214. *The Mercuration of Thionaphthen.*

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Thionaphthen and mercuric acetate in hot aqueous methyl alcohol give a *dimercuriacetate*. At the ordinary temperature a monomercuriacetate also may be isolated. This with propionyl chloride gives *thionaphthenyl ethyl ketone* identical with a specimen prepared from thionaphthen, propionyl chloride and stannic chloride. Both these ketones give the same *semicarbazone* and 2 : 4-dinitrophenylhydrazone and, on oxidation, that obtained by the direct Friedel–Crafts reaction yields thionaphthen-2-carboxylic acid. The mercuriacetate group therefore enters the 2-position in thionaphthen, replacement by the propionyl group being assumed to proceed normally. Mercuration thus falls into line with bromination, nitration, and the direct introduction of acetyl. The monomercuriacetate is converted by sodium iodide or calcium chloride into *di-2-thionaphthenylmercury*. Heating with sodium sulphide or hydrosulphide converts the dimercuriacetate into thionaphthen. Thionaphthen with hot aqueous alcoholic mercuric chloride and sodium acetate gives a *dimercurichloride*.

BEZDRIK, FRIEDLÄNDER, and KÖNIGER (*Ber.*, 1908, **41**, 232) warmed thionaphthen with mercuric acetate in acetic acid or alcohol and obtained " one or more " mercuriacetates.

The mercury content of one of them corresponded to thionaphthenyl mono-mercury acetate. No m. p. is recorded. Weissgerber and Krüber (*Ber.*, 1920, **53**, 1557) heated crude coal-tar thionaphthen containing much naphthalene with methyl-alcoholic mercuric acetate and obtained a mercuriacetate (no m. p. or analysis is recorded) which gave pure thionaphthen on decomposition with acid. This method was employed by Challenger *et al.* (*J. Inst. Pet. Tech.*, 1926, **12**, 106) for the detection of thionaphthen in Kimmeridge shale oil.

With thionaphthen and mercuric acetate in hot aqueous methyl-alcoholic solution we have obtained a *dimercuriacetate.* At the ordinary temperature the product is a mixture from which a slightly impure monomercuriacetate may be isolated along with the di-derivative.

The monomercuriacetate with propionyl chloride gives *thionaphthenyl ethyl ketone* identical with a specimen prepared from thionaphthen, propionyl chloride, and stannic chloride (compare the formation of 2-thienyl methyl ketone from 2-thienyl mercury chloride and acetyl chloride by Volhard; *Annalen*, 1892, **267**, 178). The use of stannic chloride instead of aluminium chloride is to be recommended where it is desired to restrict the Friedel–Crafts reaction to the thiophen nucleus (Stadnikoff *et al.*, *Ber.*, 1928, **61**, 268, 1996, 2341).

Both these ketones gave the same *semicarbazone* and on oxidation that specimen prepared by the direct Friedel–Crafts reaction yielded thionaphthen-2-carboxylic acid. The orientation of this derivative was established by its formation from carbon dioxide and thionaphthenylmagnesium bromide, a compound which gives 2-hydroxythionaphthen on oxidation (Komppa, *J. pr. Chem.*, 1929, **122**, 319; see also Komppa and Weckmann, *ibid.*, 1933, **138**, 109; Fries and Hemmecke, *Annalen*, 1929, **470**, 1; Crook and Davies, J., 1937, 1697).

The mercuriacetate group therefore enters the 2-position in thionaphthen, on the assumption that its replacement by propionyl proceeds normally. Mercuration of thionaphthen thus falls into line with bromination, nitration, and the direct introduction of acetyl. The introduction of sodium, however, occurs in the 1- and 1 : 2-positions and that of MgBr in the 1-position (see Weissgerber and Krüber, *loc. cit.*; Schönberg *et al.*, *Ber.*, 1933, **66**, 234).

Reaction with hot alcoholic mercuric chloride is slow (thionaphthen and thiopheno-2′ : 3′ : 2 : 3-thiophen can be separated by fractional mercuration at the ordinary temperature; see Challenger and Harrison, *J. Inst. Pet. Tech.*, 1935, **21**, 145), but in presence of sodium acetate a *dimercurichloride* may be obtained. The monomercuriacetate is converted by sodium iodide or by calcium chloride into *di-2-thionaphthenylmercury.*

Heating with sodium sulphide or hydrosulphide converts thionaphthenyl dimercuriacetate into thionaphthen. For analogous reactions with other mercurated compounds, see Otto (*Annalen*, 1870, **154**, 191).

EXPERIMENTAL.

Thionaphthen and Mercuric Chloride.—Thionaphthen (5 g.) was refluxed with mercuric chloride (30 g.; 3 mols.) in alcohol (150 c.c.) for 8 hours. As the reaction was still incomplete, sodium acetate (5 g.) in a little water was added, and the mixture refluxed for several hours. The deposit was washed with boiling water and dried. The *dimercurichloride* was insoluble in most solvents, but after two recrystallisations from nitrobenzene it melted at 279—281°. Mercury was determined in this and similar products as sulphide after decomposition with warm hydrochloric acid (Found : Hg, 66·9. C_8H_5ClSHg requires Hg, 54·3%. $C_8H_4Cl_2SHg_2$ requires Hg, 66·2%).

In an unsuccessful attempt to obtain a monomercurichloride, thionaphthen (10 g.), mercuric chloride (30 g.; 1·5 mols.) in alcohol (250 c.c.), and water (150 c.c.) were refluxed with sodium acetate (10 g.) for several hours. The washed precipitate after three crystallisations as before melted at 279—281° (Found : Hg, 65·4%).

Thionaphthen and Mercuric Acetate.—Thionaphthen (4 g.) in methyl alcohol (160 c.c.) was refluxed for 2 hours with a solution of mercuric oxide (16 g.) in acetic acid (20 c.c.) and water (120 c.c.). The white deposit (9 g.) was separated and washed with benzene and alcohol [Found :

Hg, 61·3. $C_8H_5S·Hg·O·CO·CH_3$ requires Hg, 51·1%. $C_8H_4S(Hg·O·CO·CH_3)_2$ requires Hg, 61·6%].

A *monomercuriacetate* containing a small amount of the di-derivative was obtained thus: Thionaphthen (15 g.), mercuric acetate (40 g.), water (500 c.c.), and alcohol (70 c.c.) were stirred for 2—3 days at room temperature. The deposit, after being washed with alcohol and ether, melted at 220° with previous blackening (Found: Hg, 57·5%). Refluxing with alcohol left the insoluble dimercuriacetate (Found: Hg, 61·6%). The extract deposited crystals, m. p. 208—209° after one recrystallisation from alcohol (Found: Hg, 54·1%). After two further recrystallisations these melted for the last two times at 207—208° (Found: Hg, 52·1%). Another preparation also had m. p. 207—208° (Found: C, 30·1; H, 2·2; S, 8·2. $C_8H_5S·Hg·O·CO·CH_3$ requires C, 30·6; H, 2·0; S, 8·2; Hg, 51·1%).

Thionaphthenyl Monomercuriacetate and Propionyl Chloride.—The mercury compound (2 g.) and propionyl chloride (25 c.c.) were left for 5 days at room temperature, the mixture poured into water, treated with sodium carbonate, and extracted with ether, and the residue distilled in steam, giving a volatile solid which after three crystallisations from ligroin melted at 81·5—82·5° and at 82—83° in admixture with 2-*thionaphthenyl ethyl ketone*, m. p. 82—83° (see below). The ketone gave a semicarbazone, m. p. 203·5—205° and mixed m. p. 204—205° with the semicarbazone of 2-thionaphthenyl ethyl ketone, m. p. 204—205°.

In another experiment the mercuriacetate (1 g.) and propionyl chloride (5 c.c.) were heated at 100° for an hour. Treatment as before gave an oil which did not completely solidify below 0°. This gave a 2 : 4-dinitrophenylhydrazone, m. p. 218—220°, and mixed m. p. 219—221° with synthetic thionaphthenyl ethyl ketone 2 : 4-dinitrophenylhydrazone, m. p. 220—221°.

2-*Thionaphthenyl Ethyl Ketone.*—Thionaphthen (8 g.) and propionyl chloride (12 g.) in carbon disulphide (80 c.c.) were mixed with a solution of stannic chloride (20 g.) in carbon disulphide (100 c.c.) and left for 2 days at room temperature. The mixture became deep red and a viscous black solid separated. Addition of water and ether, removal of solvents and distillation in steam gave a white volatile solid, which after three crystallisations from ligroin (b. p. 80—100°) melted constantly at 83°. Yield, 15—20% (Found: C, 69·5; H, 5·4; S, 16·8. $C_{11}H_{10}OS$ requires C, 69·5; H, 5·3; S, 16·8%). The *semicarbazone* melted constantly at 204—205° after four crystallisations from slightly diluted alcohol (Found: C, 58·4; H, 5·3. $C_{12}H_{13}ON_3S$ requires C, 58·3; H, 5·4%). The 2 : 4-dinitrophenylhydrazone formed red crystals, m. p. 220—221° after three recrystallisations from alcohol–benzene.

Oxidation of 2-*Thionaphthenyl Ethyl Ketone to Thionaphthen*-2-*carboxylic Acid.*—The ketone (0·5 g.), potassium ferricyanide (40 g.), and potassium hydroxide (15 g.) in water (125 c.c.) were warmed under reflux for 3 hours. The liquid was then filtered from a little ferric hydroxide and acidified, inorganic salts were separated and washed with alcohol and ether, and the filtrate and washings were extracted with ether. After removal of more inorganic matter evaporation of the extracts gave a residue (0·25 g.) which on crystallisation from alcohol had m. p. 170—171°. After three crystallisations from slightly diluted alcohol this melted at 174—175°. Thionaphthen-2-carboxylic acid melts at 174—175° (Found: C, 60·5; H, 3·5. Calc. for $C_9H_6O_2S$: C, 60·7; H, 3·4%).

Di-2-*thionaphthenylmercury.*—(I) Thionaphthenyl-2-mercuriacetate (3 g.), sodium iodide (6 g.), and alcohol (180 c.c.) were boiled under reflux for 3 hours, the mixture poured into water (500 c.c.), and the precipitate washed with much water. It melted at 314—317° and could be recrystallised only from nitrobenzene. Five operations gave a *product*, m. p. 322° when fairly rapidly heated. On slow heating, the m. p. varied between 313° and 320° (Found: C, 40·2; H, 2·2; S, 13·4. $C_{16}H_{10}S_2Hg$ requires C, 41·1; H, 2·1; S, 13·7%).

(II) In an attempt to convert thionaphthenyl-2-mercuriacetate into the corresponding chloride, 6 g. were boiled for some hours with calcium chloride (4 g.) in alcohol (100 c.c.). The deposit was separated, boiled with water, and recrystallised from much acetone. It darkened at about 230° and melted at 285—290° (Found: Hg, 44·7. $C_{16}H_{10}S_2Hg$ requires Hg, 43·0%. C_8H_5ClSHg requires Hg, 54·3%. $C_8H_5S·Hg·O·CO·CH_3$ requires Hg, 51·1%). The product therefore consisted of slightly impure di-2-thionaphthenylmercury.

(III) The mercuriacetate (1 g.), calcium chloride (1 g.), and alcohol (20 c.c.) were refluxed overnight and the deposit was boiled with water and then with alcohol and recrystallised twice from nitrobenzene. It was then free from halogen and melted at 320—321° alone and in admixture with di-2-thionaphthenylmercury obtained in (I).

The Action of Sodium Sulphide and Sodium Hydrogen Sulphide on Mercurated Derivatives of Thionaphthen.—A slightly impure specimen of thionaphthenyl dimercuriacetate (6·5 g. Found :

Hg, 59·35%) was distilled with a large excess of sodium sulphide (5 g.) in water (with or without previous saturation with hydrogen sulphide); thionaphthen (0·81 g.) readily volatilised.

The non-volatile solid was in each case a mixture, extraction with boiling nitrobenzene yielding fractions, m. p. 285° and 292—293°, which probably contained some di-2-thionaphthenylmercury. (Dr. J. Bruce found that the analogous thiophen derivative, dithienylmercury, is inert to boiling sodium sulphide, whereas the mono- and the di-mercurichloride give thiophen under these conditions.)

The aqueous filtrate contained sodium mercury sulphide, giving mercuric sulphide on acidification.

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