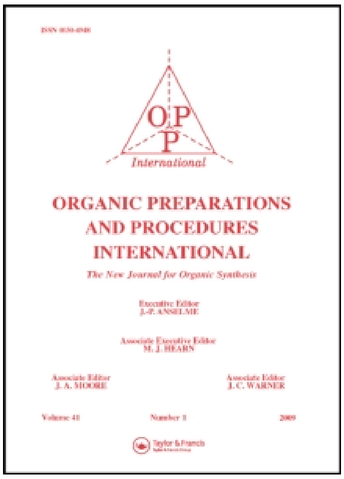

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7-(3- AND 4-CARBOXYPHENYL) BENZ [A] ANTHRACENES AND 9-(3- AND 4-CARBOXYPHENYL) ANTHRACENES

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7-(3- AND 4-CARBOXYPHENYL)BENZ[A]ANTHRACENES

AND

9-(3- AND 4-CARBOXYPHENYL)ANTHRACENES

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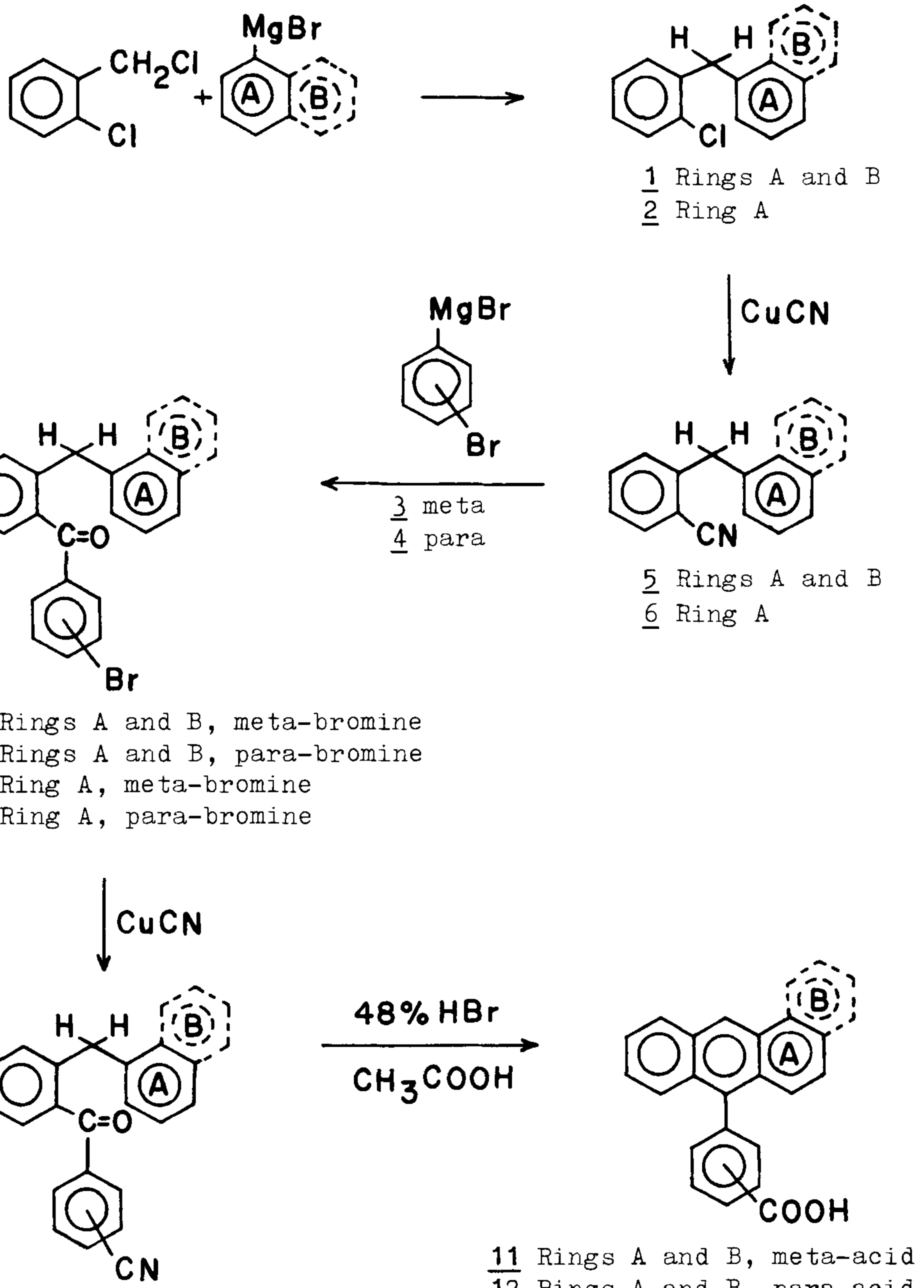
The four carboxylic acids 7-(3-carboxyphenyl)benz[a]anthracene (11), 7-(4-carboxyphenyl)benz[a]anthracene (12), 9-(3-carboxyphenyl)anthracene (13), and 9-(4-carboxyphenyl)anthracene (14), were prepared by the five step procedure illustrated in Chart I. This method, with the exception of the first step, had been successfully used previously to prepare small quantities of 11,[2] 12,[3] and 14[4]. Scaling up the procedures already in the literature created numerous problems with product purity and poor yields, which the experimental procedures described herein alleviated.

CHART I



1 Rings A and B
2 Ring A

5 Rings A and B
6 Ring A

7 Rings A and B, meta-bromine
8 Rings A and B, para-bromine
9 Ring A, meta-bromine
10 Ring A, para-bromine

11 Rings A and B, meta-acid
12 Rings A and B, para-acid
13 Ring A, meta-acid
14 Ring A, para-acid

EXPERIMENTAL

2-(1-Naphthylmethyl)chlorobenzene (1).

A Grignard reagent was prepared, under nitrogen, by the rapid addition of 207 g (1.0 mole) of 1-bromonaphthalene in 600 ml of anhydrous ether to 24.3 g (1.0 mole) of magnesium turnings contained in a 2-l, 3-necked flask, immersed in a water bath, and equipped with a mechanical stirrer, condenser, dropping funnel, and dry nitrogen inlet. After the addition was complete, the mixture was refluxed 1 hr, the ether was then replaced with 400 ml of dry benzene, and when the temperature reached 55°, 129 g (0.80 moles) of o,α-dichlorotoluene in 300 ml of benzene was added over a period of 1 hr. The reaction mixture was refluxed for 12 hrs, allowed to cool to room temperature, and the complex decomposed with 300 ml of 10% hydrochloric acid solution while cooling the reaction flask in an ice bath. The benzene layer was separated, washed three times with 300 ml portions of water, and dried over sodium sulfate. The dried solution was filtered, concentrated and distilled under reduced pressure to yield the product as an impure, yellow viscous oil, b.p. 180-188°/0.7 mm (Lit.[5] 189-192°/2.0 mm). Some α,α'-binaphthyl codistilled with the product. The distillate was dissolved in 75 ml of acetone, cooled overnight in a refrigerator and the crystallized α,α'-binaphthyl removed by vacuum filtration. Concentration of the filtrate give the product as a yellow viscous oil, yield 101 g (50%).

2-Chlorodiphenylmethane (2).

The procedure for the preparation of the phenylmagnesium bromide Grignard reagent was the same as reported above, except that 157 g (1.0 mole) of bromobenzene was used. When the temperature reached 55°, 129 g

(0.8 mole) of o,α-dichlorotoluene was added over a period of 1 hr. The reaction mixture was allowed to reflux for 10 hrs, then cooled, and the complex decomposed with 300 ml of 10% hydrochloric acid solution while cooling the reaction flask in an ice bath. The benzene layer was separated, washed twice with 300 ml portions of water, dried over sodium sulfate, filtered and concentrated. Distillation under reduced pressure afforded the product as a clear oil, b.p. 138-142°/5 mm (Lit.[11] 138-142°/5 mm); yield 124 g (61%).

2-(1-Naphthylmethyl)cyanobenzene (5).

A mixture of 253 g (1.0 mole) of 2-(1-naphthylmethyl)chlorobenzene (1), 134 g (1.5 mole) of cuprous cyanide and a few crystals of anhydrous cupric sulfate in 600 ml of freshly distilled N-methyl-2-pyrrolidone was vigorously refluxed for 48 hrs in a 2-l, 3-necked flask equipped with a mechanical stirrer and a condenser. The resultant black solution was cooled to 100° and transferred to a 5-l, 3-necked flask equipped with a condenser, mechanical stirrer and dropping funnel. A solution of 368 g (7.5 moles) of sodium cyanide in 1500 ml of water was slowly added (exothermic initially), and the mixture was stirred at 100° for 1 hr as the complex was decomposed. The mixture was poured into two 2-l separatory funnels, 200 ml of benzene was added to each, the mixtures were shaken carefully while warm and left overnight as the water and benzene layers slowly separated. An ultraviolet lamp was used to distinguish the benzene and water layers. The benzene layers were separated, the water layers extracted twice more with 100 ml portions of benzene, the benzene layers were combined, washed three times with 200 ml portions of water, and dried over sodium sulfate. The dried solution was filtered, concentrated, and distilled under reduced pressure to afford the product as a viscous yellow oil, b.p. 175-180/0.5 mm (Lit.[5] 216-217/3.0 mm). The oil was dissolved in 75 ml of acetone and cooled overnight. Any α,α'-binaphthyl which was not removed during the purification of 2-(1-naphthylmethyl)chlorobenzene (1) and which codistilled with the product was precipitated and removed by filtration. Concentration of the filtrate gave the product as a viscous yellow oil; yield 190 g (78%).

2-Cyanodiphenylmethane (6).

Using 203 g (1.0 mole) of 2-chlorodiphenylmethane (2) the procedure for the preparation of this compound was exactly the same as the one reported above. Vacuum distillation afforded the product as a light yellow oil, b.p. 160-165°/5 mm (Lit.[11] 160-164°/4 mm); yield 212 g (75%).

2-(1-Naphthylmethyl)-4'-bromobenzophenone (8).

A Grignard reagent was formed by the addition of 176.9 g (0.75 mole) of p-dibromobenzene in 600 ml of dry ether (solid is soluble in warm ether) to 18.2 g (0.75 mole) of magnesium turnings contained in a 2-l, 3-necked flask equipped with a mechanical stirrer, a condenser, dropping funnel and a nitrogen inlet, and the flask immersed in a water bath. After the addition was complete, under a nitrogen atmosphere, the solution was refluxed 1 hr. The ether was then replaced with 400 ml of dry benzene, and when the temperature reached 50°, 121.5 g (0.5 mole) of 2-(1-naphthylmethyl)-cyanobenzene (5) in 100 ml of dry benzene was added over a 1/2 hr period. The solution was refluxed 14 hrs, cooled in an ice bath, and 443 ml of 25% sulfuric acid solution was slowly added (very exothermic initially). The resultant mixture was refluxed for 48 hrs, cooled to room temperature, and transferred to a 2-l separatory funnel. The benzene layer was separated, washed with 200 ml of water, 200 ml of 10% sodium bicarbonate solution, twice with 200 ml portions of water, and dried over sodium sulfate. The dried solution was filtered, concentrated, and vacuum distilled affording the product as an impure pale greenish-yellow viscous oil, b.p. 240-245°/0.4 mm (Lit.[3] 275-278°/2 mm); yield 100 g (50%). This product was used in subsequent reactions with good results without further purification.

2-(1-Naphthylmethyl)-3'-bromobenzophenone (7).

This ketone was prepared analogously to 8 using 118 g (0.5 mole) of m-dibromobenzene to form the Grignard reagent. Vacuum distillation afforded the product as an impure reddish-brown oil, b.p. 195-197°/0.5 mm (Lit.[4] 210-220/1 mm); yield 126 g (71%). This product also was used in subsequent reactions with good results without further purification.

2-Benzyl-3'-bromobenzophenone (9).

This ketone was prepared analogously to 7 using 97 g (0.5 mole) of 2-cyanodiphenylmethane (6). Vacuum distillation afforded the product as an impure greenish-yellow oil, b.p. 193-195°/0.3 mm; yield 109 g (62%). No attempt was made to prepare an analytically pure sample for elemental analysis; however, when this product was used in subsequent reactions without further purification good results were obtained.

2-(1-Naphthylmentyl)-3'-cyanobenzophenone; 2-(1-Naphthylmethyl)-4'-cyanobenzophenone; 2-Benzyl-3'-cyanobenzophenone; 2-Benzyl-4'-cyanobenzophenone.

These four cyano ketones were prepared from the bromo ketones 7, 8, 9, and 10, respectively, by the following procedure. A mixture of 0.5 mole of bromo ketone, 90 g (1.0 mole) of cuprous cyanide and a few crystals of anhydrous cupric sulfate in 700 ml of freshly distilled N-methyl-2-pyrrolidone was refluxed vigorously for 48 hrs in a 2-l, 3-necked flask equipped with a mechanical stirrer and condenser. The reaction mixture was then cooled to 100°, transferred to a 5-l flask equipped with a mechanical stirrer, 245 g (5 mole) of sodium cyanide in 1-l of water was added slowly, and the resultant mixture was stirred at 100° for 1 hr. The mixture was then transferred to two 2-l separatory funnels and each was extracted while warm with 200 ml of benzene. The benzene layers were separated (U.V. lamp used to distinguish the layers), the aqueous layers were extracted twice more with 100 ml portions of benzene, the benzene layers combined and dried over sodium sulfate. The dried solution was filtered and concentrated to give the product as a viscous black oil (an oil was obtained in each case). The oils were isolated in 85-95% crude yields and, in each case, the products were used in subsequent reactions without any purification.

7-(4-Carboxyphenyl)benz[a]anthracene (12).

To a solution containing 104 g (0.3 mole) of 2-(1-naphthylmethyl)-4'-cyanobenzene dissolved in 2-l of refluxing glacial acetic acid in a 5-l flask equipped with a magnetic stirrer, condenser and dropping funnel, was added dropwise 500 ml of 48% hydrobromic acid over a 2 hr period. The resultant solution was refluxed 24 hrs, cooled to room temperature, and the precipitated product was isolated by vacuum filtration. The product was obtained as a light brownish-white powdery solid after one crystallization from toluene-tetrahydrofuran (THF) (8:2); m.p. 280-283°, yield 52 g (50%). This material was dried again and used with excellent results in subsequent reactions without any further purification. An analytical sample was prepared by recrystallizing this material five times from toluene-THF (8:2), m.p. 297-299 (Lit.[3] 298-300°).

Anal. Calc'd for $C_{25}H_{16}O_2$: C, 86.18; H, 4.64.

Found: C, 86.20; H, 4.66.

7-(3-Carboxyphenyl)benz[a]anthracene (11).

To a solution containing 74 g (0.21 mole) of 2-(1-naphthylmethyl)-3'-cyanobenzene dissolved in 1480 ml of refluxing glacial acetic acid contained in a 5-1 flask equipped with a magnetic stirrer and reflux condenser was added dropwise 400 ml of 48% hydrobromic acid over a 2 hr period. The resultant solution was refluxed for 30 hrs, cooled to room temperature, and the precipitated product was isolated by vacuum filtration. The product was washed with water until the washings were neutral to litmus and then dried at 94°/10 mm in a vacuum oven for 7 hrs. The product was obtained as light brown crystals after one crystallization from toluene-THF (8:2); m.p. 267-271, yield 45 g (60%). This material was dried again and used with good results in subsequent reactions without any further purification. An analytical sample was prepared by recrystallizing this material four times from toluene-THF (8:2) and treated once with charcoal; m.p. 274-275° (Lit.[2] 253-254°).

Anal. Calc'd for $C_{25}H_{16}O_2$: C, 86.18; H, 4.64.

Found: C, 86.01; H, 4.59.

9-(4-Carboxyphenyl)anthracene (14).

This compound was prepared analogously to 11 to the point of washing with water until the washings were neutral to litmus. The product was then dried at 75°/10 mm for 8 hr. One crystallization of the product from toluene-THF (7:3) afforded yellow needles, m.p. 259-262°; yield 48 g (65%). This material was dried and used in subsequent reactions without further purification. An analytical sample was prepared by recrystallizing this material twice from toluene-THF (7:3), m.p. 262-264° (Lit.[4] 262-264°).

9-(3-Carboxyphenyl)anthracene (13).

This compound was prepared analogously to 11 to the point of washing with water until the washings were neutral to litmus. The product was then dried at 85°/10 mm for 10 hrs. One crystallization of the product from toluene-THF (7:3) afforded light brown crystals, m.p. 294-297°; yield 47 g (64%). This material was dried and used in subsequent reactions without further purification. An analytical sample was prepared by recrystallizing this material four times from toluene-THF (7:3) and treating once with charcoal to give light yellowish crystals, m.p. 300-302°.

Anal. Calc'd for $C_{21}H_{14}O_2$: C, 84.46; H, 4.74.

Found: C, 84.31; H, 4.61.

REFERENCES

1. a.) Present address: Northeast Louisiana State College, Department of Chemistry, Monroe, Louisiana 71201. b.) To whom inquiries should be sent at VPI.
2. R. H. Kunkel, B. S. Thesis, Virginia Polytechnic Institute, 1958.
3. F. A. Vingiello and R. K. Stevens, J. Am. Chem. Soc., 80, 5256 (1958).
4. C. K. Bradsher and F. A. Vingiello, J. Org. Chem., 13, 786 (1948).
5. C. K. Bradsher, J. Am. Chem. Soc., 62, 1077 (1940).
6. E. Bergman, J. Org. Chem., 4, 1 (1939).
7. F. A. Vingiello, M. O. L. Spangler and J. E. Bondurant, J. Org. Chem., 25, 2091 (1960).
8. C. Koelsch and A. Whitney, J. Org. Chem., 6, 759 (1941).
9. L. Friedman and H. Shechter, J. Org. Chem., 26, 2522 (1962).
10. M. S. Newman and H. Boden, J. Org. Chem., 26, 2525 (1962).
11. C. K. Bradsher, J. Am. Chem. Soc., 62, 486 (1940).

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