We should like to acknowledge the aid of the Research Corporation of New York for financial support of this work.

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 Buû-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 $C_{10}H_8N_3S_2$: 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]

RECEIVED JANUARY 2, 1952

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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(1) Department of Chemistry, The State College of Washington, Pullman, Washington.

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The ether was removed by distillation leaving a residue of crude dihexylmethylmalonic acid amounting to 59.6 g., which partially crystallized on standing.

To this crude material, dissolved in 95 ml. of absolute ether, was added dropwise 29.2 g. (0.183 mole) of bromine as the reaction mixture was stirred and heated under reflux over a period of 45 minutes. After the addition of bromine was complete, the reaction mixture was heated for an additional one-half hour. The mixture was cooled to room temperature, and 70 ml. of water was added dropwise. The ether layer was separated, and without drying the ether was removed by distillation leaving a residue of crude bromodihexylmethylmalonic acid. This was decarboxylated by heating at 135–145° in an oil-bath for 90 minutes. The material was then heated *in vacuo* at the same temperature for an additional hour to remove volatile substances. The residue which amounted to 57.2 g. was dissolved in 200 ml. of hexane. The solution was warmed, treated with 5 g. of Darco and filtered. The hexane was removed under reduced pressure. The crude product obtained was an orange-colored oil, yield 54.2 g. (92%).

β,β-Dihexylalanine.—In the glass liner of a high pressure bomb was placed 5.0 g. (0.016 mole) of the crude bromo-acid dissolved in 30 ml. of absolute ethanol. This was cooled in a Dry Ice–Cellosolve mixture and 5.1 g. (0.30 mole) of liquid ammonia was added with stirring. The reaction mixture was heated in the bomb to 130° over a period of seven hours and then allowed to cool overnight. The contents were removed, and a light, amber solution was obtained. The ethanol and excess ammonia were then removed under reduced pressure. When about half of the ethanolic ammonia had been removed, a voluminous, white precipitate began to form. This precipitate was removed by filtration and washed thoroughly with anhydrous ether. The crude material was of a spongy consistency, m.p. 211–223°, yield 2.6 g. A sample for analysis was recrystallized twice from 50% aqueous acetic acid. The material sintered at 215° and melted at 222–223° (cor.).

Anal. Calcd. for $C_{15}H_{31}NO_2$: C, 69.99; H, 12.14; N, 5.44. Found: C, 70.05; H, 12.05; N, 5.42.

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The Reaction of a *p*-Substituted *o*-Methylolphenol with Oleic Acid

BY G. R. SPRENGLING

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The heat reaction of *o*-hydroxymethyl phenols with unsaturated compounds has been found by K. Hultzsch[1] to result in the formation of chroman rings in the case of simple unsaturates such as styrene. Many other authors[2] join Hultzsch in assuming that the same formation of chromans takes place in reaction with drying oils, but no definite proof of this has been advanced. Others assume a reaction of unspecified nature between the methylol groups and "active methylene hydrogen,"[3] or a transesterification accompanied by reaction with polyunsaturated centers only,[4] or with formation of methylene bridges.[5] Some authors[6] dispute the fact that a reaction takes place with a drying oil at all.

To avoid complications this reaction was investigated using monofunctional reagents. Being conveniently available, the *o*-methylol derivative of *p*-*t*-butyl-*o*-cresol and oleic acid or its methyl ester were employed.

When these two reagents, the latter in large excess, were heated together to 180° for 3–4 hr. in a slow stream of dry CO_2, a reaction took place with the evolution of almost exactly one mole of water per mole of methylol phenol used. No evolution of formaldehyde could be detected. After removal of excess oleic acid and volatile self-condensation products of the methylolphenol by vacuum distillation, a residue greater than the original amount of methylolphenol used remained. This residue was shown by potentiometric titration and esterification to contain a considerable amount of carboxylic acid groups, though only a very small amount of oleic acid could be recovered from it by extraction with alkali. Contrary to the assertion of Hultzsch,[1] the extraction with alkali yielded no high molecular weight acids. The carboxyl groups must be bound to some molecule other and presumably larger than oleic acid, which yields water insoluble soaps.

By the use of a Duolite A-2 anion exchange resin column, the residue could be separated into three fractions, two of which evidently resulted from self-condensation of the methylolphenol. The larger of these latter fractions was neutral, had an

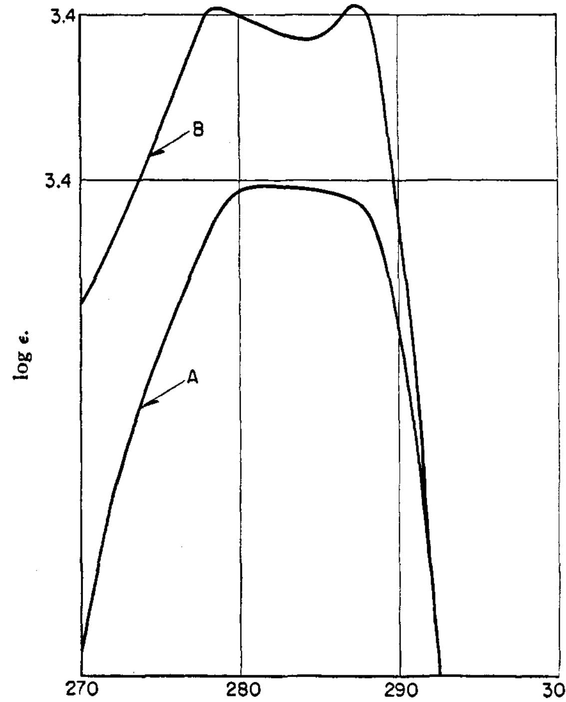

Fig. 1.—Ultraviolet spectra of 2-methyl-4-*t*-butyl-6-methylolphenol (A) and the corresponding chroman ester (B).

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