Experimental[15]

General Procedure for Preparation of the Enol Acetates.—A solution of 1 g. of the appropriate keto (or aldehydo) steroid and 0.15 g. of *p*-toluenesulfonic acid monohydrate in about 20 ml. of isopropenyl acetate[16] was placed in a 50-ml. flask fitted with a six-inch fractionating column. This solution was slowly distilled for about 10 hours. More isopropenyl acetate was added from time to time to keep the volume above 10 ml. After cooling the solution remaining in the flask, about 1 g. of solid sodium bicarbonate was added and the remaining isopropenyl acetate was removed by distillation under reduced pressure at less than 30°. The residue was shaken with ether[17] and ice-water and the aqueous layer was extracted with more ether. The combined ether solution was washed with water, then with saturated sodium chloride solution and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure at less than 30° and the residue crystallized from the solvent indicated in Table I.

3β,21-Diacetoxy-5-pregnen-20-one (IV).—A solution of 1 g. (0.0025 mole) of 3β,20-diacetoxy-5,20-pregnadiene (II) in 25 ml. of methylene chloride was cooled to below −10° in an ice–salt-bath. To this was added dropwise during 25 minutes with stirring 16.6 ml. (0.005 mole) of a 0.602 normal bromine solution in methylene chloride. The resulting colorless solution was distilled to dryness under reduced pressure at a temperature below 20°. The residue of crude bromo compound (III) was dissolved in 25 ml. of benzene and a solution of 5 g. of sodium iodide in 25 ml. of absolute ethanol was added.[18] After standing at room temperature for 26 hours the mixture was diluted with water and extracted twice with ether. The ether solution was washed twice with cold 1% sodium hydroxide solution, then well with water and dried over anhydrous sodium sulfate. Removal of the ether under reduced pressure at a temperature below 30° gave crude crystalline 3β-acetoxy-21-iodo-5-pregnen-20-one. This was dissolved in 35 ml. of acetone and 5 g. of potassium bicarbonate and 3 ml. of glacial acetic acid were added.[19] The mixture was refluxed with stirring for 12 hours and then diluted with ice-water and extracted twice with ether. The ether solution was washed with water, then with cold dilute sodium thiosulfate, then twice with water and dried over anhydrous sodium sulfate. The ether was removed under reduced pressure at a temperature below 30° and the residue was reacetylated with 5 ml. of pyridine and 3 ml. of acetic anhydride at room temperature for one hour. Ice-water was added and the mixture was extracted twice with ether. The ether solution was washed with cold dilute hydrochloric acid, water, cold dilute sodium bicarbonate solution, twice with water, and dried over anhydrous sodium sulfate. The ether solution was distilled at atmospheric pressure. When the volume of the solution was about 10 ml. crystallization started. After cooling the crystals were collected, washed with ether and dried giving 0.44 g. of white crystals, m.p. 159–162°. A mixed melting point with an authentic sample of 3β,21-diacetoxy-5-pregnen-20-one gave no depression. An additional yield of 0.07 g. was obtained from the filtrate.

Dimethyl Ester of the Maleic Anhydride Adduct of 3β-Acetoxy-5,7,9(11)-etiocholatrienic Acid (VII).—A solution of 0.69 g. (1.27 millimoles) of the dimethyl ester of the maleic anhydride adduct of 3β,20-diacetoxy-5,7,9(11),20-pregnatetraene (VI) in 35 ml. of methylene chloride was cooled by a Dry Ice–acetone mixture and ozonized oxygen was passed in until 61 mg. (17% excess) of ozone was absorbed. The reaction mixture was diluted with 20 ml. of acetic acid and concentrated under reduced pressure below 40° to a volume of about 10 ml. This was diluted with 25 ml. more acetic acid and 5 g. of zinc dust was added in several portions. After filtering, the solution was poured into about 20 ml. of water. The white precipitate which formed was collected and dried, weight 0.55 g., m.p. 231–248°.[20]

This was recrystallized first from acetone and then from methanol giving white crystals m.p. 255–259° (dec.), $[\alpha]^{25}\text{D}$ +80.6° (0.57% in $CHCl_3$).

Anal. Calcd. for $C_{28}H_{36}O_8$: C, 67.17; H, 7.25; neut. equiv., 501. Found: C, 67.16; H, 7.13; neut. equiv., 520.

The filtrates were worked up for neutral product but only a small amount of unchanged enol acetate was obtained.

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[15] All melting points were taken on a Fisher–Johns melting point block. Elementary analyses and rotations are by Mr. Wm. A. Struck and associates of our Microchemical Laboratory.

[16] In some cases the ketosteroids were not soluble in isopropenyl acetate but they dissolved as the reaction proceeded.

[17] In a few cases the enol acetates were not soluble in ether and methylene chloride was used for the extraction.

[18] This conversion of the tribromide to 3β-acetoxy-21-iodo-5-pregnen-20-one is essentially the method described by P. L. Julian and W. J. Karpel [THIS JOURNAL, **72**, 362 (1950)] for an analogous conversion.

[19] This method for converting a 21-iodo compound to a 21-acetoxy compound is essentially that of G. Rosenkranz, J. Pataki, St. Kaufmann, J. Berlin and C. Djerassi, *ibid.*, **72**, 4081 (1950).

[20] The above part of this experiment was carried out by Dr. A. Vern McIntosh, Jr., in these laboratories.

KALAMAZOO, MICHIGAN RECEIVED NOVEMBER 23, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

Reactions of 3-Thianaphthenylmethylmagnesium Chloride

BY RUSSELL GAERTNER

Mixtures of the products formed by both the normal and abnormal reactions were obtained when this Grignard reagent was treated with carbon dioxide, formaldehyde and ethylene oxide. Benzoyldurene and benzophenone reacted normally. Exclusively abnormal reaction occurred with ethyl chlorocarbonate. The implications concerning the aromaticity of thianaphthene are considered.

If, as suggested in preceding reports,[1,2] the extent of abnormal reaction of an heteroarylmethyl Grignard reagent is a criterion of the aromatic character of the nucleus, or more accurately a measure of the interaction of the neighboring unsaturation with the remainder of the nucleus, the position of the halomethyl group in an unsymmetrical nucleus should not affect the ratio of the two types of product. Since 2-thianaphthenylmethylmagnesium chloride reacted exclusively with rearrangement,[2] a comparison with the properties of the 3-isomer afforded a test of the hypothesis.

3 - (Chloromethyl) - thianaphthene (I) was smoothly converted to the Grignard reagent (II) in the cyclic reactor; in some runs a small amount of a coupling product, probably 1,2-bis-(3-thianaphthenyl)-ethane, was isolated. The reagent was treated with carbon dioxide, ethyl chlorocarbonate, ethylene oxide, formaldehyde, benzoyldurene and benzophenone. Only ethyl chlorocarbonate gave exclusively the abnormal product, 3-methyl-2-thianaphthoic acid (III), also prepared

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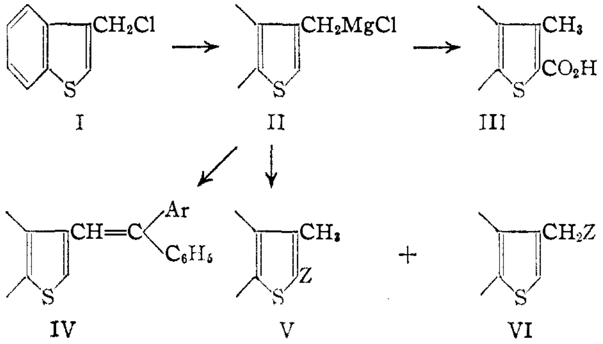
[1] R. Gaertner, THIS JOURNAL, **73**, 3934 (1951). This paper contained a summary of previous work in the field.

[2] R. Gaertner, *ibid.*, **74**, 766 (1952). Benzoyldurene was an exception in that it reacted normally; the carbinol was isolated and dehydrated.

by carbonating the Grignard reagent obtained from 2-bromo-3-methylthianaphthene.



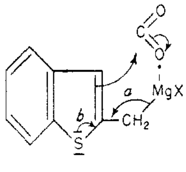
As in the case of the isomeric reagent,[2] the normal product was obtained with benzoyldurene; however, the intermediate carbinol was not obtained but dehydrated during isolation to give the corresponding triarylethylene (IV, Ar-duryl). Similar results were obtained with benzophenone.

With the other reagents, mixtures of both abnormal (V) and normal (VI) products resulted. Carbonation led to III and 3-thianaphthenylacetic acid in a ratio of 3.4 or 3.8 to 1 in two runs. The liquid mixture obtained using ethylene oxide contained both 2-(3-methyl-2-thianaphthenyl)-ethanol (V, Z-CH_2CH_2OH) and 3-(3-thianaphthenyl)-1-propanol (VI, Z-CH_2CH_2OH); recrystallization of the mixture of phenylurethans gave either pure derivative by appropriate seeding techniques but no estimate of the ratio was justifiable on this basis. The expected products were also prepared by reduction with lithium aluminum hydride of the appropriate acids, both of which were in turn obtained by the Kindler–Willgerodt process with 3-methyl-2-acetothianaphthone or 3-propiothianaphthone, respectively.

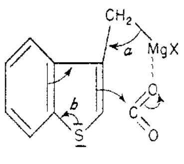
Similarly, with formaldehyde both 2-(3-thianaphthenyl)-ethanol (VI, Z-CH_2OH) and 3-methyl-2-thianaphthenylcarbinol (V, Z-CH_2OH) were present in the mixture of products. The latter was prepared for comparison by reduction of III. A third product was probably 2-(2-hydroxymethyl-3-thianaphthenyl)-ethanol.[3]

Clearly these results necessitate modification of the earlier view that the tendency toward abnormal reaction is a criterion of aromaticity. Thus the decreasing order based on carbonation for arylmethyl reagents[1,2] is: 2-thianaphthenylmethyl, 3-furfuryl, 3-thianaphthenylmethyl, 2-thenyl, benzyl. Of course, the order is different for other reactants; for example, formaldehyde and ethylene oxide gave no detectable normal products with the 2-thenyl reagent.

The reason for the greater extent of abnormal reaction of the 2 as compared to the 3 isomer in the thianaphthene series is uncertain. It may be pointed out, however, that the observed behavior is in agreement with the hypothesis that rearrangement will occur more extensively into a position which is attacked preferentially in electrophilic substitution.[4] Thus the reactive 3-position of thianaphthene accepts the reagent more extensively than does the 2-position. Theoretically the two types of reaction are not unrelated; aromatic substitution involves separation of charge, a carbanion being induced on the position attacked. Analogously, the abnormal Grignard reaction results from the contribution of an ortho carbanion to the cyclic complex with the reactant. The polarizability of a nucleus in a given position should be related in both reactions. That is, the electromeric shift **a** within the complex VII occurs more extensively than in VIII, due to bolstering contributions from the polarizability **b**. Only in VII can shift **b** occur without interrupting the resonant system in the fused benzene nucleus.



VII



VIII

The investigation of substituted reagents in the thiophene and thianaphthene series continues in this Laboratory.

Acknowledgments.—This work was made possible by a grant-in-aid from the Graduate School for the 1950–1951 and 1951–1952 academic years. Gifts of thianaphthene by Jefferson Chemical Company and of durene by The Humble Oil and Refining Company were of great aid.

Experimental Part[5]

3-Thianaphthenylmethylmagnesium Chloride (II).—3-(Chloromethyl)-thianaphthene[6] (I) was converted to the Grignard reagent using the cyclic reactor.[1,2] The highest yield, determined by titration, was 99%. By conventional means, only a 36% yield of reagent was produced from 35.7 g. of chloride; 12 g. of crude 1,2-bis-(3-thianaphthenyl)-ethane, first isolated in the carbonation reaction, was also isolated.

Reactions of II.—The procedures were similar to those which have been described previously[1,2]; yields may not have been optimum. Hydrolysis of 0.144 mole of the reagent with saturated ammonium chloride solution and ice gave 17.6 g. (83%) of 3-methylthianaphthene[7]; b.p. 63–72° (0.3 mm.); n^{20}D 1.6268; d^{20}_4 1.137; *MR* (calcd.) 44.31, (obsd.) 46.18. The picrate[7] melted at 122.5–123.5°.

A. **Carbonation.**—From 0.300 mole of reagent, by acidification of the alkaline extracts, was obtained a wet mixture of acids which was triturated twice with acetone and twice with benzene. The filtrates were diluted with water and again filtered; the insoluble acid weighed 32.2 g. (56% yield) and melted at 240–243°. After recrystallization from

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[3] S. Siegel, W. M. Boyer and R. R. Jay, THIS JOURNAL, **73**, 3237 (1951), found that aldehydes, but not formaldehyde, gave compounds of this type with benzylmagnesium chloride.

[4] E. Campaigne and W. M. LeSuer, *ibid.*, **70**, 1555 (1948), referred briefly to the "high activity of the alpha position in the thiophene nucleus" in connection with their tentative observation of rearrangement with 3-thenylmagnesium bromide. A search of the literature revealed no other references in this connection; nor could data be found to test the hypothesis.

[5] Melting points, but not boiling points, are corrected. Properties of previously known compounds agreed satisfactorily with those reported in the references. Microanalyses were by Micro-Tech Laboratories, Skokie, Illinois.

[6] F. F. Blicke and D. G. Sheets, THIS JOURNAL, **70**, 3768 (1948); in the chloromethylation of thianaphthene, concd. hydrochloric acid and trioxane can be substituted conveniently for formalin and hydrogen chloride. These authors listed only a boiling point; our once-distilled product solidified in the deep-freeze and melted at 34–35°.

[7] F. Krollpfeiffer, H. Hartmann and F. Schmidt, *Ann.*, **563**, 15 (1949).

acetic acid, 3-methyl-2-thianaphthoic acid (III) formed compact colorless prisms; m.p. 244–244.5°.

Anal. Calcd. for $C_{10}H_8O_2S$: C, 62.48; H, 4.10. Found: C, 62.41; H, 4.28.

The acid in the benzene layer was recrystallized from carbon tetrachloride–hexane (9.4 g., 16%); m.p. 108–109° (no depression with authentic 3-thianaphthenylacetic acid[6]). The amide[6] melted at 172.4–174°. In a smaller run, 0.200 mole of reagent gave these products in a ratio of 9.6 to 2.6 g. From the neutral fraction in the larger run, besides 3-methylthianaphthene, by recrystallization from hexane of the residue in the distillation was isolated 0.20 g. of colorless needles; m.p. 141.5–142.5°. The product of coupling was probably 1,2-bis-(3-thianaphthenyl)-ethane.

Anal. Calcd. for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79. Found: C, 73.32; H, 4.94.

To 23.2 g. of 3-methylthianaphthene in 50 ml. of carbon tetrachloride was added dropwise, with stirring and cooling in ice, 27.2 g. of bromine in 25 ml. of the solvent. The mixture was heated to 50° and the solvent aspirated; the residue was stirred overnight at 90° with 200 ml. of 10% potassium hydroxide. 2-Bromo-3-methylthianaphthene (b.p. 114–115°; 32.9 g., 92% yield) was a faintly yellow liquid; $n^{20}\text{D}$ 1.6548; $d^{20}{}_4$ 1.555; *MR* (calcd.) 52.08, (obsd.) 53.57.

Anal. Calcd. for C_9H_7BrS: C, 47.59; H, 3.11. Found: C, 47.55; H, 3.33.

The Grignard reagent was obtained by allowing 22.7 g. of the compound to react with magnesium (2.7 g.) in 100 ml. of ether; a bulky tan solid separated during conversion. By carbonation, 7.9 g. (41%) of 3-methyl-2-thianaphthoic acid, m.p. 243–244°, was obtained; 6.1 g. of 3-methylthianaphthene was present in the neutral fraction. This reagent did not react with benzoyldurene in ether.

B. **Benzoyldurene.**—A solution (100 ml. containing 0.0825 mole) of reagent was pipetted onto 11.9 g. of the ketone. The purple solution changed to brown when heated two hours. The product mixture did not crystallize from hexane and was distilled. After removal of 5.1 g. of 3-methylthianaphthene at 94–95° (1.5 mm.), the residual amber gum was dissolved in hot acetone. A total of 3.9 g. (20%) of colorless crystals, m.p. 203–205°, separated from hexane-acetone. 1-Duryl-1-phenyl-2-(3-thianaphthenyl)-ethene was recrystallized from acetone–benzene; m.p. 206–207°. It was attacked only very slowly by neutral permanganate, and not at all by hydrogen at 30° with Adams catalyst or palladium-on-charcoal.

Anal. Calcd. for $C_{26}H_{24}S$: C, 84.74; H, 6.56. Found: C, 84.81; H, 6.51.

C. **Benzophenone.**—To a solution of 5.0 g. of the ketone in 50 ml. of ether was added 25 ml. of a solution containing 0.0274 mole of reagent; during the vigorous reaction a tan precipitate separated. After being heated for 2 hours the mixture was hydrolyzed. The oily product did not crystallize and was distilled to a temperature in the bath of 150° at 0.1 mm. The residue was dissolved in acetone and 1.64 g. (19%) of a yellow powder separated. Recrystallization of 1,1-diphenyl-2-(3-thianaphthenyl)-ethene from benzene–acetone gave nearly colorless prisms; m.p. 234–235°.

Anal. Calcd. for $C_{22}H_{16}S$: C, 84.57; H, 5.16. Found: C, 84.64; H, 5.37.

Two unsuccessful approaches to the synthesis of phenyl 3-thianaphthenylmethyl ketone, a likely intermediate for independent preparations of the two triarylethylenes, were investigated. The condensation of 3-thianaphthenylacetyl chloride with benzene (aluminum chloride) or with phenylmagnesium bromide gave only unresolved uninviting mixtures.

D. **Ethyl Chlorocarbonate.**—From 33 ml. of the ester and 0.164 mole of reagent was obtained, after hydrolysis of the crude ester, a total of 13.6 g. (43%) of 3-methyl-2-thianaphthoic acid, m.p. 240–243°. No 3-thianaphthenylacetic acid could be detected.

E. **Formaldehyde.**—The reagent from 45 g. of I was treated with the gas from 40 g. of paraformaldehyde. The solution of the product in hexane–benzene deposited a total of 5.19 g. of very crude material; m.p. 133–138°. By repeated recrystallization from acetone–benzene, the melting point of the compound, probably 2-(2-hydroxymethyl-3-thianaphthenyl)-ethanol, was raised to 141–142°. (*Anal.* Calcd. for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81. Found: C, 63.22; H, 5.83.) When 3.4 g. was desulfurized[7a] with about 48 g. of Raney nickel in ethanol, 1.83 g. of an impure oil (b.p. 160–164° at 0.9 mm.) was isolated; it did not give a crystalline phenylurethan.

The original mother liquors were distilled. The viscous distillate (b.p. 134–150° at 0.4 mm., $n^{20}\text{D}$ 1.6445) weighed 22.1 g. (50%). A sample of the fraction boiling at 139–140° was submitted for analysis.

Anal. Calcd. for $C_{10}H_{10}OS$: C, 67.38; H, 5.66. Found: C, 67.20; H, 5.71.

All cuts crystallized slowly and only partially. From the above fraction, which weighed 7.4 g., by filtration and two recrystallizations from hexane, was obtained 1.3 g. (18% of this fraction) of 3-methyl-2-thianaphthenylcarbinol, m.p. 90–92°, identical with the compound described below. No further separation could be effected by recrystallization. An attempt to obtain the known phenylurethan of 2-(3-thianaphthenyl)-ethanol[8] from the viscous filtrate of the same cut gave oils.

The ether-insoluble 3-methyl-2-thianaphthoic acid (32.2 g.) was reduced with 8 g. of lithium aluminum hydride in about 400 ml. of ether using a pressure-equalized dropping funnel as a continuous-return extractor. The excess hydride was destroyed with ethyl acetate, and the product recrystallized from hexane. 3-Methyl-2-thianaphthenylcarbinol (28.1 g., 95%) formed colorless rods, m.p. 90.6–91.6°, which were sublimed at 100° and 0.2 mm. for analysis.

Anal. Calcd. for $C_{10}H_{10}OS$: C, 67.38; H, 5.66. Found: C, 67.60; H, 5.71.

F. **Ethylene Oxide.**—From 0.0405 mole of reagent and 10 ml. of ethylene oxide was obtained 2.76 g. (35%) of a viscous oil; b.p. 130–138° (0.3 mm.). (*Anal.* Calcd. for $C_{11}H_{12}OS$: C, 67.71; H, 6.29. Found: C, 68.53; H, 6.21.) It (0.8 g.) was treated with 0.4 g. of phenyl isocyanate, and the mixture of phenylurethans recrystallized repeatedly from hexane with final seeding with the authentic derivative of 2-(3-methyl-2-thianaphthenyl)-ethanol. A total of 0.10 g. of this derivative (m.p. 127–129°) was obtained. The remaining material melted at 90–95° and was recrystallized from hexane with seeding with the phenylurethan of 3-(3-thianaphthenyl)-propanol, giving 0.06 g. of this pure compound (m.p. 95–96°). Further separation was not attempted; no depressions were noted in the mixed melting points with authentic compounds.

A mixture of 12.2 g. of 3-methylthianaphthene, 10.2 g. of acetic anhydride and 3.0 g. of boron trifluoride etherate was heated an hour at 100°. After hydrolysis, distillation gave 6.8 g. (44%; b.p. 129–131° at 0.5 mm.) of an oil which solidified; m.p. 70–75°. After recrystallization from hexane–methanol, the needles of 3-methyl-2-acetothianaphthone were sublimed at 60° (1 mm.); m.p. 76.5–77.5°.

Anal. Calcd. for $C_{11}H_{10}OS$: C, 69.44; H, 5.30. Found: C, 69.33; H, 5.51.

The ketone (5.0 g.), 7 g. of morpholine and 1.3 g. of sulfur were heated under reflux for 12 hours. Addition of ethanol and water gave 7.5 g. of a tarry solid. A sample of the thiomorpholide of 3-methyl-2-thianaphthenylacetic acid was recrystallized from ethanol; m.p. 112–113°.

Anal. Calcd. for $C_{15}H_{17}NOS_2$: C, 61.82; H, 5.88. Found: C, 62.10; H, 6.06.

The solid and mother liquors were recombined and heated for 10 hours with 5 g. of potassium hydroxide in ethanol. 3-Methyl-2-thianaphthenylacetic acid (3.1 g., 57%) was recrystallized from benzene–hexane; m.p. 150.4–152°. It sublimed at 140° and 0.1 mm.

Anal. Calcd. for $C_{11}H_{10}O_2S$: C, 64.05; H, 4.89. Found: C, 64.28; H, 4.92.

Reduction of the acid (2.50 g.) with lithium aluminum hydride gave 2.06 g. (89%) of 2-(3-methyl-2-thianaphthenyl)-ethanol, a viscous oil; $n^{20}\text{D}$ 1.6237; $d^{20}{}_4$ 1.190.

Anal. Calcd. for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.62; H, 6.56.

The phenylurethan formed fine needles from hexane–benzene; m.p. 128.6–129.6°.

(7a) The procedure was that of F. F. Blicke and D. G. Sheets, THIS JOURNAL, **71**, 4010 (1949).

(8) P. Cagniant, *Bull. soc. chim. France*, 382 (1949), prepared this alcohol (phenylurethan, m.p. 110°) and, from it, the propionic acid, m.p. 145°.

Anal. Calcd. for $C_{18}H_{17}NO_2S$: C, 69.42; H, 5.50. Found: C, 69.33; H, 5.58.

A mixture of 26.8 g. of thianaphthene, 19.6 g. of propionyl chloride and 100 ml. of carbon disulfide, stirred and cooled in ice, was treated with 32 g. of aluminum chloride in small portions during one hour. After decomposition with ice and distillation, the product mixture (b.p. 125–145° at 0.3 mm.) weighed 21.7 g. (57%); m.p. 50–75°. By recrystallization from methanol–hexane, a total of 8.4 g. of 3-propiothianaphthone,[9] m.p. 79–81°, was obtained. No further separation of the isomers could be effected.

The ketone (8.4 g.) was subjected to the Kindler–Willgerodt procedure described above. No crystalline thiomorpholide was obtained and the entire mixture was hydrolyzed. A total of 3.9 g. (43%) of plates of 3-(3-thianaphthenyl)-propionic acid[8] crystallized from benzene; m.p. 147–148.5°. It sublimed at 140° (0.2 mm.).

Anal. Calcd. for $C_{11}H_{10}O_2S$: C, 64.05; H, 4.89. Found: C, 64.00; H, 4.96.

By reduction with lithium aluminum hydride, 3.6 g. of the acid gave 2.77 g. (83%) of 3-(3-thianaphthenyl)-1-propanol; b.p. 139–142° (0.3 mm.); $n^{20}D$ 1.6174.

Anal. Calcd. for $C_{11}H_{12}OS$: C, 68.71; H, 6.29. Found: C, 68.45; H, 6.44.

The phenylurethan, m.p. 96.5–97.5°, was recrystallized from benzene–hexane.

Anal. Calcd. for $C_{13}H_{17}NO_2S$: C, 69.42; H, 5.50. Found: C, 69.54; H, 5.63.

Reactions of 3-(Chloromethyl)-thianaphthene (I).—To a solution of 24.2 g. of the halide in 70 ml. of dioxane was added a solution of 61 g. of stannous chloride in 70 ml. of concd. hydrochloric acid and 70 ml. of dioxane; it was heated at 70° for an hour. 3-Methylthianaphthene (11.6 g., 59% yield) was obtained. From the residue after distillation, 4.5 g. of a solid was isolated by crystallization from hexane. This compound, presumably 3-methyl-2-(3-thianaphthenylmethyl)-thianaphthene, melted at 121–122°.

Anal. Calcd. for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79. Found: C, 73.55; H, 4.93.

Several experiments were conducted to improve the yield (28%) of 3-thianaphthenylacetic acid previously obtained[6] from the chloride by the cyanide synthesis. In one run, a mixture of 18.3 g. of halide with sodium cyanide in anhydrous acetone was heated overnight, but no reaction occurred since attempted hydrolysis with alcoholic alkali led only to ethyl 3-thianaphthenylmethyl ether (11.4 g., 59%; b.p. 104–105° at 0.5 mm.). It had the following properties: $n^{20}D$ 1.5921; d^{20}_4 1.135; *MR* (calcd.) 55.19, (obsd.) 57.25.

Anal. Calcd. for $C_{11}H_{12}OS$: C, 68.71; H, 6.29; S, 16.67. Found: C, 68.72; H, 6.34; S, 16.88.

However, a mixture of 23.2 g. of chloride, 13 g. of powdered potassium cyanide and 20 ml. of 1% sodium iodide in acetone, when stirred and heated under reflux for 4 hours, then diluted with 10 ml. of water and heated and stirred for 12 hours, gave after hydrolysis[6] with alkali 17.5 g. (72% based on the chloride) of the acetic acid; m.p. 107–109°.

Attempted Reaction[10] of 3-Methyl-2-thianaphthenylmagnesium Bromide with Duryl *o*-Methoxyphenyl Ketone.[11]—The ketone (3.8 g.) in 40 ml. of dry benzene was added to the Grignard reagent (containing unchanged magnesium) from 4.0 g. of halide and 0.5 g. of magnesium in 25 ml. of ether. The ether was removed by distillation and the residual mixture was heated and stirred 7 hours. After volatile materials had been removed from the oily product by distillation *in vacuo*, addition of acetone precipitated 1.0 g. of a white powder. Recrystallization from benzene gave 2,2′-diduroylbiphenyl[12] in plates; m.p. 257–258.6°.

Anal. Calcd. for $C_{34}H_{34}O_2$: C, 86.04; H, 7.22. Found: C, 86.10; H, 7.26.

To a mixture of 9.0 g. of mercuric bromide and 4.8 g. of magnesium powder in 40 ml. of ether was added 3.0 g. of duryl *o*-methoxyphenyl ketone in 40 ml. of benzene. The ether was removed by distillation; after heating for two hours the mixture was deep blue. The product was recrystallized from ethanol, and the crystals triturated with benzene. The benzene-soluble compound was 2,2′-diduroylbiphenyl; m.p. 248–251°. The insoluble 9,10-diduryl-9,10-dihydro-10-hydroxy-1-methoxyphenanthrene[13] formed plates from acetone–benzene; m.p. 256–263° (dec.).

Anal. Calcd. for $C_{35}H_{38}O_2$: C, 85.67; H, 7.81. Found: C, 85.55; H, 7.92.

The diphenoyl chloride from 4.8 g. of diphenic acid and 11 ml. of thionyl chloride was mixed with 6.7 g. of durene and 60 ml. of carbon disulfide and treated with stirring and cooling by ice with 6.7 g. of aluminum chloride; the mixture was allowed to warm to room temperature and hydrolyzed with ice. The product, 2,2′-diduroylbiphenyl (6.3 g., 66%; m.p. 251–254°), did not depress the melting points of samples isolated previously.

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[9] F. Challenger and S. A. Miller, *J. Chem. Soc.*, 1005 (1939), prepared the compound in low yield using stannic chloride as the catalyst.

[10] This experiment was intended as an independent synthesis performed before the nature of the product of the reaction of II with benzoyldurene was apparent.

[11] R. C. Fuson and W. C. Hammann, THIS JOURNAL, **73**, 1851 (1951).

[12] Subsequent to our identification of this compound, Prof. R. C. Fuson kindly informed us that it had been prepared in his laboratory by two still different methods. The isolation of this product of coupling is interesting in connection with the observation of R. C. Fuson and C. Hornberger, Jr., *J. Org. Chem.*, **16**, 637 (1951), that reduction of mesityl o-methoxyphenyl ketone with the magnesium-magnesium iodide couple gave 9,10-dimesitylphenanthrene and other related products. Presumably the diketone is an intermediate in this reaction, *i.e.*, coupling occurs before other conceivable steps.

[13] This compound is analogous to one isolated by Fuson and Hornberger, ref. 12, in a similar experiment with the mesityl analog.