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

Abnormal Reactions of 2-Thianaphthenylmethylmagnesium Chloride

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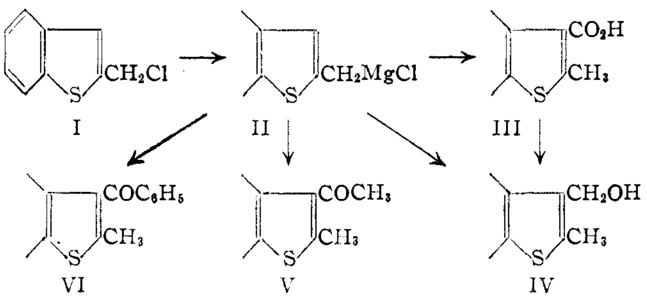
Treatment of the Grignard reagent obtained from 2-(chloromethyl)-thianaphthene with carbon dioxide, acetyl chloride, formaldehyde, and ethyl benzoate led exclusively to products substituted in the 3-position. The reagent added to benzoyldurene in the 1,2 manner and normally. The results are discussed in terms of the aromaticity of thianaphthene.

Previous reports described abnormal reactions of 2-thenylmagnesium chloride[1]—which produced predominantly 2-methyl-3-substituted-thiophenes—and the reaction of 2-(chloromethyl)-benzofuran[2] with magnesium—which yielded exclusively *o*-allenylphenol. The analogous derivative of thianaphthene has been investigated to determine the effect of the fused structure in the thiophene series.

2-(Chloromethyl)-thianaphthene (I in Chart A) was converted efficiently in the cyclic reactor to the Grignard reagent (II), also obtained in fair yield by conventional means. The reactions of I with carbon dioxide, formaldehyde, acetyl chloride and ethyl benzoate were carried out. The resulting derivatives were solids with favorable properties, permitting more conclusive characterizations than were possible in the thiophene series where some of the products were liquids of uncertain isomeric purity.[1] The products, III, IV, V and VI, respectively, resulted exclusively from abnormal reactions. Only in the case of acetyl chloride could a second product be isolated—in trace amounts; its composition was that of 1,3-bis-(2-thianaphthenyl)-2-methylpropene or an isomer, and the compound was apparently analogous to a secondary product in the thiophene work.[1]

CHART A



The structure of 2-methyl-3-thianaphthoic acid (III) was demonstrated by oxidation and conversion to thianaphthene-2,3-dicarboanhydride. 2-Methyl-3-thianaphthenylcarbinol (IV) was also obtained by reduction of the acid (III) with lithium aluminum hydride. 2-Methyl-3-acetothianaphthone (V) and 3-benzoyl-2-methylthianaphthene (VI) were the products of acetylation and benzoylation, respectively, of 2-methylthianaphthene.

With the apparently great tendency of I toward the rearrangement in mind, it was allowed to react with benzoyldurene.[3] The only isolated product was 1-duryl-1-phenyl-2-(2-thianaphthenyl)-ethanol the result of normal 1,2-addition. The structure was evident from the observation that the alcohol was easily dehydrated by heating with a trace of iodine, giving a compound which could only be 1-duryl-1-phenyl-2-(2-thianaphthenyl)-ethylene.

The order of decreasing tendency toward rearrangement of α-arylmethyl Grignard reagents[1] based on carbonation may be expanded as follows: 2-thianaphthenylmethyl, 3-furfuryl, 2-thenyl, benzyl. On this basis, one concludes that thianaphthene is less "aromatic" than furan, or, in other words, that the vinyl sulfide linkage interacts less with the rest of the molecule than does the vinyl ether portion of furan. This surprising conclusion is being tested by other related approaches.

Acknowledgment.—The author is indebted to the Graduate School for grants-in-aid for the 1950–1951 and 1951–1952 academic years. Generous gifts of thianaphthene by the Jefferson Chemical Company, New York, N. Y., and of durene by The Humble Oil and Refining Company, Houston, Texas, are greatly appreciated.

Experimental Part[4]

2-(Chloromethyl)-thianaphthene (I).—2-(Hydroxymethyl)-thianaphthene, prepared previously by reaction of 2-thianaphthenylsodium with formaldehyde,[5] was obtained by similar treatment of the lithium derivative.[6] From 67 g. of thianaphthene was obtained 39 g. (48% yield or 89% based on recovery), m.p. 97–99°; by vacuum distillation of the mother liquors 31 g. of thianaphthene (46%) was reclaimed. The alcohol was converted to the known chloride (I) by thionyl chloride.[5]

2-Thianaphthenylmethylmagnesium Chloride (II).—Use of the cyclic reactor in this Laboratory has been described.[1] In this case, it was necessary to prepare a freshly amalgamated column of magnesium turnings for each run, since reinitiation of an old charge gave lower yields. The best yield of reagent from 5–10 g. of halide was 93%. By a conventional procedure a 61% yield was obtained; a search for the expected product of coupling was fruitless.

Reactions of II.—The procedures were similar to those outlined for the 2-thenyl reagent.[1] Precautions designed to prevent incidental loss of reagent were more important than in the earlier work since smaller amounts of halide

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(1) R. Gaertner, THIS JOURNAL, **73**, 3934 (1951).

(2) R. Gaertner, *ibid.*, **73**, 4400 (1951).

(3) Benzyl Grignard reagents ordinarily add in the conjugate manner to such highly hindered ketones; thus, R. C. Fuson and B. C. McKusick, *ibid.*, **65**, 60 (1943), found that benzylmagnesium chloride adds 1,6 to benzoyldurene, giving *p*-benzylphenyl duryl ketone. Professor Fuson kindly suggested an investigation of the possibility that the 2-thenyl reagent, for example, might behave similarly, with rearrangement. Although a number of examples of 1,2-addition to hindered ketones are available, II appears to be the first benzyl-type Grignard reagent to react in this fashion. For a review of this chemistry, see R. Gaertner, *Chem. Revs.*, **45**, 493 (1949).

(4) 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.

(5) F. F. Blicke and D. G. Sheets, THIS JOURNAL, **71**, 2856 (1949), reported 29.5% recovery and 56.5% yield (based on thianaphthene consumed).

(6) D. A. Shirley and M. D. Cameron, *ibid.*, **72**, 2788 (1950), described only carbonation of this reagent, which is superior for the present purposes by reason of safety, solubility of the alcoholate in ether, and recovery.

were used. The solutions were generally 50–100% less concentrated but no apparent dilution effects were noted. Conditions and yields may not have been optimum.

A. **Carbonation.**—From a solution containing 0.0256 mole of reagent was isolated an acidic fraction which was recrystallized from benzene. A total of 2.16 g. (45% yield) of tan crystals, m.p. 192–194°, separated. By sublimation of the gummy residue in the mother liquors, 0.04 g. of colorless material, m.p. 130–140°, was obtained; it may have been 2-thianaphthenylacetic acid[7] but there was too little for study. Recrystallization of 2-methyl-3-thianaphthoic acid (III) from benzene–acetone and sublimation at 130° (0.1 mm.) gave colorless needles; m.p. 195.8–196.4°.

Anal. Calcd. for $C_{10}H_8O_2S$: C, 62.48; H, 4.10. Found: C, 62.67; H, 4.33.

Oxidation[1] of 1.0 g. of the acid yielded 0.27 g. of thianaphthene-2,3-dicarboxylic acid[8]; m.p. 249.5–251.5°. The anhydride[8] was obtained in good yield by treatment with acetic anhydride and isolated by sublimation; m.p. 169–171°.

From the neutral fraction, by recrystallization from hexane, was isolated 0.47 g. of crude 2-(hydroxymethyl)-thianaphthene, m.p. 95–98°, and 1.17 g. (b.p. 105–108° at 10 mm.) of crude 2-methylthianaphthene,[9] m.p. 49–50°. The picrate[9] formed canary-yellow needles; m.p. 108.5–109.5°. A resin remained in the still-pot.

B. **Formaldehyde.**—The gas generated from 10 g. of paraformaldehyde was passed into a solution containing 0.0167 mole of reagent. Besides 2-methylthianaphthene, only 2-methyl-3-thianaphthenylcarbinol (IV) was isolated (1.05 g., 35% yield; m.p. 144–146°). By recrystallization from hexane–benzene and sublimation at 100° (0.2 mm.), colorless needles were obtained; m.p. 145.8–147.4°.

Anal. Calcd. for $C_{10}H_{10}OS$: C, 67.38; H, 5.66. Found: C, 67.45; H, 5.61.

Reduction of 0.78 g. of 2-methyl-3-thianaphthoic acid with lithium aluminum hydride in ether produced 0.31 g. of the alcohol (m.p. 146–147°, no depression with above product), 0.30 g. of acid being recovered.

C. **Acetyl Chloride.**—The oily product obtained from the treatment of 0.0277 mole of reagent with 28 ml. of acetyl chloride failed to crystallize and was distilled in a small sausage flask. Besides the low-boiling 2-methylthianaphthene, a total of 1.95 g. of very crude distillate, boiling principally at 127–129° (0.2 mm.) and melting at 69–73°, was collected. By recrystallization from hexane 1.51 g. (29%) of colorless plates, m.p. 69–70°, was formed, leaving intractable material in the mother liquors. 2-Methyl-3-acetothianaphthone (V) was sublimed twice at 70° (0.1 mm.) for analysis.

Anal. Calcd. for $C_{11}H_{10}OS$: C, 69.44; H, 5.30. Found: C, 69.68; H, 5.47.

Acetylation[10] of 2-methylthianaphthene with acetic anhydride and boron trifluoride etherate gave a poor yield of the ketone; m.p. 68.5–70° (no depression with above compound).

From the residue in the original distillation, by dissolving the black resin in chloroform, decolorizing, recrystallizing from ethanol and then from hexane, and finally distilling in a sublimation apparatus at 140° (0.1 mm.) was obtained 0.22 g. of colorless plates with a double melting point: 111.6–113° and 121–122°. The composition was that of 1,3-bis-(2-thianaphthenyl)-2-methylpropene or an isomer.

Anal. Calcd. for $C_{20}H_{16}S_2$: C, 74.96; H, 5.03; S, 20.01. Found: C, 75.13; H, 5.21; S, 20.10.

D. **Ethyl Benzoate.**—A solution (95 ml.) containing 0.0343 mole of reagent was added dropwise to a solution of 41 g. of the ester in 100 ml. of anhydrous ether stirred mechanically and cooled in a Dry Ice–acetone-bath. When the solution had warmed to 0°, dilute hydrochloric acid was added. The residue did not solidify after the excess ester had been removed by distillation at 1 mm. and it was distilled twice in a small sausage flask. The tan distillate (b.p. 150–175°; 3.5 g.) solidified and was recrystallized from hexane. A total of 2.03 g. (23% yield) of light yellow crystals separated; m.p. 72.5–75°. The gummy residue in the mother liquors was intractable. Recrystallization from methanol–hexane and distillation in a sublimation apparatus at 110° (0.7 mm.) produced colorless prisms of 3-benzoyl-2-methylthianaphthene; m.p. 74.8–76.5°.

Anal. Calcd. for $C_{16}H_{12}OS$: C, 76.16; H, 4.80. Found: 76.02; H, 4.91.

This compound (m.p. 74–76°; no depression) was also prepared by treatment of 2-methylthianaphthene with benzoyl chloride in the presence of stannic chloride.

E. **Benzoyldurene.**—A solution (100 ml.) containing 0.0361 mole of the reagent was pipetted onto 11.9 g. of the ketone. The initially deep purple solution changed rapidly to red-brown; it was heated under reflux for two hours and treated with dilute hydrochloric acid. A solution (35 ml.) of the product mixture in ethanol deposited 1.8 g. of unchanged benzoyldurene. The mother liquor was diluted with about 200 ml. of hexane and this solution deposited crystals overnight. By distilling the solvents, redissolving the residue in hexane, and seeding, additional crops were obtained. The combined material was recrystallized from ethanol–benzene, giving a total of 4.27 g. (31% yield) of colorless plates, m.p. 126–127.5°. Further recrystallization from ethanol–acetone gave pure 1-duryl-1-phenyl-2-(2-thianaphthenyl)-ethanol; m.p. 126.4–127.4°.

Anal. Calcd. for $C_{26}H_{26}OS$: C, 80.79; H, 6.78; S, 8.29. Found: C, 81.19, 81.02; H, 6.69, 6.78; S, 8.15.

It did not reduce neutral permanganate in acetone. When 0.70 g. was heated to 150° in a metal-bath and a small crystal of iodine added, water vapor was rapidly evolved. After being heated to 200° and cooled, the black glass was dissolved in benzene. Addition of ethanol precipitated the crude product, which was recrystallized from hexane. Colorless needles, m.p. (after sublimation at 160° and 0.1 mm.) 163.8–164.6°, of 1-duryl-1-phenyl-2-(2-thianaphthenyl)-ethylene resulted.

Anal. Calcd. for $C_{26}H_{24}S$: C, 84.74; H, 6.56. Found: C, 84.77; H, 6.75.

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RECEIVED SEPTEMBER 10, 1951

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[7] The melting point of the pure compound is 141–142°.[4]

[8] A. Bezdrik, P. Friedländer and P. Koeniger, *Ber.*, **41**, 227 (1908).

[9] C. Hansch and W. A. Blondon, THIS JOURNAL, **70**, 1561 (1948).

[10] The procedure was similar to that of M. W. Farrar and R. Levine, *ibid.*, **72**, 4433 (1950), for acetylation of thianaphthene.