[Contribution from the Chemical Laboratory of Duke University]

AROMATIC CYCLODEHYDRATION. XXI. *ortho-* AND *para-* (9-ANTHRYL)BENZOIC ACIDS[1]

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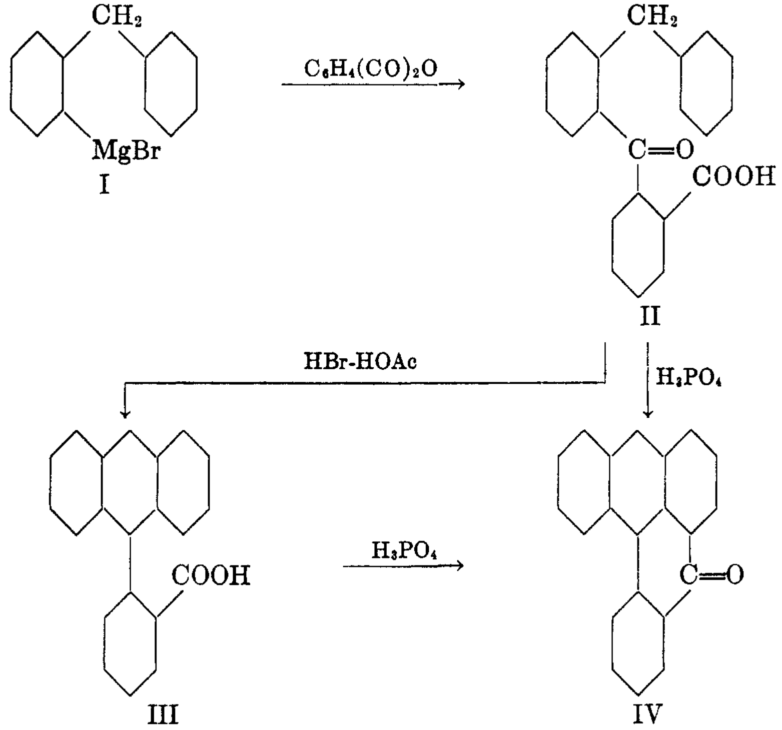
Received June 16, 1948

With the exception of a single complex example, the cyclization of 1-(diphenylmethyl)anthraquinone described by Scholl and Donat (1), the *o*-benzylphenone cyclization appears to have been applied only to the synthesis of hydrocarbons (2). Our present communication describes the preparation of *ortho-* and *para-* (9-anthryl)benzoic acids by this reaction. One of the acids, the *ortho* (III), has been prepared previously by Cook (3) and by Scholl and Donat (1) through reduction of the lactone of 9-hydroxy-9-(*o*-carboxyphenyl)anthrone.



In the present work, the Grignard reagent (I) prepared from 2-bromodiphenylmethane was allowed to react with phthalic anhydride to yield 2-benzylbenzophenone-2′-carboxylic acid (II). This compound underwent cyclodehydration readily to yield the expected *o*-(9-anthryl)benzoic acid (III). From the structure of this acid, it might be predicted that it could be cyclized to coeranthrone (IV). Scholl and Donat (1) attempted this ring closure using warm

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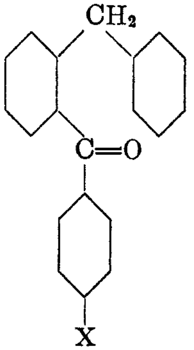
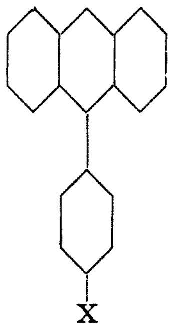
[1] For the preceding communication of this series see Bradsher, Rapoport, and Anderson, *J. Am. Chem. Soc.*, **68**, 2152 (1946).

concentrated sulfuric acid but obtained only very impure dirty-red coeranthrone (IV). Our experiments with the same reagent were no more promising, and it appeared that sulfur dioxide was being given off in the reaction. When *o*-(9-anthryl)benzoic acid (III) was heated at 195° with the less strongly oxidizing phosphoric acid, it was found that cyclization to coeranthrone could be effected in 47% yield. A mixture of phosphoric acid and phosphorus pentoxide was used to bring about the elimination of two moles of water from 2-benzylbenzophenone-2'-carboxylic acid (II), giving a 66% yield of coeranthrone.



V, X = Cl
VI, X = CN
VII, X = Br



VIII, X = Br
IX, X = CN
X, X = COOH

The *p*-(9-anthryl)benzoic acid (X) was prepared in two ways. In the first, 2-benzyl-4'-chlorobenzophenone (V) was prepared by the reaction of *p*-chlorophenylmagnesium iodide with *o*-benzylbenzonitrile and converted to the corresponding nitrile (VI) by the action of cuprous cyanide. Cyclization of this keto-nitrile was accompanied by hydrolysis, yielding the free acid (X).

In the alternate procedure, 9-(*p*-bromophenyl)anthracene (VIII) was prepared by the *o*-benzylphenone cyclization and converted to the nitrile (IX) which, on hydrolysis, gave the expected acid (X).

EXPERIMENTAL

o-Bromodiphenylmethane. It was found that this halide could be prepared in better yield when *o*-bromobenzophenone was reduced by the action of hydriodic acid rather than by the Clemmensen reduction employed previously (4, 5). A mixture of 10 g. of *o*-bromobenzophenone, 10 ml. of 47% hydriodic acid, and 10 g. of red phosphorus was refluxed and stirred for forty hours. After neutralization, the mixture was extracted with ether. The ethereal extract was filtered, dried, and concentrated. The residue was fractionated under reduced pressure, yielding 9.5 g. (82%) of colorless liquid, b.p. 179–183° (21.5 mm.) [Lit. (5) 175° (22 mm.)].

2-Benzylbenzophenone-2'-carboxylic acid (II). A Grignard reagent prepared in ether from 18 g. of *o*-bromodiphenylmethane was transferred slowly under nitrogen pressure to a stirred boiling solution containing 9.8 g. of phthalic anhydride in 200 ml. of anhydrous benzene. The mixture was stirred and refluxed for two hours and then allowed to stand overnight. After decomposition in the usual way, the benzene solution was extracted twice with sodium carbonate solution. Careful acidification of the carbonate extract gave a pale yellow precipitate which, once recrystallized from benzene, gave 14.3 g. (68%) of fine white needles, m.p. 170–171°. An analytical sample was obtained by repeated recrystallization, m.p. 172–174°.

Anal. Calc'd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10.
Found: C, 79.80; H, 5.30.

o-(9-Anthryl)benzoic acid (III). A solution of 0.5 g. of the above keto-acid (II) was refluxed for twenty hours in a mixture containing 4 ml. of 48% hydrobromic acid, 1 ml. of water, and 15 ml. of acetic acid. The mixture was cooled and the crystalline product collected, m.p. 238–242°; yield 0.38 g. (81%). It was twice recrystallized from ethanol, m.p. 242–243° [Lit. (1) 242–243.5°].

Anal. Calc'd for $C_{21}H_{14}O_2$: C, 84.55; H, 4.73.
Found: C, 84.36; H, 4.63.

The methyl ester was prepared by the action of diazomethane, m.p. 156–157°.

Anal. Calc'd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16.
Found: C, 84.59; H, 5.53.

Coeranthrone (IV). (a) *By cyclization of o-(9-anthryl)benzoic acid (III).* A mixture consisting of 0.35 g. of the acid (III) and 20 ml. of 85% phosphoric acid was heated for two and one-half hours in an oil-bath at 195°. The red solution was poured on ice and the red product collected and recrystallized from acetic acid as dark red needles, m.p. 177–178.5° [Lit. (1) 178°]; yield 0.15 g. (47%).

(b) *By cyclization of 2-benzylbenzophenone-2'-carboxylic acid (II).* To a mixture of 0.5 g. of the keto-acid (II) and 5 ml. of phosphoric acid, phosphorus pentoxide was added until the mixture had a pasty consistency. It was then heated at 190–200° for one and three-quarters hours and at 250° for an additonal quarter hour. On decomposition with ice-water, a brick-red precipitate was obtained. This was collected and boiled with ammonium hydroxide to remove unchanged acid, then collected and recrystallized from acetic acid as flat, dark, red-brown needles, m.p. 178–180°; yield 0.29 g. (66%). This product gave no depression of melting point when mixed with that obtained with (a).

2-Benzyl-4'-chlorobenzophenone (V). A Grignard reagent was prepared from 37 g. of *p*-chloroiodobenzene, and after removal of most of the ether, a solution of 10 g. of *o*-benzylbenzonitrile was added. The mixture was refluxed for fourteen hours, cooled, and decomposed with 20% ammonium chloride solution. The benzene layer was separated and refluxed with 200 ml. of 2 *N* hydrochloric acid for ten hours. The organic layer was separated, washed, dried, concentrated, and the residue distilled under reduced pressure. The fraction boiling at 237–239° (8 mm.) was collected. Recrystallized from ethanol (using Norit), the product was obtained as long white needles, m.p. 73°; yield 9.4 g. (59%).

Anal. Calc'd for $C_{20}H_{15}ClO$: C, 78.30; H, 4.93.
Found: C, 78.62; H, 5.31.

2-Benzyl-4'-cyanobenzophenone (VI). A mixture containing 7 g. of 2-benzyl-4'-chlorobenzophenone, 4.1 g. of cuprous cyanide, 0.01 g. of cupric sulfate, and 10 ml. of pyridine was heated in an oil-bath at 250° for fifteen hours, the pyridine being allowed to escape. At the end of this period, the mixture was cooled and poured into dilute ammonium hydroxide solution, extracted with benzene, the benzene extract concentrated, and the residue distilled under reduced pressure. The distillate was recrystallized several times from ethyl alcohol (using Norit), as long white needles, m.p. 104.5–105°; yield 1.8 g. (27%).

Anal. Calc'd for $C_{21}H_{15}NO$: C, 84.83; H, 5.09; N, 4.71.
Found: C, 84.62; H, 5.02; N, 4.80.

2-Benzyl-4'-bromobenzophenone (VII). A Grignard reagent prepared from 24.7 g. of *o*-bromodiphenylmethane was added dropwise with stirring to a solution of 20 g. of *p*-bromobenzoyl chloride in 400 ml. of anhydrous benzene heated to 45°. After addition was complete, the mixture was refluxed for two hours, during which most of the ether was allowed to escape. After standing overnight, the mixture was decomposed, the benzene layer separated, washed, concentrated, and the residue fractionated under reduced pressure. The portion boiling at 210–220° (1 mm.) solidified on standing, yield 16 g. (50%). Recrystallization from ethanol yielded white plates, m.p. 83–84.5°.

Anal. Calc'd for $C_{20}H_{15}BrO$: C, 68.39; H, 4.31; Br, 22.75.
Found: C, 68.52; H, 4.56; Br, 22.78.

9-(p-Bromophenyl)anthracene (VIII). Cyclization of the above ketone (VII) was carried out as in the preparation of *o*-(9-anthryl)benzoic acid (III), except that refluxing was continued for forty hours. The product crystallized from the reaction mixture and was washed with water, m.p. 176–178°; yield 0.4 g. (84%). Repeated recrystallization from ethanol gave long white needles, m.p. 178–179°.

Anal. Calc'd for $C_{20}H_{13}Br$: C, 72.08; H, 3.93.
Found: C, 72.15; H, 3.63.

9-(p-Cyanophenyl)anthracene (IX). One gram of the above halide (VIII) was converted to the nitrile as in the preparation of VI except that heating was continued for sixty-four hours. The entire reaction mixture was subjected to distillation under reduced pressure, and the distillate recrystallized from ethanol, yield 0.4 g. (48%). An analytical sample was prepared by repeated recrystallization from ethanol; white crystals, m.p. 125–126°.

Anal. Calc'd for $C_{21}H_{13}N$: C, 90.30; H, 4.69; N, 5.02.
Found: C, 90.46; H, 5.02; N, 5.13.

p-(9-Anthryl)benzoic acid (X). (a) *By hydrolysis of 9-(p-cyanophenyl)anthracene (IX).* A small sample (50 mg.) of the above nitrile was refluxed for sixty hours in the usual hydrobromic-acetic acid mixture. The product was crystallized from ethanol as pale yellow needles, m.p. 260–261° (with previous sublimation).

(b) *By combined cyclization and hydrolysis of the keto-nitrile (VI).* One gram of 2-benzyl-4′-cyanobenzophenone (VI) was refluxed for seventy hours in the usual hydrobromic-acetic acid mixture. On cooling, there was obtained a nearly quantitative yield of *p*-(9-anthryl)-benzoic acid (X), which was crystallized from ethanol, m.p. 262–264°. This is probably a slightly purer preparation than that obtained in (a). There was no depression of melting points on mixing samples prepared by both methods.

The methyl ester obtained by action of diazomethane was crystallized from ethanol, m.p. 176–177°.

Anal. Calc'd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16.
Found: C, 84.85; H, 5.43.

SUMMARY

para and *ortho*-(9-Anthryl)benzoic acids have been prepared by reactions involving aromatic cyclodehydration. It has been found that the *ortho* isomer may be cyclized to coeranthrone by the use of phosphoric acid.

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