Anal. Calcd. for $C_{14}H_6O_4Br_4$: Br, 57.3. Found: Br, 57.4.

Racemization Experiments.—A sample of *l*-4,6,4′,6′-tetrachlorodiphenic acid having $[\alpha]D$ −129° (in chloroform) was refluxed in a 1 *N* sodium hydroxide solution for six hours. It was recovered by acidification and dried. It then showed $[\alpha]D$ −126°. The decrease is probably not significant.

A sample of *d*-4,6,4′,6′-tetrabromodiphenic acid having $[\alpha]D$ +6.7° (in alcohol) was dissolved in a 1 *N* sodium hydroxide solution and kept at 80° for five days. It was recovered by acidification and had the same rotation.

Summary

1. The biaryl synthesis involving the action of reducing agents on aqueous solutions of diazotized amines has been applied to the synthesis of resolvable diphenic acids. The method constitutes a rapid and direct synthesis of these substances.

2. *d,l*-4,6,4′,6′-Tetrachlorodiphenic acid and the analogous tetrabromodiphenic acid have been prepared by this method in one step from the appropriate 3,5-dihalogeno-2-aminobenzoic acids. Net yields obtained were 61 and 53%, respectively. The acids were resolved into their active forms by means of brucine.

DURHAM, N. H. RECEIVED APRIL 24, 1940

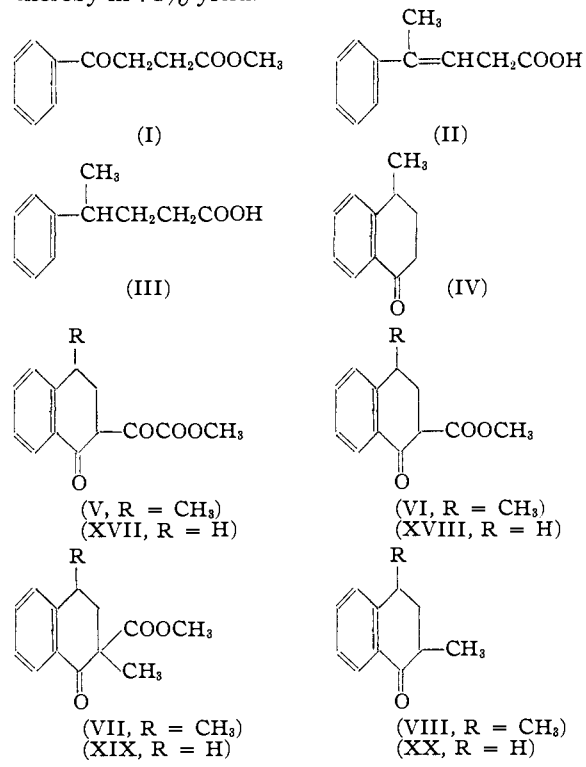
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Polymethyl Aromatic Hydrocarbons. I. Synthesis of 1,2,4-Trimethylnaphthalene and 1,2-, 1,3- and 1,4-Dimethylnaphthalene

BY M. C. KLOETZEL

Research now in progress required the preparation of certain di- and tri-methylnaphthalenes in sizable quantity and free from isomers. Herein is described the synthesis of 1,2,4-trimethylnaphthalene (XVI) and 1,2-, 1,3- and 1,4-dimethylnaphthalene by new methods which fulfil these requirements.

The readily available β-benzoylpropionic acid was utilized as the starting material for the preparation of 4-methyl-1-tetralone (IV) and from this cyclic ketone in turn were synthesized 1,3- and 1,4-dimethylnaphthalene and 1,2,4-trimethylnaphthalene (XVI). When methyl β-benzoylpropionate (I) was treated with methylmagnesium iodide 4-phenylpenten-3-oic acid (II) was produced. This acid has been prepared previously by Mayer and Stamm[1] but in only 26% yield. It was therefore of primary importance that this step in the synthetic scheme be improved. Consistent 70–75% yields of 4-phenylpenten-3-oic acid (II) finally were afforded by means of strict adherence to certain precautions, notably the use of 1.38 moles of methylmagnesium iodide per mole of methyl β-benzoylpropionate, and maintenance of the reaction temperature near 0° during addition of the Grignard reagent. An acetic acid solution of (II) rapidly absorbed hydrogen in the presence of Adams catalyst to give a quantitative yield of 4-phenylpentanoic acid (III). Inasmuch as the cyclization of 4-phenylpentanoyl chloride with aluminum chloride has been reported[1,2] to give (IV) in yields of 70–75%, the simpler direct cyclization of the acid (III) with 80% sulfuric acid was employed and the desired cyclic ketone (IV) was obtained thereby in 74% yield.



(1) Mayer and Stamm, *Ber.*, **56**, 1424 (1923).

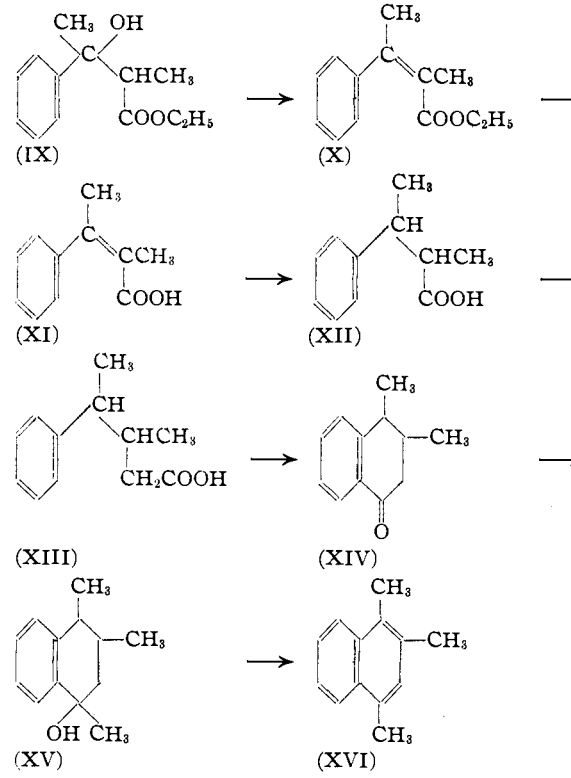
(2) Von Braun and Stuckenschmidt, *ibid.*, **56**, 1724 (1923).

1,4-Dimethylnaphthalene was prepared readily in 90% over-all yield from 4-methyl-1-tetralone (IV) by treatment of the cyclic ketone with methylmagnesium iodide, followed by dehydration of the resulting tertiary carbinol with anhydrous formic acid and subsequent catalytic dehydrogenation of the 1,4-dimethyl-1,2-dihydronaphthalene.

The excellent method used by Bachmann and Thomas[3] to prepare 2-methyl-2-carbomethoxy-1-tetralone (XIX) was applied to the preparation of 2,4-dimethyl-2-carbomethoxy-1-tetralone (VII) with great success. This method is illustrated by formulas (IV) to (VII). Yields were in excess of 95% throughout this series of reactions. Hydrolysis of the ester (VII) with dilute alkali and decarboxylation of the resulting acid afforded a 97% yield of 2,4-dimethyl-1-tetralone (VIII).

Reduction of the cyclic ketone (VIII) by the Clemmensen method yielded the expected 1,3-dimethyltetralin, which was successfully dehydrogenated both with sulfur and catalytically over palladium–charcoal; dehydrogenation with sulfur was found to give superior yields of 1,3-dimethylnaphthalene. Previous descriptions of this hydrocarbon show some discrepancies. Vesely and Stursa[4] give 88–89° as the melting point of 1,3-dimethylnaphthalene picrate while Barnett and Sanders[5] report 118°; our observation of m. p. 117–118° for this picrate is in good agreement with the latter authors.

1,2,4-Trimethylnaphthalene (XVI) was prepared from 2,4-dimethyl-1-tetralone (VIII) in practically quantitative over-all yield by reactions similar to those described for the preparation of 1,4-dimethylnaphthalene from 4-methyl-1-tetralone. In addition it seemed advisable to prepare 1,2,4-trimethylnaphthalene by a second method for comparison. The synthetic scheme which was employed (IX → XVI) is in some respects similar to that of Ruzicka and Ehmann[6] but contains numerous modifications of our own. The hydroxy ester (IX), which was prepared from acetophenone and ethyl α-bromopropionate by means of a Reformatsky reaction, was dehydrated by heating it with potassium bisulfate, and the α,β-dimethylcinnamic acid (XI) which resulted from subsequent hydrolysis of the unsaturated ester (X) was hydrogenated catalytically to give 2-methyl-3-phenyl-*n*-butyric acid (XII). The method of Arndt and Eistert[7] was then employed to lengthen the acid chain by one carbon atom. The acid chloride of (XII) reacted with diazomethane to give a liquid diazoketone which was converted to the acid (XIII) by warming it with silver oxide in a solution of sodium thiosulfate. Ring closure was then effected in the usual manner with 80% sulfuric acid to give the desired 3,4-dimethyl-1-tetralone (XIV). By treatment of this cyclic ketone (XIV) with methylmagnesium iodide there was obtained the tertiary carbinol (XV) which was dehydrated and dehydrogenated with sulfur to give (XVI). While this second synthetic method (IX → XVI) is not adapted to the preparation of large quantities of 1,2,4-trimethylnaphthalene as is the previously described method (involving the steps I → VIII), it nevertheless gave a sample suitable for comparison, and the hydrocarbons prepared by the two methods were identical in every respect.



1,2-Dimethylnaphthalene was prepared from 1-tetralone by means of a series of reactions (XVII → XX) similar to those already described for the synthesis of 1,2,4-trimethylnaphthalene. 2-Methyl-2-carbomethoxy-1-tetralone (XIX) was

(3) Prof. Bachmann and Dr. Thomas kindly furnished details of their procedure before publication of their paper. See also Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 825 (1940).

(4) Vesely and Stursa, *Chem. Zentr.*, **104, I**, 3079 (1933).

(5) Barnett and Sanders, *J. Chem. Soc.*, 434 (1933).

(6) Ruzicka and Ehmann, *Helv. Chim. Acta*, **15**, 145 (1932).

(7) Arndt and Eistert, *Ber.*, **68**, 200 (1935).

prepared by the method of Bachmann and Thomas[3] and was hydrolyzed with dilute alkali to give 2-methyl-1-tetralone (XX) in 95% yield. In this instance likewise, treatment of the cyclic ketone with methylmagnesium iodide followed by dehydration of the tertiary carbinol and subsequent catalytic dehydrogenation resulted in a 95% over-all yield of 1,2-dimethylnaphthalene.

The reactions used in these syntheses appear to be of general applicability and are being extended to the synthesis of other methylnaphthalenes as well as methyl derivatives of the anthracene, phenanthrene and acenaphthene series.

Experimental

Methyl β-Benzoylpropionate (I).—A solution of 47.5 g. of β-benzoylpropionic acid in 75 cc. of anhydrous methanol containing 4.5 cc. of concentrated sulfuric acid was refluxed for five hours on a steam-bath; most of the methanol was then distilled off, water was added and the ester was extracted with ether. The ester distilled at 132° (0.4 mm.[8]); yield, 45.7 g. (89%). The **semicarbazone** crystallized from 95% ethanol in colorless needles, m. p. 138–139°.

Anal. Calcd. for $C_{12}H_{15}O_3N_3$: N, 16.8. Found: N, 16.6.

4-Phenylpenten-3-oic Acid (II).—To an ice-cold solution of 19.2 g. of methyl β-benzoylpropionate (0.1 mole) in 100 cc. of ether was added dropwise and with continuous swirling the Grignard reagent (0.138 mole) prepared from 3.36 g. of magnesium, 19.6 g. of methyl iodide and 65 cc. of ether. Each drop of the Grignard reagent reacted vigorously with the ester causing immediate separation of a colorless precipitate, and care was taken to keep the reaction mixture near 0° during the addition. The mixture was kept ice-cold for thirty minutes after complete addition of the Grignard reagent; it was then allowed to warm up to 25° over a period of thirty minutes and was finally heated on a water-bath at 55–60° for three hours. During the period of heating the precipitate was converted to a viscous semi-solid mass. The entire mixture was hydrolyzed with ice and dilute hydrochloric acid and the red ether layer was washed with water and extracted several times with dilute aqueous sodium carbonate. Boiling with charcoal removed all the color from the combined alkaline solution and the colorless **4-phenylpenten-3-oic acid** was precipitated by adding dilute hydrochloric acid to the mechanically-stirred alkaline solution cooled in an ice-bath; yield, 13.2 g. (75%); m. p. 74–76° (Mayer and Stamm[1] reported 75–78°). The product obtained in this manner is sufficiently pure to be used in the next step.

The preparation of this unsaturated acid (II) was attempted by adding one, one and one-quarter, one and one-half, two, and finally two and one-half moles of methylmagnesium iodide to one mole of methyl β-benzoylpropionate in the described manner: the yields of 4-phenylpenten-3-oic acid were 27, 69, 69, 63, and 43%, respectively. Continued heating beyond the three-hour period caused no increase in yield.

(8) Kugel, *Ann.*, **299**, 62 (1898).

4-Phenylpentanoic Acid (III).—When a solution of 96.5 g. of 4-phenylpenten-3-oic acid in 250 cc. of glacial acetic acid containing 500 mg. of Adams catalyst was shaken with hydrogen at approximately 8 lb. (0.5 atm.) pressure the requisite volume of hydrogen for one double bond was absorbed within two hours. After removal of the acetic acid under reduced pressure 95.5 g. (98%) of **4-phenylpentanoic acid** distilled as a colorless liquid at 165–166° (12 mm.) or at 138° (0.4 mm.); v. Braun and Stuckenschmidt[2] who prepared this acid by hydrolysis of the corresponding nitrile reported b. p. 165° (12 mm.), and Mayer and Stamm[1] reported a b. p. of 169–170° (14 mm.) for the acid obtained by hydrogenation of the sodium salt of 4-phenylpenten-3-oic acid.

4-Methyl-1-tetralone (IV).—When 95.5 g. of 4-phenylpentanoic acid was heated on a steam-bath for two hours with 488 cc. of 80% sulfuric acid there was obtained a clear brown-orange solution. The cooled solution was poured into 1600 cc. of water and the ketone was extracted with ether; most of the yellow color was removed from the ethereal extract by shaking it with dilute sodium hydroxide. **4-Methyl-1-tetralone** distilled as a colorless liquid at 110–111° (1 mm.); yield, 63.5 g. (74%); **semicarbazone**, m. p. 209–211°. Mayer and Stamm[1] reported 210° as the m. p. of this semicarbazone and v. Braun and Stuckenschmidt[2] reported 204°.

Synthesis of 1,4-Dimethylnaphthalene.—To the ice-cold Grignard reagent prepared from 37.2 g. of methyl iodide, 6.36 g. of magnesium and 100 cc. of ether was added a solution of 20.9 g. of 4-methyl-1-tetralone in 75 cc. of ether. The reaction mixture was refluxed for one hour and then hydrolyzed with ice and ammonium chloride. Spontaneous evaporation of the ether layer at room temperature left behind a quantitative yield (23.7 g.) of colorless, crystalline **1,4-dimethyl-1-tetralol.** The carbinol is very soluble in ether but may be crystallized readily from 30–60° petroleum ether, from which it separates in hexagonal prisms; m. p. 82–82.5°.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.8; H, 9.1. Found: C, 81.5; H, 9.1.

When 23 g. of the crude, finely-pulverized tertiary carbinol was dissolved in 78 cc. of anhydrous formic acid a rapid dehydration took place and within one minute **1,4-dimethyl-1,2-dihydronaphthalene** began to separate as an oil. Reaction was completed by allowing the mixture to stand at 25° for two hours, after which the mixture was diluted with 400 cc. of water. The mixture was extracted with ether and the extract was washed with aqueous sodium bicarbonate to remove formic acid. 1,4-Dimethyl-1,2-dihydronaphthalene was obtained as a colorless oil boiling at 87–88° (0.8 mm.); yield, 18.9 g. (92%).

1,4-Dimethylnaphthalene was obtained readily when 18.5 g. of 1,4-dimethyl-1,2-dihydronaphthalene was heated to 260–280° with 1.85 g. of palladium–charcoal catalyst.[9] Evolution of hydrogen was practically complete within thirty minutes and the mixture was then heated to 280–290° for fifteen minutes to complete the dehydrogenation; yield, 18 g. (98%); b. p. 108–109° (1 mm.). **1,4-Dimethylnaphthalene picrate** forms orange needles from methanol; m. p. 143–144°. Barnett and Sanders[5] reported a m. p.

(9) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

of 144° for this picrate and Robinson and Thompson[10] reported 143–144°.

1,4-Dimethylnaphthalene styphnate separates from methanol in orange, rectangular prisms; m. p. 125–126°.

Anal. Calcd. for $C_{12}H_{12}\cdot C_6H_3O_8N_3$: N, 10.5. Found: N, 10.8.

The **1,3,5-trinitrobenzene derivative of 1,4-dimethylnaphthalene** was obtained from methanol in yellow needles; m. p. 165–166°.

Anal. Calcd. for $C_{12}H_{12}\cdot C_6H_3O_6N_3$: N, 11.4. Found: N, 11.8.

Synthesis of 2,4-Dimethyl-1-tetralone (VIII). (a) 2,4-Dimethyl-2-carbomethoxy-1-tetralone (VII).—Employing the procedure of Bachmann and Thomas[3] 4-methyl-1-tetralone was condensed with dimethyl oxalate to give a quantitative yield of **4-methyl-1-tetralone-2-glyoxalate.** When 35 g. of the aforementioned glyoxalate was heated to 175–185° with half its weight of powdered soft glass a vigorous evolution of carbon monoxide took place. The **4-methyl-2-carbomethoxy-1-tetralone (VI)** was purified by distillation in vacuum and was obtained as a nearly colorless liquid which crystallized in the receiver; yield, 29.6 g. (95%) boiling at 150–152° (2 mm.). The keto ester crystallized readily from 30–60° petroleum ether in colorless, hexagonal prisms; m. p. 66–67°.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.5; H, 6.5. Found: C, 71.8; H, 6.6.

When the aforementioned keto ester (29.1 g.) was treated with sodium methoxide and methyl iodide,[3] **2,4-dimethyl-2-carbomethoxy-1-tetralone (VII)** was obtained; b. p. 158–159° (2 mm.); yield, 29.6 g. (96%).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.4; H, 6.9. Found: C, 72.2; H, 6.9.

(b) 2,4-Dimethyl-1-tetralone (VIII).—2,4-Dimethyl-2-carbomethoxy-1-tetralone (42 g.) was hydrolyzed by stirring it vigorously (mechanically) for one and one-quarter hours at 50–55° with a solution of 15.8 g. of sodium hydroxide in 295 cc. of water and 6 cc. of ethanol. The solution never became quite clear and continued treatment with alkali only served to increase the precipitation of an insoluble oil. The precipitate was evidently the desired ketone (VIII) for the apparent purity and high yield (97%) precluded any significant side reaction. It has, moreover, been observed[11,12] that keto esters of the type (VII) are susceptible to cleavage by alkali. Acidification of the hydrolysis mixture precipitated the β-keto acid as a nearly colorless, crystalline solid and this acid was readily decarboxylated by means of steam distillation. The **2,4-dimethyl-1-tetralone** was volatile with steam and was purified by vacuum distillation; yield, 30.5 g. (97%) of colorless liquid boiling at 112° (1 mm.). This ketone has a sweet odor reminiscent of licorice and gives a yellow color with concentrated sulfuric acid. The **semicarbazone** of **2,4-dimethyl-1-tetralone,** prepared by refluxing for five hours a mixture of 1.74 g. of the ketone, 1.5 g. of semicarbazide hydrochloride, 2 cc. of anhydrous pyridine and 30 cc. of absolute ethanol, crystallized from ethanol in broad, colorless needles; m. p. 218–220° dec.

Anal. Calcd. for $C_{13}H_{17}ON_3$: C, 67.5; H, 7.4. Found: C, 67.5; H, 7.2.

Synthesis of 1,3-Dimethylnaphthalene.—When 2,4-dimethyl-1-tetralone was reduced by the Clemmensen method, **1,3-dimethyltetralin** was obtained in 77% yield. The hydrocarbon, which has a sweet, faintly-camphoraceous odor, was purified by distilling it under reduced pressure over sodium; b. p. 78° (1 mm.).

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.97; H, 10.06.

Hydrogen sulfide was evolved smoothly for one and one-quarter hours when 10.3 g. of 1,3-dimethyltetralin was heated to 230–240° with 4.2 g. of sulfur. The melt finally was heated to 250–270° for five minutes to complete the reaction and the **1,3-dimethylnaphthalene** was distilled from the reaction mixture under reduced pressure. The pure hydrocarbon was obtained as a colorless, practically odorless liquid by distillation under reduced pressure over sodium; yield, 9.8 g. (98%) boiling at 117° (2 mm.). Dehydrogenation of 1,3-dimethyltetralin with palladium–charcoal catalyst did not proceed as smoothly as dehydrogenation with sulfur. Hydrogen was evolved for twenty-five minutes at 200–250° when 3.6 g. of 1,3-dimethyltetralin was heated with 360 mg. of catalyst. The mixture was then heated to 280–320° for thirty minutes to complete the reaction. Inasmuch as only 65% of the theoretical volume of hydrogen was evolved the **1,3-dimethylnaphthalene** was purified through the picrate; yield, 2.61 g. (74%) of purified hydrocarbon.

1,3-Dimethylnaphthalene picrate crystallized from methanol in orange needles; m. p. 117–118°. Barnett and Sanders[5] reported 118° for the m. p. of this picrate and Vesely and Stursa[4] reported 88–89°.

1,3-Dimethylnaphthalene styphnate was prepared by dissolving equivalent quantities of the components in hot methanol; orange-yellow needles; m. p. 116–118°.

Anal. Calcd. for $C_{12}H_{12}\cdot C_6H_3O_8N_3$: N, 10.5. Found: N, 10.9.

Synthesis of 1,2,4-Trimethylnaphthalene (XVI) from 2,4-Dimethyl-1-tetralone.—To the cold Grignard reagent prepared from 2.8 g. of magnesium, 17 g. of methyl iodide and 50 cc. of ether was added dropwise a solution of 10 g. of 2,4-dimethyl-1-tetralone in 50 cc. of ether. The mixture was refluxed for one hour, hydrolyzed with ice and ammonium chloride and worked up in the usual manner. Evaporation of the ether layer yielded 11.4 g. (100%) of colorless, crystalline **1,2,4-trimethyl-1-tetralol.** The carbinol crystallized readily in colorless prisms from 30–60° petroleum ether; m. p. 84–86°. Concentrated sulfuric acid gives a yellow color with this tertiary carbinol.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.0; H, 9.5. Found: C, 81.9; H, 9.5.

When 13.5 g. of 1,2,4-trimethyl-1-tetralol was dehydrated with 50 cc. of anhydrous formic acid in the manner previously described there was obtained 12 g. (98%) of **1,2,4-trimethyl-3,4-dihydronaphthalene** boiling at 86–88° (0.4 mm.) after one previous distillation under reduced pressure over sodium.

1,2,4-Trimethylnaphthalene (XVI) was obtained in quantitative yield when 1,2,4-trimethyl-3,4-dihydronaphthalene was catalytically dehydrogenated in the manner previously

(10) Robinson and Thompson, *J. Chem. Soc.*, 2017 (1932).
(11) Bachmann, Cole and Wilds, THIS JOURNAL, **62**, 826 (1940).
(12) Titley, *J. Chem. Soc.*, 2578 (1928).

described. Purification of the hydrocarbon was effected by vacuum distillation (b. p. 125–126° (0.6 mm.)) and subsequent crystallization from methanol gave colorless, nacreous leaflets; m. p. 54–55° (Ruzicka and Ehmann[6] reported 50°). **1,2,4-Trimethylnaphthalene picrate** formed orange needles from methanol; m. p. 148–148.5° (Ruzicka and Ehmann[6] reported 147.5°). **1,2,4-Trimethylnaphthalene styphnate** separated from methanol in orange needles; m. p. 123–124° (Ruzicka and Ehmann,[6] 123.5°).

The **1,3,5-trinitrobenzene derivative** of **1,2,4-trimethylnaphthalene** separated from methanol in yellow needles; m. p. 166.5–167.5°.

Anal. Calcd. for $C_{18}H_{14}\cdot C_6H_3O_6N_3$: N, 10.95. Found: N, 11.07.

Synthesis of 1,2,4-Trimethylnaphthalene (XVI) from Acetophenone. (a) **2-Methyl-3-phenyl-*n*-butyric Acid (XII).**—Ethyl 3-hydroxy-2-methyl-3-phenyl-*n*-butyrate (IX) was prepared in 78% yield from acetophenone and ethyl α-bromopropionate by means of the Reformatsky reaction.[13] This hydroxy ester was then dehydrated with potassium bisulfate and was hydrolyzed to give α,β-dimethylcinnamic acid (XI) according to the method of Burton and Shoppee.[14] The unsaturated acid (XI, 7.4 g.) was hydrogenated readily in acetic acid solution (25 cc.) in the presence of Adams catalyst (80 mg.) to give a 95% yield (7.2 g.) of pure **2-methyl-3-phenyl-*n*-butyric acid (XII).** The acid was effectively purified by vacuum distillation (b. p. 124–125° (0.2 mm.)) and subsequent crystallization from ligroin; thick, colorless, rectangular plates; m. p. 131–132°. The acid (XII) is slightly soluble in cold petroleum ether or ligroin, moderately soluble in benzene, and very soluble in cold chloroform or hot ligroin.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.9. Found: C, 74.2; H, 8.0.

(b) **Arndt–Eistert Reaction on the Acid (XII).**—An ethereal solution (20 cc.) of pure 2-methyl-3-phenyl-*n*-butyryl chloride (from 3.56 g. of the acid XII) was added dropwise to an ice-cold ethereal solution of diazomethane (prepared from 12.6 cc. of nitrosomethylurethan according to the method of Meerwein and Burneleit[15]). The solution was allowed to stand at room temperature for two hours and then excess diazomethane and ether were removed under reduced pressure (employing a bath maintained at 30°). A solution of the residual yellow, liquid diazoketone in 30 cc. of dioxane was added dropwise over a period of twenty-five minutes to a mechanically-stirred suspension of 2.6 g. of silver oxide in an aqueous solution (130 cc.) containing 3.8 g. of sodium thiosulfate. The suspension was heated to 65–70° throughout the addition of the diazoketone and stirring at 65–70° was continued for one additional hour. Potassium hydroxide was then added to the solution (to ensure alkalinity) which was filtered through alumina and was finally acidified with acetic acid. Crude **3-methyl-4-phenylpentanoic acid,** which was isolated by extracting the acidified solution with ether, was purified by reprecipitation from a sodium bicarbonate solution with hydrochloric acid; evaporation of the dried ethereal extract left 3.1 g. (81%) of the acid (XIII) in a sufficiently pure condition for cyclization. Von Braun[16] first prepared this acid by hydrolysis of the corresponding nitrile.

(c) **Preparation of 3,4-Dimethyl-1-tetralone (XIV).**—The acid (XIII) was cyclized with 80% sulfuric acid and isolated in the manner previously described for 4-methyl-1-tetralone; 2.0 g. (72% yield) of the cyclic ketone distilled as a colorless liquid at 96–97° (0.3 mm.). This ketone has been prepared previously in a different manner by Ruzicka and Ehmann[6] and by v. Braun.[16]

(d) **1,2,4-Trimethylnaphthalene (XVI).**—To the Grignard reagent prepared from 0.6 g. of magnesium, 2 cc. of methyl iodide and 6 cc. of ether was added a solution of 2 g. of the aforementioned ketone in 10 cc. of ether, and the mixture was refluxed for one hour. The crude **1,3,4-trimethyl-1-tetralol (XV),** isolated in the usual manner, was dehydrated with 7 cc. of formic acid in the manner previously described, and the **1,2,4-trimethyl-1,2-dihydronaphthalene** (1.35 g.) so obtained was dehydrogenated by heating it with the theoretical weight of sulfur to 220–230° for forty-five minutes; 1.3 g. of **1,2,4-trimethylnaphthalene** distilled in vacuum and crystallized in the receiver. Mixed m. p. determinations made with the hydrocarbon and the picrate, styphnate and trinitrobenzene derivative indicated that this hydrocarbon was identical with the 1,2,4-trimethylnaphthalene which was prepared from 2,4-dimethyl-1-tetralone.

Synthesis of 1,2-Dimethylnaphthalene. (a) **2-Methyl-1-tetralone (XX).**—2-Methyl-2-carbomethoxy-1-tetralone (XIX), prepared from 1-tetralone[17] according to the procedure of Bachmann and Thomas,[3] was hydrolyzed in the manner described for the hydrolysis of 2,4-dimethyl-2-carbomethoxy-1-tetralone. In this instance likewise, steam distillation sufficed to decarboxylate the resulting β-keto acid, and a 95% yield of **2-methyl-1-tetralone** distilled with the steam; b. p. 115–116° (2.5 mm.). The **semicarbazone** crystallized from ethanol in colorless leaflets; m. p. 203–205°. Krollpfeiffer and Schaefer[18] reported 199–201° for the m. p. of this semicarbazone, and Mayer and Stamm[1] reported 200–201°.

(b) **1,2-Dimethylnaphthalene.**—To the Grignard reagent from 3.52 g. of magnesium, 20.6 g. of methyl iodide and 60 cc. of ether was added a solution of 11.6 g. of 2-methyl-1-tetralone in 80 cc. of anhydrous ether. **1,2-Dimethyl-1-tetralol,** isolated in the usual manner, crystallized in square, colorless plates from 30–60° petroleum ether; yield, quantitative; m. p. 65.5–66° (Schroeter, Lichtenstadt and Irineu[19] reported 64–66°). This tertiary carbinol (17.8 g.) was dehydrated with formic acid in the previously described manner; yield, 15.7 g. (98%) of **1,2-dimethyl-3,4-dihydronaphthalene** boiling at 101° (1.5 mm.). When 15.4 g. of the aforementioned hydrocarbon was heated to 245–290° with 1.5 g. of palladium–charcoal catalyst for forty-five minutes there was obtained 14.75 g. of pure **1,2-dimethylnaphthalene** (97% yield). The **picrate** separated from methanol in orange needles; m. p. 130–131°. This m. p. is in accord with the observations of previous investigators.

(13) Rupe, Steiger and Fiedler, *Ber.*, **47**, 68 (1914).
(14) Burton and Shoppee, *J. Chem. Soc.*, 1160 (1935).
(15) Meerwein and Burneleit, *Ber.*, **61**, 1845 (1928).
(16) Von Braun, *Ann.*, **451**, 48 (1926).
(17) "Organic Syntheses," Vol. 20, John Wiley and Sons, New York, N. Y., 1940, p. 94.
(18) Krollpfeiffer and Schaefer, *Ber.*, **56**, 631 (1923).
(19) Schroeter, Lichtenstadt and Irineu, *ibid.*, **51**, 1600 (1918).

1,2-Dimethylnaphthalene styphnate crystallized from methanol in yellow-orange needles; m. p. 142–143°.

Anal. Calcd. for $C_{12}H_{12}\cdot C_6H_3O_8N_3$: N, 10.5. Found: N, 10.6.

The **1,3,5-trinitrobenzene derivative** of **1,2-dimethylnaphthalene** crystallized from methanol in yellow needles; m. p. 147–148°.

Anal. Calcd. for $C_{12}H_{12}\cdot C_6H_3O_6N_3$: N, 11.4. Found: N, 11.5.

Summary

A method is described for the synthesis of 1,3- and 1,4-dimethylnaphthalene and 1,2,4-trimethylnaphthalene, starting from the readily available β-benzoylpropionic acid. A similar synthesis, starting from 1-tetralone, is described for 1,2-dimethylnaphthalene.

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[CONTRIBUTION FROM THE SCHOOL OF PHARMACY, UNIVERSITY OF PITTSBURGH]

Preparation of Fatty Acid beta-Monoglycerides

BY B. F. DAUBERT

The preparation and identification of beta-monoglycerides of aromatic acids was first accomplished by Helferich and Sieber[1] by acid hydrolysis of the ditrityl ether derivatives. These investigators prepared the beta-monobenzoate and beta-mono-(*p*-nitrobenzoate) of glycerol. Jackson and King[2] and Verkade and associates[3] found that application of this method to the preparation of aliphatic beta monoesters resulted in a shifting of the acyl group to produce the alpha ester. By catalytic hydrogenation of the esterified α,α-benzylidene glycerol, Bergmann and Carter[4] were the first to prepare a beta monoglyceride of a fatty acid. The method has been verified by a number of other investigators.

Verkade and associates[5] suggested a new method for preparing beta monoglycerides that involves the catalytic detritylation of the β-acyl-α,α'-dityrityl ether of glycerol. The purpose of this investigation, since their work has not been reported in detail, is to verify the method and report the experimental data. beta-Monobutyrin also has been prepared and identified as a new compound in the fatty acid series.

Experimental

Preparation of β-Palmityl-α,α'-ditritylglycerol.—The α,α'-ditrityl ether of glycerol was prepared according to the method of Verkade, van der Lee and Meerburg.[6] The ditrityl ether (12 g.) was dissolved in a mixture of 15 ml. of quinoline and 15 ml. of chloroform. After cooling the mixture to approximately 0° in an ice-bath, there was added slowly a solution containing 6.0 g. of palmityl chloride in 15 ml. of chloroform. The mixture was allowed to stand at room temperature for twenty-four hours and then taken up in 250 ml. of ether. The ether solution was washed successively with cold 0.5 *N* sulfuric acid, saturated sodium bicarbonate solution, and water, and finally dried over anhydrous calcium sulfate (Drierite). The ether was removed by distillation under reduced pressure and the residue dissolved in 200 ml. of dry acetone. The solution was filtered, the acetone removed by distillation under reduced pressure and the residue redissolved in a warm mixture of alcohol and acetone (25–1). On cooling to 0–5° for twenty-four hours and scratching the inside of the flask, crystallization was induced. The crystal mass was suction filtered and recrystallized from a similar mixture of alcohol and acetone; yield 13.5 g. (80%), m. p. 71° (Jackson and King,[2] 71.5°).

Preparation of beta-Monopalmitin.—Twelve grams of β-palmityl-α,α'-ditritylglycerol was suspended in 250 ml. of absolute alcohol and transferred to a hydrogenation bottle together with 1 g. of palladium black. The reduction was carried out at 45 lb. (3 atm.) pressure, 45–50°. Reduction was complete after approximately four hours. The progress of the reduction was followed easily by means of the pressure gage. The warm solution was filtered immediately to remove the catalyst and then evaporated to dryness *in vacuo*. The residue was redissolved in a mixture of alcohol and ether (1–1). After repeated fractional crystallizations from cool mixtures of alcohol and ether, 4 g. (85%) of beta-monopalmitin and 5 g. (69%) of triphenylmethane were obtained. The beta-monopalmitin on recrystallization from absolute alcohol melted at 68° and the triphenylmethane at 92.5°. The same procedure was equally successful with platinum (1 g. PtO_2) as the catalyst.

Preparation of β-Butyryl-α,α'-benzylidene Glycerol.—*n*-Butyryl chloride (11.8 g.) was added slowly to 20 g. of α,α'-benzylidene glycerol dissolved in 30 ml. of dry pyridine, with cooling in an ice-bath. The mixture was allowed to stand for four hours at room temperature. When water was added (400 ml.), the compound separated as an oil. After the excess water was poured off, the residue was taken up in ether and washed successively with 0.5 *N* sulfuric acid, saturated sodium bicarbonate solution, and

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(2) Jackson and King, THIS JOURNAL, **55**, 678 (1933).
(3) Verkade and Meerburg, *Rec. trav. chim.*, **54**, 716 (1935).
(4) Bergmann and Carter, *Z. physiol. Chem.*, **191**, 211 (1930).
(5) Verkade, van der Lee, de Quant and Zuydewijn, *Proc. Acad. Sci., Amsterdam*, **40**, 580 (1937).
(6) Verkade, van der Lee and Meerburg, *Rec. trav. chim.*, **56**, 619 (1937).