sorption shown by anthracene[7] could well account for the qualitative maxima reported[5] beyond 290 mμ, even if anthracene were present to the extent of 10% or less.

The compounds reported herein have been prepared by established methods and the physical properties are in agreement with those reported in the recent literature. Since the absorption spectrum of 2,9-dimethylanthracene has not been previously reported, the curve is given in Fig. 2 although the corresponding 9,10-dihydride was not obtained.

Experimental[8]

9-Methylanthracene.—9-Anthraldehyde (Eastman Kodak Co.) was converted to 9-methylanthracene in 92% yield by means of the modified[9] Wolff–Kishner reduction. The hydrocarbon crystallized from ethanol as pale yellow needles, m.p. 79.2–79.7°, lit.[10] m.p. 81.5°.

9-Methyl-9,10-dihydroanthracene.—9-Methylanthracene was reduced in 85% yield to the dihydro derivative by heating with sodium in amyl alcohol according to the procedure of Schlenk and Bergmann.[11] The dihydride thus obtained crystallized from ethanol as colorless needles, m.p. 58.8–59.8°, lit.[10] m.p. 61.5°.

2,9-Dimethylanthracene.[12]—The preparation of this hydrocarbon was patterned after the following sequence of previously[13] reported reactions: toluene + phthalic anhydride → *o*-(*p*-toluyl)-benzoic acid (I) → *o*-(*p*-methylbenzyl)-benzoic acid (II) → 2-methyl-9-anthrone (III) → 2,9-dimethylanthracene (IV). Improvements in the procedure included the reduction of keto acid I in 92% yield by hydrogenolysis in acetic acid solution in the presence of platinum oxide catalyst,[14] and the conversion in 86% yield of acid II to anthrone III by treatment with anhydrous hydrogen fluoride.[15] The use of concentrated sulfuric acid for this cyclization reportedly[13] gave anthrone III in less than 50% yield. When anthrone III was allowed to react with methylmagnesium bromide, IV was obtained in only 29% yield, whereas the use of methyllithium raised this yield to 50%. 2,9-Dimethylanthracene crystallized from methanol as orange needles, m.p. 83.0–84.0°, lit.[13] m.p. 85°.

Attempted reduction of 2,9-dimethylanthracene with sodium and amyl alcohol[11] gave no dihydro derivative, but there was obtained a low yield of a high-melting yellow solid whose identity was not established.

9,10-Dimethylanthracene.[16]—The hydrocarbon was prepared by the procedure used for the synthesis of 9,10-dimethyl-1,2-benzanthracene.[17] The use of benzene as solvent was a necessary modification to accommodate the low solubility of anthraquinone in ether.

To a large excess of methylmagnesium iodide in 200 ml. of ether was added a suspension of 21.0 g. (0.1 mole) of anthraquinone in 300 ml. of dry benzene. Approximately 100 ml. of ether was removed from the green solution by rapid distillation and was replaced by 100 ml. of benzene. The solution was heated under reflux for one hour, allowed to stand overnight, and then poured slowly into a cold (0°) mixture of 240 ml. of hydriodic acid (sp. gr. 1.7) and 800 ml. of methanol. After the vigorous reaction had subsided 800 ml. of glacial acetic acid was added. The iodomethyl intermediate, which separated as bright yellow needles, was rapidly filtered and dried without heating, in the absence of light. The yield of crude material was quantitative.

The iodomethyl intermediate was then dissolved in a mixture of 2 l. of dioxane and 100 ml. of concentrated hydrochloric acid and added to a solution of 330 g. of stannous chloride in 1.5 l. of dioxane. The resultant red solution was heated under gentle reflux for 10 minutes during which time the color changed to a pale yellow. After 45 minutes at room temperature, this solution was diluted with water to yield 22 g. (99%) of crude 9,10-dimethylanthracene. Two recrystallizations from benzene gave brilliant yellow needles, m.p. 182.0–183.8°, lit.[18] m.p. 183.5–184.5°.

9,10-Dimethyl-9,10-dihydroanthracene.[19]—To a refluxing solution of 0.80 g. of 9,10-dimethylanthracene in 200 ml. of absolute ethanol was added 6 g. of sodium. The yellow solution was heated under reflux for 16 hours, filtered and poured into 500 ml. of water. There was collected 0.45 g. (55%) of yellow powdery crystals, m.p. 100–140°. These were dissolved in 30 ml. of benzene containing 2.0 g. of maleic anhydride and the mixture was heated under reflux for 8 hours. The adduct was filtered and the filtrate washed with dilute sodium hydroxide solution and water, and finally dried over anhydrous magnesium sulfate. The benzene solution was then passed through a small column of alumina and the eluate concentrated and sublimed at 140° (0.5 mm.) to remove traces of high-melting material. The sublimate crystallized from methanol to give 0.2 g. of 9,10-dimethyl-9,10-dihydroanthracene as colorless plates, m.p. 126.2–128.0°, lit.[19] m.p. 130°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.55.

When 9,10-dimethylanthracene was reduced by heating with sodium and amyl alcohol,[11] there was obtained, in 50% yield, a compound which crystallized from methanol in fine needles, m.p. 270–273°. Analysis (C, 88.98; H, 6.52) indicated that oxygen had been introduced into the molecule.

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The Synthesis of 2-Thianaphthaldehyde and Some of its Derivatives

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In spite of considerable research activity in the field of thianaphthene chemistry in recent years, no one has reported the 2-aldehyde derived from thianaphthene. 3-Thianaphthaldehyde has been prepared by Komppa and Weckman[1] from the 3-thianaphthylmagnesium bromide and ethyl orthoformate or ethoxymethyleneaniline in yields of 17 and 25%, respectively.

We have prepared the 2-aldehyde from 2-thianaphthyllithium, from the metalation of thianaphthene with *n*-butyllithium,[2] and N-methylformanilide in 62% yield based on starting thianaphthene.

2-Thianaphthaldehyde was carried through several typical aromatic aldehyde reactions such as benzoin condensation, thiosemicarbazone formation, anil formation, and condensation with benzyl cyanide.

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Experimental

2-Thianaphthaldehyde.—Thianaphthene (20 g., 0.15 mole) was metalated with *n*-butyllithium as described earlier,[2] and to the ethereal solution of the organometallic compound was added slowly with stirring a solution of 20 g. (0.15 mole) of N-methylformanilide[3] in 30 ml. of ether. After completion of the addition, the mixture was heated to reflux for one hour and then hydrolyzed by pouring into 80 ml. of 3 *N* hydrochloric acid mixed with crushed ice. The ether layer was separated and the aqueous layer washed three times with ether. The combined ether extracts were washed three times with 1 *N* hydrochloric acid followed by washing with 10% aqueous sodium bicarbonate solution. The resulting ether solution was dried over anhydrous magnesium sulfate and the ether removed by distillation. To the residue was added a small amount of ethanol and then approximately 125 ml. of saturated aqueous sodium bisulfite solution. The resulting mixture was mixed thoroughly and allowed to stand for 20 minutes. The crystalline bisulfite addition compound was filtered off, washed with ether and dried. The aldehyde was regenerated by addition of excess saturated aqueous sodium carbonate to a cool aqueous solution of the bisulfite addition compound. The precipitated solid aldehyde was filtered off and dried yielding 14.7 g. (62%) based on thianaphthene of 2-thianaphthaldehyde, m.p. 34–34.5°. Recrystallization from ethanol did not raise the melting point.

Anal. Calcd. for C_9H_6OS: S, 19.8. Found: S, 19.8, 19.6.

A small sample of the aldehyde was oxidized with a dilute solution of potassium permanganate in acetone to 2-thianaphthenecarboxylic acid identical in melting point and mixed melting point (234–236°) with an authentic specimen.[1,4]

2-Thianaphthal-4′-carboxyaniline.—A solution of 1.0 g. (0.006 mole) of 2-thianaphthaldehyde and 0.82 g. (0.006 mole) of *p*-aminobenzoic acid in 10 ml. of ethanol was allowed to stand for two hours. The precipitated solid was removed by filtration to give 0.95 g. (56%) of the anil melting slowly with decomposition in the range 300–305°. Recrystallization from xylene did not change the melting range.

Anal. Calcd. for $C_{16}H_{11}NO_2S$: N, 4.98. Found: N, 5.04 and 5.07.

2-Thianaphthal-3′-hydroxy-4′-carboxyaniline.—This anil was prepared as described above from equivalent amounts of the aldehyde and *p*-aminosalicylic acid. Product melting at 204–205° (dec.) was obtained in 22% yield. Recrystallization of this material from xylene raised the melting point to 208.5–209°.

Anal. Calcd. for $C_{16}H_{11}NO_3S$: N, 4.71. Found: N, 4.42 and 4.48.

1-(2′-Thianaphthyl)-2-cyano-2-phenylethylene.—Four drops of a 30% aqueous potassium hydroxide solution was added with stirring to a solution of 2 g. (0.012 mole) of 2-thianaphthaldehyde and 1.4 g. (0.012 mole) of benzyl cyanide in 8.5 ml. of alcohol. The yellow precipitate which formed immediately was filtered off and dried. It consisted of 2.5 g. (80%) of condensation product m.p. 127–128°. Recrystallization from ethanol did not raise the melting point.

Anal. Calcd. for $C_{17}H_{11}NS$: N, 5.36. Found: N, 5.36 and 5.46.

A similar reaction between 3-thianaphthaldehyde and benzyl cyanide has been reported by Buu-Hoi and Hoan.[5]

Thiosemicarbazone of 2-Thianaphthaldehyde.—A solution of 5 g. (0.031 mole) of 2-thianaphthaldehyde and 2.8 g. (0.031 mole) of thiosemicarbazide in 200 ml. of alcohol-water mixture containing 60% of alcohol was heated under reflux overnight. The mixture was cooled and the precipitated solid filtered off and dried yielding 6 g. (83%) of the thiosemicarbazone, m.p. 218–220°. A recrystallization from alcohol raised the m.p. to 219–220°.

Anal. Calcd. for $C_{10}H_9N_3S_2$: N, 17.9. Found: N, 17.8 and 17.7.

2,2′-Thianaphthoin.—A solution of 1.5 g. (0.009 mole) of 2-thianaphthaldehyde in 10 ml. of 50% alcohol-water was heated to boiling and 0.05 g. of potassium cyanide was added with stirring. After the exothermic reaction had subsided, the mixture was heated to reflux for 20 minutes. The cooled mixture was acidified with acetic acid, and the solid removed by filtration. The thianaphthoin melted at 153.5–155° and weighed 1.35 g. (92%). Recrystallization from alcohol raised the m.p. to 154–156°.

Anal. Calcd. for $C_{18}H_{12}O_2S_2$: S, 19.8. Found: S, 19.6 and 19.5.

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Synthesis of β,β-Dihexylalanine

BY GARDNER W. STACY[1]

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In an extension of earlier work[2,3] we have synthesized β,β-dihexylalanine. The preparation of dialkylmethylmalonic esters and symmetrical β,β-dialkylsubstituted-alanines by these methods, therefore, would appear to be useful as a general procedure. Because of this it seemed appropriate to report the experimental details for the synthesis of this higher homolog.

Experimental

Ethyl Dihexylmethylmalonate.—Hexylmagnesium bromide was prepared by the addition of 99 g. (0.6 mole) of hexyl bromide dissolved in 165 ml. of absolute ether to 14.6 g. (0.6 atom) of magnesium suspended in 95 ml. of absolute ether over a period of two hours. After the addition was complete, the reaction mixture was warmed under reflux for one-half hour. To the solution of hexylmagnesium bromide was added over a period of one-half hour 43.2 g. (0.225 mole) of ethyl ethoxymethylenemalonate[4] dissolved in 30 ml. of absolute ether. The reaction mixture was then heated under reflux for 20 minutes. After the contents of the flask had cooled, they were poured into a mixture of 400 g. of ice and 70 ml. of 12 *N* hydrochloric acid. The ether layer was separated and the aqueous layer extracted with three 150-ml. volumes of ether. The combined extracts were then dried over anhydrous magnesium sulfate. The ether was removed by distillation and the residue distilled *in vacuo*. A forerun boiling at 70–147° (0.2 mm.) amounted to 19.8 g. The main fraction distilled at 148–152° (0.2 mm.), yield 37.8 g. (55%). A sample boiling over a one degree range 151–152° (0.2 mm.), n^{20}_{D} 1.4422, was submitted for analysis.

Anal. Calcd. for $C_{20}H_{38}O_4$: C, 70.13; H, 11.18. Found: C, 70.04; H, 11.37.

α-Bromo-β,β-dihexylpropionic Acid.—Saponification of the malonic ester was accomplished by slowly adding 62.6 g. (0.183 mole) to a solution of 39 g. of potassium hydroxide in 91 ml. of water and by heating the mixture under reflux with stirring for five hours. After the reaction mixture had cooled, it was diluted with 40 ml. of water and then a layer of 200 ml. of ether was added. With stirring the mixture was acidified to congo red with 58.5 ml. of 12 *N* hydrochloric acid. The ether layer was separated, and then the aqueous layer was extracted consecutively with three 100-ml. portions of ether. The extracts were combined with the original ether layer and dried over anhydrous calcium chloride.

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