[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

SYNTHESES IN THE *PERI*-SUBSTITUTED NAPHTHALENE SERIES[1]

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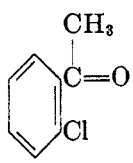
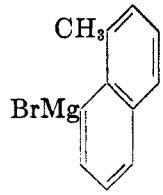
The initial objective of these investigations was synthesis of 1′,9-dimethyl-1,2-benzanthracene. The desirability of obtaining this compound, in order to permit its testing for possible carcinogenic activity, has already been discussed by Fieser and Seligman (1), and these investigators attempted unsuccessfully (1, 2) to accomplish its synthesis. There seems little doubt that the difficulties encountered in these syntheses are associated with the very pronounced steric hindrance between the two methyl groups, and it has become of considerable interest to learn whether the synthesis of the molecule is at all possible. The possibility of such a synthesis is strongly indicated by the work of Newman and collaborators, who have synthesized 4,5-dimethylphenanthrene derivatives. For example, 4,5,8-trimethyl-1-phenanthrylacetic acid was obtained by Newman and Hussey (3), and resolved into an optically active form. This shows that the methyl groups are forced out of the plane of the ring and overlap each other, thus creating an asymmetric molecule. It may be stated, at the outset, that the present work has not resulted in synthesis of the desired 1′,9-dimethyl-1,2-benzanthracene, but a number of the previously encountered difficulties have been overcome, and a study has been made of several highly hindered *peri*-substituted naphthalene derivatives.

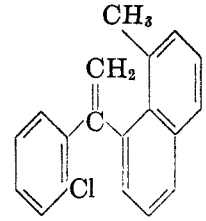
In one of the previous approaches (2) to the above-mentioned synthesis, an attempt was made to obtain the chloroalkene III by way of reaction of *o*-chloroacetophenone (I) with 8-methyl-1-naphthylmagnesium bromide (II) or the analogous lithium reagent. Addition of the Grignard reagent to the carbonyl group, followed by dehydration of the resulting carbinol, would give compound III, but no identifiable product was obtained from this reaction. In view of recent work



I



II



III

on Grignard reactions involving hindered molecules, especially that of Arnold and co-workers (4), it seems probable that ketone I would react entirely as the

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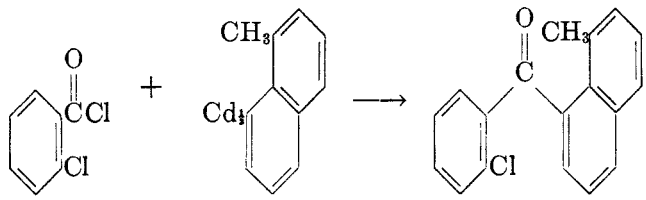
enol with the Grignard reagent II, although *para*-substitution of the 8-methyl-1-naphthyl group might be encountered (5). In the present work, a reaction between *o*-chlorophenylmagnesium bromide and 1-acetylnaphthalene resulted in very little addition to the carbonyl group, and most of the 1-acetylnaphthalene was recovered.

In order to avoid difficulty with the enolization reaction, we proposed to prepare the chloroalkene III by way of reaction of a methyl Grignard or lithium reagent with ketone IV, which has no *alpha* hydrogens. The simplest approach to this ketone appeared to be reaction of *o*-chlorobenzoyl chloride with the 8-



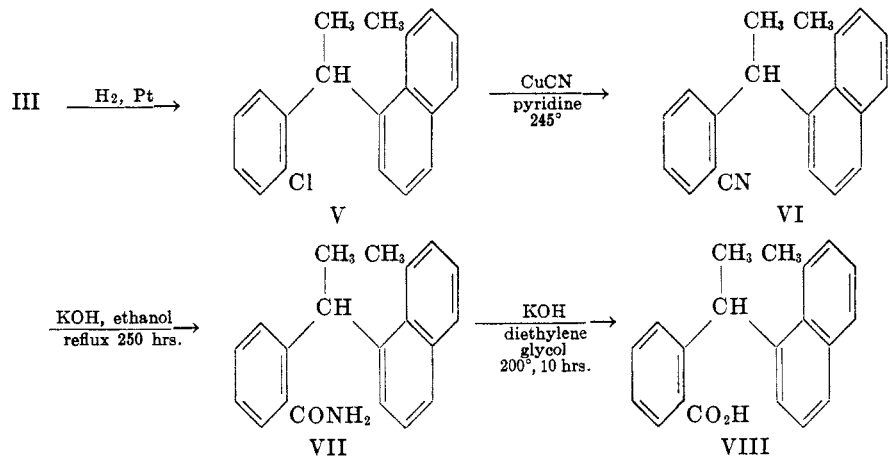
IV

methyl-1-naphthyl cadmium reagent. Since 1-chloro-8-methylnaphthalene seemed less inaccessible than the 1-bromo compound, the chloro compound was used for preparation of the cadmium reagent. This chloronaphthalene was prepared by the previously-described procedure (2), proceeding from 1-nitronaphthalene by way of 1-chloro-8-nitronaphthalene, 1-chloro-8-aminonaphthalene, and 1-chloro-8-bromonaphthalene to the desired 1-chloro-8-methylnaphthalene. Difficulty was experienced with the second step of this sequence, but a reproducible procedure was worked out.

1-Chloro-8-methylnaphthalene was converted to the cadmium reagent by way of the lithium reagent. The chloronaphthalene in dilute ether solution reacted with freshly cut lithium very sluggishly, if at all, but when the solution was concentrated a vigorous reaction set in and proceeded with no further difficulty. Reaction of the cadmium reagent with *o*-chlorobenzoyl chloride proceeded exothermally, but the ketone obtained from the reaction melted at 74.5–105°, and no pure compound could be isolated. Apparently, migration from the hindered 1-position had occurred at some stage of the preparation, presumably during formation or reaction of the lithium reagent. When 1-(*o*-chlorobenzoyl)naphthalene was prepared from *o*-chlorobenzoyl chloride and di-1-naphthylcadmium obtained from 1-chloronaphthalene *via* the lithium reagent, a small amount of migration appears to have occurred. The ketone was not readily purified sufficiently to give the melting point observed when the preparation was from 1-naphthoyl chloride and bis-(*o*-chlorophenyl)cadmium. It seems probable that this migration would not occur, even with the hindered naphthalene derivative, if the Grignard reagent were used, but the preparation of 1-bromo-8-methylnaphthalene appears so tedious that a different approach was adopted. The lithium reagent may be avoided if the carboxyl is shifted to the naphthalene ring and the cadmium reagent prepared from *o*-chlorophenylmagnesium bromide. The prepa-

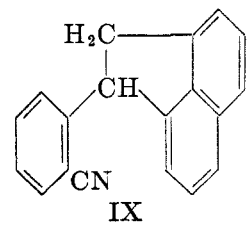
ration of 8-methyl-1-naphthoic acid, required for this alternative synthesis, has been described in the preceding paper (6).

The reaction of 8-methyl-1-naphthoyl chloride with bis-(*o*-chlorophenyl)cadmium gave a 76% yield of distilled ketone IV free from isomers, and crystallization readily yielded material melting at 73.8–74.4°. Although the methyl Grignard reagent reacted very slowly and unsatisfactorily with this ketone, lithiummethyl reacted as rapidly as it was added, and there appeared to be no tendency for a competing reaction with the chlorine. Dehydration of the resultant carbinol and fractionation of the product through a column gave a 69% yield of the chloroalkene, III. Conversion of this chloroalkene to 1-(*o*-carboxyphenyl)-1-(8-methyl-1-naphthyl)ethane (VIII), the acid desired for cyclization experiments, was accomplished by the indicated sequence of reactions.



The first two steps, to yield V and VI, were accomplished without difficulty, following the procedures used previously (7) for a similar compound, except that in the hydrogenation step there was some attack on chlorine. Removal of the chlorine-free by-product was accomplished by fractional distillation.

As indicated in the chart, heating under reflux with alcoholic potassium hydroxide for 250 hours hydrolyzed the nitrile only as far as the amide. None of acid VIII was isolated at this stage. Since it has previously been reported (7) that hydrolysis of *o*-7-(acenaphthyl)benzonitrile (IX) under identical conditions



IX

gives a 69% yield of the corresponding acid, it is apparent that VI is far more hindered than IX. A study of models indicates that this is entirely reasonable.

The presence of the methylene bridge in IX holds all the carbons in one plane except for the benzene portion of the molecule. The phenyl grouping is free to swing into a plane at approximately right angles to the plane of the remainder of the molecule, and this somewhat relieves the crowding around the nitrile grouping. On the other hand, in VI the naphthyl group is free to rotate, and interference between the methyls forces the naphthalene ring into a position of serious interference with the nitrile grouping.

We were unable to convert the amide, VII, to the acid with nitrite, following the improved procedure recently published (8), but high-temperature saponification gave a nearly quantitative conversion to the acid. The latter procedure appears to be the favored method for conversion of highly hindered amides to the acids, in instances where the molecule can withstand alkali at the required temperatures. The course of the reaction is easily followed by titration of the ammonia evolved.

In the low-temperature hydrolysis yielding the amide VII, there was also obtained about 7% yield of an acid which was isomeric, but not identical, with acid VIII. Shorter periods of hydrolysis did not decrease the yield of this acid, and it seems certain that the substance is the isomer of VIII having the carboxyl group in the unhindered *para* position. This isomer would arise from a small amount of *p*-bromochlorobenzene present in the *o*-bromochlorobenzene used as starting material and prepared from technical *o*-chloroaniline. Although intermediates III, IV, and V were crystallized to a constant melting point for analysis, distilled samples were used for subsequent steps in the synthesis. This is no disadvantage since the *p*-isomer is easily removed if the two-stage hydrolysis is used.

All efforts to cyclize acid VIII were unsuccessful, although there were utilized what appear to be the most powerful methods of cyclization known at present. These were anhydrous hydrogen fluoride, zinc chloride and acetic anhydride (9), and the inverse Friedel and Crafts procedure (10). In the first and last procedures, the crude reaction products from the cyclization were reduced with zinc and alkali (11), in hopes that the hydrocarbon would be more easily isolated than the anthrone, but no compound with the properties expected for the desired hydrocarbon could be obtained. The principal products in all instances were insoluble, high molecular weight materials.

A study of models suggests that failure of acid VIII to cyclize is due to the fact that interference between the methyl groups prevents the two aromatic systems from approaching the same plane, thus preventing the carboxyl from coming sufficiently near for reaction with the 2-position in the naphthalene ring system. It is further suggested by a study of models that if 8-methyl-5,6,7,8-tetrahydro-1-naphthoic acid (6) were used as starting material for synthesis of an acid analogous to VIII but containing the tetralin ring system, cyclization should be possible, for the methyl in the angular ring would then be out of the plane of the rest of the molecule. The final step introducing the strain would then be dehydrogenation, and this appears hopeful, for no new carbon-carbon bonds would be established. This latter procedure will be explored in this laboratory as soon as

there has been developed a procedure suitable for supplying 8-methyl-5,6,7,8-tetrahydro-1-naphthoic acid in sufficient quantity.

Before 8-methyl-1-naphthoic acid was used in the preparations just described, model experiments were carried out starting with 1-naphthoic acid. In this work there were prepared the chloroketone, chloroalkene, and chloroalkane differing from III, IV, and V by lacking the methyl group in the 8-position in the naphthalene ring. There was also prepared 1-acetyl-8-methylnaphthalene by reaction between 8-methyl-1-naphthoyl chloride and dimethylcadmium.

EXPERIMENTAL

All melting points are corrected, and all boiling points are uncorrected. Analyses are by the Microanalytical Division of the Department of Chemistry of the University of California.

1-Chloro-8-nitronaphthalene.[3] 1-Nitronaphthalene was chlorinated as has been previously described (2), but direct crystallization of the product separating from the chlorination mixture gave the reported yield (36%) of 1-chloro-8-nitronaphthalene only after prolonged systematic crystallization. If the precipitate was first fractionated through a 65-cm. Vigreux column and the fraction boiling above 170° (1–2 mm.) used for recrystallization, a yield of 25–30% was readily obtained. Material melting at 91° or higher was used for reduction. For the best sample, m.p. 94.0–94.6°.

1-Chloro-8-aminonaphthalene.[3] The previously-reported procedure (12) for the preparation of this compound seems not sufficiently detailed to permit reproducible results. The following procedure consistently gave very little recovered starting material or reductive removal of chlorine.

A mixture of 60 g. of 1-chloro-8-nitronaphthalene, 48.4 g. of iron powder reduced with hydrogen, and 80 ml. of water was stirred vigorously with a Hershberg stirrer and heated under reflux for eight hours, the flask being immersed in a steam-bath or boiling-water bath. At the beginning of the reduction 4 ml. of concentrated hydrochloric acid was added, and during the reduction an additional 8 ml. of acid was added in 2-ml. portions. The cooled reaction mixture was treated with 20 ml. of concentrated aqueous ammonium hydroxide, then the total precipitate was extracted with portions of boiling ethanol until dilution of the extract with water gave no precipitate. The ethanol filtrates were concentrated and diluted with water, and the precipitated amine was dissolved in a boiling mixture of 290 ml. of 1 *N* hydrochloric acid and 900 ml. of water. After removal of a small amount of insoluble oil (unreduced nitro compound), addition of ammonium hydroxide precipitated 44.0 g. of amine, m.p. 74–80°. Systematic crystallization from ethanol yielded 33 g. (64%) of amine melting at 92° or above, and suitable for use in the next step. The best sample melted at 93.5–94.7°. This yield of purified amine is below previous reports (2, 12).

1-Chloro-8-bromonaphthalene.[3]. A hot mixture of 69.0 g. of 1-chloro-8-aminonaphthalene and 140 ml. of 48% hydrobromic acid was rapidly chilled to 0° with stirring and diazotized at this temperature by the addition of a cold solution of 30 g. of sodium nitrite in 175 ml. of water. After addition was complete the mixture was stirred 40 minutes at the same temperature, then 48 g. of urea was added and stirring continued for 20 minutes. The diazonium solution was added in one portion to 67 g. of cuprous bromide dissolved in 640 ml. of 48% hydrobromic acid cooled to 0°. After stirring for 15 minutes at 0° and an additional 15 minutes after removal of the cooling-bath, the mixture was heated on a steam-bath. The reaction mixture was diluted with 500 ml. of water, the precipitate removed by filtration, and the aqueous solution extracted with benzene. The precipitate was added to the benzene

[3] In this preparation, the authors were assisted by Mr. Charles F. Allen.

extract, and after filtration of a little insoluble material, the benzene solution was washed with sodium carbonate solution, water, concentrated sulfuric acid, water, and sodium bicarbonate solution. Removal of solvent and distillation from a Claisen flask yielded 70.3 g. (75%) of a light yellow product, b.p. 150–160° (5–6 mm.). Crystallization from 300 ml. of ethanol yielded 57.8 g. (62%) of colorless plates, m.p. 93.0–95.0°. Only small amounts of satisfactory material could be obtained by systematic working of material obtained from the filtrate. The best sample of 1-chloro-8-bromonaphthalene melted at 94.6–96.6° [literature: 96.5–97° (2), 94–95° (13)].

The somewhat different procedure previously used (2) for this preparation gave only a 49% yield of distilled product.

1-Chloro-8-methylnaphthalene was prepared by reaction of 8-chloro-1-naphthylmagnesium bromide with methyl sulfate essentially as has been described (2), except that the product was distilled through a 65-cm. Podbielniak type column to give 52% yield of a product of b.p. 134–136° (10 mm.), m.p. 67.2–70.3°, and suitable for use in the subsequent synthesis. Fieser and Seligman (2) reported a 60% yield of distilled product, which melted at 68–69° after recrystallization.

Reaction of bis-(8-methyl-1-naphthyl)cadmium with o-chlorobenzoyl chloride was carried out essentially as described below for the preparation of 1-(*o*-chlorobenzoyl)naphthalene, procedure B. Distillation of the products through a 65-cm. Podbielniak type column yielded 8.7 g. of an oil, b.p. 102–140° (10.5 mm.), 0.8 g. of intermediate, and 4.4 g. (32%) of a viscous oil, b.p. 195–205° (2 mm.). The latter fraction solidified slowly on standing, and crystallization from hexane gave 1.5 g. of fine needles, m.p. 74.5–105°. This material was not further investigated.

1-(o-Chlorobenzoyl)-8-methylnaphthalene (IV). A Grignard reagent was prepared from 0.12 mole of *o*-bromochlorobenzene and 0.12 mole of magnesium in 60 ml. of ether, and this was converted to the cadmium reagent with 0.066 mole of anhydrous cadmium chloride in the usual manner (14). After distillation of ether and addition of 100 ml. of benzene, there was added during 10 minutes, in 50 ml. of benzene, the acid chloride prepared from 0.04 mole of 8-methyl-1-naphthoic acid (6) and 2 mole-equivalents of thionyl chloride. During the addition, the temperature of the reaction mixture rose from 28 to 45°. The mixture was stirred for 4 hours at 40–45°, then worked up in the usual manner (14), and the product was distilled from a Claisen flask to yield 8.2 g. (76%) of ketone IV, b.p. 165–195° (2 mm.).

This material was used for further synthesis, but a crystalline sample could not be obtained until a sample was distilled through the 65-cm. Podbielniak type column. From 8.2 g. obtained as above there resulted 6.5 g. of material, b.p. 195–200° (3 mm.), which slowly crystallized on standing. One crystallization from hexane yielded material of m.p. 73.8–74.4°, not altered by further crystallization.

Anal. Calc'd for $C_{18}H_{13}ClO$: C, 77.01; H, 4.67; Cl, 12.63.

Found: C, 76.90; H, 4.79; Cl, 12.85.

1-(o-Chlorophenyl)-1-(8-methyl-1-naphthyl)ethene (III). To a solution of 11.1 g. (0.04 mole) of ketone IV in 50 ml. of ether, in an atmosphere of nitrogen, there was added, with stirring during 15 minutes, 40 ml. of approximately 0.9 *N* methyllithium in ether. The reaction caused gentle refluxing, and after stirring 15 minutes the Gilman test was negative. After addition of an additional 20 ml. of the methyllithium solution and continued stirring under reflux, the Gilman test was positive after 20 minutes. The reaction mixture was decomposed by the addition of 10 ml. of saturated aqueous ammonium chloride. Removal of ether left a red oil which was heated under reflux for one hour with 70 ml. of glacial acetic acid, to effect dehydration of the carbinol which is the reaction product. The acetic acid solution was diluted with water, the product was extracted with benzene, and after removal of benzene the ethylene III was distilled from a Claisen flask, b.p. 180–195° (2.5 mm.), wt. 10.2 g. Since this material could not be hydrogenated, it was distilled through the 65-cm. Podbielniak type column to yield 7.1 g. (69%) of a pale yellow oil, b.p. 187–192° (2 mm.), which soon began to crystallize. This material was hydrogenated at once as described below.

For analysis, a sample was crystallized from acetic acid and obtained as small, colorless cubes, m.p. 81.0–81.6°.

Anal. Calc'd for $C_{19}H_{15}Cl$: C, 81.86; H, 5.42.
Found: C, 81.85; H, 5.51.

1-(o-Chlorophenyl)-1-(8-methyl-1-naphthyl)ethane (V). A solution of 7.1 g. of freshly distilled ethylene III in 85 ml. of glacial acetic acid and 15 ml. of anhydrous ether was hydrogenated at room temperature and atmospheric pressure in the presence of 0.2 g. of commercial platinum oxide catalyst. After absorption of one mole-equivalent of hydrogen (10 hours) the reaction was interrupted, and after filtration and distillation of solvent the residual oil was fractionated through the 65-cm. Podbielniak type column. There was a forerun of 1.5 g., distilling principally at 160–170° (2 mm.), and the product (V) was collected at 185–190° (2 mm.), wt. 5.4 g. (75%). This distilled sample was used for the next step, but for analysis a sample was crystallized twice from methanol to yield colorless blades of m.p. 63.4–65.0°.

Anal. Calc'd for $C_{19}H_{17}Cl$: C, 81.27; H, 6.10.
Found: C, 81.29; H, 5.71.

1-(o-Cyanophenyl)-1-(8-methyl-1-naphthyl)ethane (VI). A mixture of 4.7 g. of ethane V, 1.5 g. of cuprous cyanide (dried in a vacuum at 100°), 0.4 ml. of acetonitrile (distilled from phosphorus pentoxide), and 4 ml. of pyridine (distilled from barium oxide) was heated in a sealed tube at 242–246° for 28 hours. The reaction mixture was shaken out with benzene and a 3% aqueous solution of sodium cyanide, some insoluble tar being removed by suction filtration. The benzene layer was washed with dilute hydrochloric acid, sodium bicarbonate solution, and water, then distilled from a Claisen flask to yield 3.1 g. (68%) of a yellow oil, b.p. 180–200° (2.5 mm.). Since this product was not obtained crystalline, it was not further characterized except by conversion to the amide, VII.

1-(o-Amidophenyl)-1-(8-methyl-1-naphthyl)ethane (VII). The distilled nitrile VI (3.1 g.) was hydrolyzed by heating under reflux in a steel flask for 250 hours with a solution of 18.2 g. of potassium hydroxide in 120 ml. of ethanol and 70 ml. of water. Solid present in the reaction mixture was filtered, and the filtrate was diluted with water and extracted with benzene. The solid and residue from distillation of most of the benzene was crystallized (charcoal) from hexane to yield 0.91 g. (28%) of colorless needles, m.p. 197–199°. The yield of amide under different hydrolytic conditions was not improved, and the low yield is ascribed in part to the accumulation of impurities in the distilled samples of III and V used for the synthesis.

For analysis there was used a sample of m.p. 203.5–203.9°, obtained by one additional crystallization.

Anal. Calc'd for $C_{20}H_{19}NO$: C, 83.01; H, 6.62.
Found: C, 83.36; H, 6.43.

The alkaline solution remaining after extraction of the above amide was acidified to yield 0.33 g. of acidic material. After two crystallizations (charcoal) from benzene-hexane (1:2), there was obtained 0.14 g. of nearly colorless needles, m.p. 183.4–185.6°. Since the composition of this acid is the same as that of VIII, but a mixture of the two gives a depressed m.p., this acid is *1-(p-carboxyphenyl)-1-(8-methyl-1-naphtyhl)ethane.*

Anal. Calc'd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25.
Found: C, 82.56; H, 6.25.

1-(o-Carboxyphenyl)-1-(8-methyl-1-naphthyl)ethane (VIII). In a steel vessel there was heated under reflux at a bath temperature of 190–200° a mixture of 393 mg. of amide VII, 3.0 g. of potassium hydroxide, and 20 ml. of diethylene glycol. The vessel was swept out with a slow stream of nitrogen which was bubbled through boric acid solution, and evolution of ammonia was followed by titration as has been previously described (15). After 80% of the theoretical amount of ammonia had been evolved (usually 8–10 hours), the cooled reaction mixture was diluted with 150 ml. of water and 52 mg. of unsaponified amide was filtered. Acidification of the clear alkaline filtrate precipitated 320 mg., (94%, based on amide consumed) of acid VIII, m.p. 179.0–181.4°. This m.p. was not altered by recrystallization from benzene-hexane, and a sample immersed in a bath at 180.5° melted completely; thus polymorphism is indicated.

Anal. Calc'd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25.
Found: C, 82.38; H, 6.37.

Attempts at cyclization of acid VIII. A. With acetic anhydride and zinc chloride. Following the method of Fieser and Hershberg (9), a mixture of 50 mg. of VIII, 0.3 ml. of glacial acetic acid, 0.25 ml. of acetic anhydride, and a trace of anhydrous zinc chloride was heated under reflux for two hours, then diluted with water. The sticky precipitate was dissolved in ether, and extracted with aqueous carbonate but no acidic material was recovered. No crystalline material could be isolated from this substance, so it was reduced with zinc and alkali according to Martin (11), a procedure frequently used (7) for reduction of an anthrone to an anthracene.

No acidic material was recovered after the reduction. On chromatography on activated alumina, the tower retained a narrow red band and a broad yellow band, while a substance giving a blue fluorescence in ultraviolet light passed rapidly through the tower. The green-yellow oil remaining after evaporation of the eluate was insoluble in 15 ml. of hot ethanol, and gave no sublimate at 2 mm. pressure and a bath temperature of 200°. Apparently, cyclization to higher molecular weight substances had occurred.

B. With anhydrous hydrogen fluoride (16). A mixture of 88 mg. of acid VIII and 5 ml. of anhydrous hydrogen fluoride was allowed to stand for 2.5 hours, then poured on ice. The crude reaction product, which contained no carbonate-soluble material, was reduced with zinc and alkali, and the product was worked up as described above. The yellow band was washed out of the column to yield 11 mg. of non-fluorescent material, while the fluorescent eluate yielded 40 mg. of oil. The latter fraction did not sublime at 200° and 2 mm., and the sublimate collected at 220° and 1.5 mm. was an insoluble, noncrystalline material.

C. Inverse Friedel and Crafts procedure. A 185-mg. sample of acid was cyclized according to the procedure of Johnson and Glenn (10), and the crude cyclization product was reduced with zinc and alkali. After chromatography, the fluorescent eluate yielded 45 mg. of material similar to that encountered in the other procedures, and elution of the large yellow zone yielded 165 mg. of orange oil. The latter fraction, at 170° and 1.5 mm., gave 145 mg. of sublimate which after precipitation from alcohol melted at 45–50° and gave an analysis indicating the presence of oxygen in the molecule. The behavior and weight of material recovered indicates reaction with the benzene solvent although this was never observed by Johnson and Glenn.

1-Acetyl-8-methylnaphthalene. A cadmium reaction was carried out as described for preparation of IV, starting with 0.02 mole of 8-methyl-1-naphthoic acid and the methylmagnesium bromide prepared from 0.025 mole of magnesium. The reaction product was saponified with alcoholic potassium hydroxide in order to remove any methyl 8-methyl-1-naphthoate formed as a by-product in the cadmium reaction (14), but no acidic material was recovered. Distillation of the neutral product from a Claisen flask yielded 2.8 g. (76%) of a yellow oil which slowly crystallized, m.p. 40.0–43.0°. Crystallization from methanol-water (5:2) gave small colorless plates, m.p. 47.9–48.9°.

Anal. Calc'd for $C_{13}H_{12}O$: C, 84.75; H, 6.57.
Found: C, 84.69; H, 6.59.

The *picrate* crystallized from ethanol as yellow needles, m.p. 84.0–84.4°.

Anal. Calc'd for $C_{19}H_{15}N_3O_8$: C, 55.21; H, 3.66.
Found: C, 55.02; H, 3.62.

1-(o-Chlorobenzoyl)naphthalene. A. A cadmium reaction was carried out as described for preparation of IV, starting with 0.33 mole of 1-naphthoic acid and the Grignard reagent from 1 mole of magnesium and 1.1 mole of *o*-bromochlorobenzene. Distillation from a Claisen flask yielded 57.4 g. (65%) of a yellow oil, b.p. 195–203° (1.5 mm.). After standing several days, crystallization set in, and a sample crystallized three times from hexane melted at 83.4–83.9°.

Anal. Calc'd for $C_{17}H_{11}ClO$: Cl, 13.30. Found: Cl, 13.58.

B. A total of 8.1 g. (0.05 mole) of 1-chloronaphthalene (b.p. 115.2–115.8° at 10 mm.) was converted to the lithium derivative with 0.8 g. (0.11 mole) of lithium cut from lithium

wire into very small pieces, in an atmosphere of nitrogen. Initially, a mixture of 50 ml. of ether, 0.2 g. of lithium, and 5 ml. of a 10% solution of 1-chloronaphthalene in ether was heated under reflux for 30 minutes, without any evidence of reaction. Since Vesely and Stursa (17) had prepared this lithium derivative in rather concentrated ether solution, ether was distilled until a volume of about 25 ml. remained, whereupon a reaction set in immediately as evidenced by red spots on the lithium and a deep red solution. Addition of 25 ml. of ether stopped reaction essentially completely, and reduction of volume again gave a vigorous reaction. The remainder of the chloronaphthalene, diluted with an equal volume of ether, was added during about three hours, the lithium was added in 0.2-g. lots at one-hour intervals, and finally the mixture was stirred under reflux for an additional two hours. To the cooled reaction mixture, containing a small amount of lithium, was added 5.1 g. (0.028 mole) of anhydrous cadmium chloride. After heating under reflux for 25 minutes the Gilman test was positive, so an additional 1.0 g. of cadmium chloride was added, but the Gilman test was positive after heating for an additional 90 minutes. After adding 100 ml. of ether and 1.0 g. of additional cadmium chloride, followed by 90 minutes heating, the Gilman test was negative. Such a procedure seems necessary to obtain a negative Gilman test; initial addition of 7 g. of cadmium chloride is no advantage.

Ether solvent was replaced with benzene, and reaction with *o*-chlorobenzoyl chloride was carried out essentially as described for the preparation of IV. Distillation of the product through the 65-cm. Podbielniak type column gave 7.4 g. (55%) of product, b.p. 198–205° (2.5 mm.). After one crystallization from hexane, the m.p. was 75.5–77.5°, and the mixture with a sample of m.p. 80.4–82.4°, obtained by Procedure A after one crystallization, melted at 77.5–80.5°.

1-(o-Chlorophenyl)-1-(1-naphthyl)ethene. In the manner described for the preparation of ethylene III, a reaction was carried out between methyllithium and 1-(*o*-chlorobenzoyl)naphthalene, and the resultant carbinol was dehydrated by heating with acetic acid. Distillation of the alkene through the 65-cm. Podbielniak type column gave a 55% yield of a viscous, pale yellow oil, b.p. 168–170° (1.5 mm.). This substance was not obtained in a crystalline condition.

Anal. Calc'd for $C_{18}H_{13}Cl$: C, 81.66; H, 4.95; Cl, 13.39.
Found: C, 81.82; H, 5.03; Cl, 13.11.

1-(o-Chlorophenyl)-1-(1-naphthyl)ethane. A solution of 7.3 g. of freshly distilled alkene (described above) in 45 ml. of glacial acetic acid was hydrogenated at atmospheric pressure and room temperature in the presence of 0.2 g. of commercial platinum oxide catalyst. After absorption of 0.67 mole-equivalent of hydrogen in 23 hours hydrogenation had ceased, and was completed in an additional 2 hours after an additional 0.2 g. of catalyst was added. Distillation of the product through the 65-cm. Podbielniak type column gave 6.6 g. (89%) of a colorless oil, b.p. 167–169° (1.7 mm.). This oil had become only partly crystalline after standing several months.

Anal. Calc'd for $C_{18}H_{15}Cl$: Cl, 13.29. Found: Cl, 13.32.

SUMMARY

In the course of syntheses leading to the preparation of 1-(*o*-carboxyphenyl)-1-(8-methyl-1-naphthyl)ethane, several hindered *peri*-substituted naphthalene derivatives have been prepared. All attempts to convert the above acid to 1′,9-dimethyl-1,2-benzanthracene were unsuccessful.

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