal solution of anisylmagnesium bromide (from *p*-bromoanisole, 0.63 g., and magnesium, 0.08 g.) and the reaction mixture was treated as in (a). The product was crystallized from methyl alcohol to give 0.8 g. of colorless crystals, m.p. 210°. This product (0.7 g.) was heated under reflux for 2 hr. with a mixture of ethyl alcohol (20 ml.) and hydrochloric acid (7 ml.). On cooling, VIb was filtered and crystallized from petroleum ether (80–100°) to give 0.7 g. as colorless crystals, m.p. 276°.

Anal. Calcd. for $C_{32}H_{32}O_4$: C, 79.97; H, 6.71. Found: C, 79.80; H, 6.68.

Action of naphthylmagnesium bromide on I. A solution of anthraquinone anil (14.1 g.) in a hot mixture of dry benzene and dry ether (150 ml.) was added to an ethereal solution of naphthylmagnesium bromide (α-bromonaphthalene, 10.35 g., and magnesium, 1.21 g.) and the reaction mixture was treated as in (a). IIc was crystallized from petroleum ether (40–60°) to give 16.2 g. of yellow crystals, m.p. 161–162°.

Anal. Calcd. for $C_{30}H_{21}NO$: C, 87.56; H, 5.14; N, 3.4. Found: C, 87.47; H, 5.37; N, 3.60.

Hydrolysis of IIc. IIc (1.6 g.) was treated as in (b). The product was crystallized from petroleum ether (60–80°) to give 1.3 g. of IIIc as colorless crystals, m.p. 256°.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 86.01; H, 5.36.

Action of methylmagnesium iodide on I. A solution of anthraquinone anil (9.43 g.) in hot mixture of dry benzene and dry ether (150 ml.) was added to an ethereal solution of methylmagnesium iodide (from methyl iodide, 4.73 g., and magnesium, 0.81 g.) and the reaction was completed as in (a). IId was crystallized from petroleum ether (60–80°) to give 5.4 g. of yellow crystals, m.p. 224°.

Anal. Calcd. for $C_{21}H_{17}ON$: C, 84.25; H, 5.72; N, 4.68. Found: C, 83.75; H, 5.61; N, 4.72.

Action of ethylmagnesium bromide on I. A solution of anthraquinone anil (7.1 g.) in a hot mixture of dry benzene and dry ether (100 ml.) was added to an ethereal solution of ethylmagnesium bromide (ethyl bromide, 2.72 g., and magnesium, 0.6 g.) and the reaction mixture was treated as in (a). IIe was crystallized from petroleum ether (60–80°) to give 4.3 g. of yellow crystals, m.p. 176°.

Anal. Calcd. for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.38; H, 5.94; N, 4.59.

Action of anisylmagnesium bromide on III. A solution of III (2.1 g.) in a mixture of dry benzene and dry ether (50 ml.) was added to an ethereal solution of anisylmagnesium bromide (from *p*-bromoanisole, 1.24 g., and magnesium, 0.16 g.) and the reaction mixture was treated as in (a). IXa was crystallized from ethyl alcohol to give 0.6 g. of colorless crystals, m.p. 186°.

Anal. Calcd. for $C_{29}H_{26}O_3$: C, 82.46; H, 6.16. Found: C, 82.38; H, 6.36.

Action of naphthylmagnesium bromide on III. A solution of III (3.14 g.) in a mixture of dry ether and dry benzene (100 ml.) was added to an ethereal solution of naphthylmagnesium bromide (from α-bromonaphthalene, 2.07 g., and magnesium, 0.24 g.) and the reaction mixture was treated as in (a). IXb was crystallized from a mixture of petroleum ether (40–60°) and benzene to give 1.2 g. of colorless crystals, m.p. 265°.

Anal. Calcd. for $C_{32}H_{26}O_2$: C, 86.87; H, 5.88. Found: C, 86.74; H, 5.93.

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[12] C. K. Ingold and P. C. Marshall, *J. Chem. Soc.*, 3080 (1926).