(XIII). Almost colorless, yielding solutions with marked blue fluorescence, it melts on recrystallization from acetone and methyl alcohol at 160°.

Anal. Calcd. for $C_{29}H_{22}O_2$: C, 86.52; H, 5.52. Found: C, 86.57; H, 5.68.

Reaction with Hydrogen Halides.—Treatment of (VII) in ether solution with dry hydrogen chloride and hydrogen bromide yields the ω-chloro and bromo derivatives (XIII). Treatment with thionyl chloride in the cold yields the same chloride, m. p. 189°, as yellow needles, highly fluorescent.

Anal. Calcd. for $C_{27}H_{19}Cl$: C, 85.55; H, 5.07. Found: C, 85.35; H, 5.06.

The bromide, m. p. 188°, was obtained as described above, and also by brominating 9-phenyl-10-benzylanthracene in carbon disulfide solution. No bromine was absorbed in the cold in the latter reaction and when reaction began on warming slightly, hydrogen bromide evolution immediately took place. It was recrystallized from carbon disulfide and ether.

Anal. Calcd. for $C_{27}H_{19}Br$: C, 76.56; H, 4.54. Found: C, 76.14; H, 4.81.

9-Phenyl-10-ω-oxybenzylanthracene (VIII).—A solution of 7 g. of the dihydroanthranol (VII) in 40 cc. of acetone and 5 cc. of 10% sulfuric acid was warmed on the water-bath until insoluble and high melting material began to separate (one hour). The solution was then filtered, poured into water and extracted with ether. The residue from evaporation of the washed and dried ether solution was recrystallized, first from alcohol, then from acetone and petroleum ether, m. p. 187°; yield 6.2 g., highly fluorescent in solution.

Anal. Calcd. for $C_{27}H_{20}O$: C, 89.96; H, 5.60. Found: C, 89.65; H, 5.68.

This compound seems to crystallize both with alcohol and acetone of crystallization, the solvent being lost between 70 and 80°. Recrystallization from acetone first, then from hot ethyl alcohol, or *vice versa*, seems to give a solvent-free product. No fluorescence of the original carbinol (VII) in solution could be detected, but on addition of acid and slightest warming, a marked blue fluorescence was noticeable.

On bromination, oxidation, acetylation, and treatment with dry hydrogen halides, this substance behaves exactly like the dihydroanthranol (VII) and yields identically the same products as have already been described.

Molecular Silver on Bromo Compound (XIII).—The bromide (XIII), warmed for a short time in benzene solution with molecular silver, is converted into a yellow, highly fluorescent substance, m. p. 252–253°, recrystallized from benzene–petroleum ether.

Anal. Calcd. for $C_{54}H_{38}$: C, 94.46; H, 5.54; mol. wt. 686. Found: C, 94.06; H, 5.53; mol. wt. (Rast, camphor), 524.

Summary

1. The Grignard reagent adds 1,6- to methyleneanthrone.

2. 10-Alkylanthranols readily yield crystalline peroxides with atmospheric oxygen and these peroxides suffer smooth pyrolysis to anthraquinone and alcohols formed by 1,4-elimination.

3. 10-Alkyl-9,10-dihydroanthranols are readily converted into anthracene derivatives, either by 1,4-elimination of substituents or by migration of groups.

4. A five-carbon atom isomerism in anthracene derivatives similar to the three-carbon atom isomerism in allyl compounds is conclusively demonstrated in the case of 9-phenyl-10-benzylidene-9,10-dihydroanthranol-9.

GREENCASTLE, INDIANA RECEIVED JUNE 17, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Comparison of Heterocyclic Systems with Benzene.[1] IV. Thionaphthenequinones

BY LOUIS F. FIESER AND R. GRICE KENNELLY

This series of investigations was undertaken with the idea that a comparison of the lowering in the reduction potential of a quinone resulting from the fusing of an unsaturated heterocyclic ring to the quinonoid ethylene linkage, with the lowering in potential produced by a benzene ring in the corresponding position, might afford a means of determining the degree of aromaticity of the heterocycle with respect to benzene. Fieser and Ames[1b] studied two quinones containing the thiophene nucleus, but each of these was of a rather special structural type. The purpose of the present work was to prepare and characterize simple ortho and para quinones derived from thionaphthene with the quinone grouping located in the carbocyclic ring.

The problem was largely a preparative one, for few quinones of the desired type have been described previously, and hydroxythionaphthenes suitable for use as starting materials are either unknown or rather inaccessible. The only route to the hydroxy compounds is by synthesis, since

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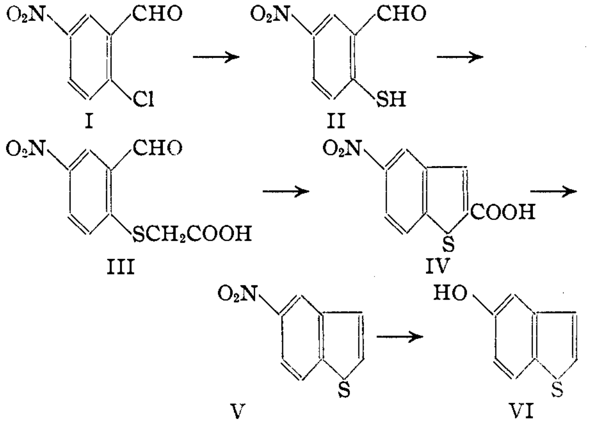
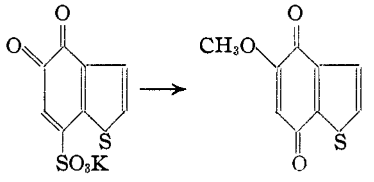
[1] Previous papers: (a) Fieser, THIS JOURNAL, **48**, 1097 (1926); (b) Fieser and Ames, *ibid.*, **49**, 2604 (1927); (c) Fieser and Peters, *ibid.*, **53**, 4080 (1931).

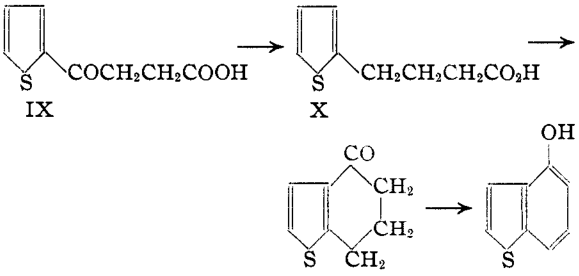
substitutions attack thionaphthene at the C_3 position[2] in the heterocyclic ring.[3] A synthesis of 5-hydroxythionaphthene (VI) recently has been reported by Fries[4] and described in detail by Hemmecke,[5] and we have found the method of great service in obtaining a typical ortho quinone of the series. The starting material, 2-chloro-5-nitrobenzaldehyde, I, is converted through the disulfide to the sulfhydryl compound II, and on reaction with chloroacetic acid and ring closure 5-nitrothionaphthene-2-carboxylic acid, IV, is obtained. Hemmecke reduced the nitro compound and decarboxylated the resulting amine, but we found it somewhat more convenient to decarboxylate IV with copper powder in quinoline solution[6] and to reduce the 5-nitro compound, V. Our over-all yield of 5-hydroxythionaphthene in five steps from *o*-chlorobenzaldehyde was 5%.


I II III IV V VI

All attempts to prepare 4,5-thionaphthenequinone were unsuccessful. 4-Amino-5-hydroxythionaphthene hydrochloride was obtained in a highly pure condition (through the azo dye), but it yielded only a black, sparingly soluble substance on oxidation. We were able to characterize potentiometrically the oxidation step to the quinoneimine, but the quinone itself was not obtained. A stable derivative suitable for potentiometric study was found, however, in potassium 4,5-thionaphthenequinone-7-sulfonate, VII, which was prepared as follows. The nitrosation of 5-hydroxythionaphthene by the usual method proceeded poorly, but the zinc salt of the nitroso compound was obtained easily by the method of Henriques and Ilinski,[7] and it could be converted into the sodium salt with little loss. The sodium salt reacted easily with sodium bisulfite to give 4-amino-5-hydroxythionaphthene-7-sulfonic acid, and this on oxidation yielded the *o*-quinone, which was isolated as the crystalline red potassium salt VII. The reaction of this quinone with methyl alcohol and sulfuric acid proceeded as in the naphthalene series,[8] giving the methoxy-*p*-thionaphthenequinone VIII.


VII VIII

As the starting point for the preparation of the unsubstituted para quinone, either 4-hydroxythionaphthene or 7-hydroxythionaphthene was required. The former compound has been obtained previously in very poor yield[9] by the condensation of α-thiophene aldehyde with sodium succinate, and the isomer is not known. We decided to attempt a new synthesis. The Friedel and Crafts reaction of thiophene with succinic anhydride in either nitrobenzene or carbon bisulfide gave in fair yield a keto acid which very probably has the structure of IX. That the substitution occurs at the α-position is inferred from the course of the condensations with phthalic anhydride[10] and with acyl halides.[11,12] All types of substitutions, in fact, yield chiefly the α-derivatives. Reduction of the keto acid to γ-(α-thienyl)-butyric acid (X) by the Clemmensen


IX X XI XII

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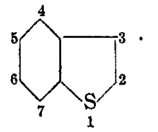
[2] Numbering system (German convention):



[3] Fries and Hemmecke, *Ann.*, **470**, 1 (1929); Komppa and Weckman, *J. prakt. Chem.*, **138**, 109 (1933).

[4] Fries, *Ann.*, **454**, 126 (1927).

[5] E. Hemmecke, Dissertation, Braunschweig, 1929.

[6] Shepard, Winslow and Johnson, THIS JOURNAL, **52**, 2083 (1930).

[7] Henriques and Ilinski, *Ber.*, **18**, 704 (1885).

[8] Fieser, THIS JOURNAL, **48**, 2922 (1926).

[9] Biedermann, *Ber.*, **19**, 1617 (1886).

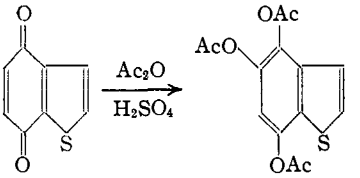
[10] Steinkopf, *Ann.*, **407**, 94 (1915).

[11] Scheibler and Rettig, *Ber.*, **59**, 1194 (1926).

[12] V. Meyer, Die "Thiophengruppe," 1888, pp. 155, 166

method was best accomplished by the low-temperature procedure,[13] for the thiophene nucleus appears to be sensitive to the action of strong hydrochloric acid at the boiling point. For the same reason aluminum chloride proved to be too active a reagent for the ring closure of X through the acid chloride. Using anhydrous stannic chloride, a milder reagent which has been used with success in the thiophene series[14] and with other particularly reactive aromatic systems,[15] 4-keto-4,5,6,7-tetrahydrothionaphthene, XI, was obtained in 90% yield. Dehydrogenation of the ketone to the desired 4-hydroxythionaphthene was accomplished in 46% yield with the use of sulfur. The hydroxy compound always was accompanied by a neutral fraction probably containing thionaphthene formed by the elimination of the elements of water. The yield was very poor when selenium was used, probably because of the slower dehydrogenating action and because of the destruction of the phenolic substance at the higher reaction temperature. The best over-all yield of 4-hydroxythionaphthene from thiophene was 14.5%.

An amino group was introduced by the reduction of the *p*-sulfobenzeneazo compound, and on oxidation there was obtained 4,7-thionaphthenequinone, XIII, a crystalline, yellow compound very similar in properties to α-naphthoquinone.



XIII XIV

Since the conjugated system of the quinone is unsymmetrical, there are two paths open for 1,4-addition reactions. In the one example studied, namely, the Thiele reaction, the only product isolated (33% yield) was that formed by addition to the system terminating in the C_7-carbonyl group, giving the triacetate XIV. The structure was established by converting the substance into a methoxythionaphthenequinone which proved to be identical with the compound VIII obtained in the other series of experiments.

A summary of the results of the potentiometric study of the new quinones is given in Table I, which includes for comparison values for the normal potentials of the corresponding naphthoquinones.

TABLE I

NORMAL REDUCTION POTENTIALS (25°)

Solvents: A, aqueous buffer; B, 50% alcohol, 0.1 *N* in HCl and 0.2 *N* in LiCl; C, 37% alcohol, 0.047 *M* in KH_2PO_4 and 0.047 *M* in Na_2HPO_4. Titrating agents: TB = tetrabromo-*o*-benzoquinone; KD = $K_2Cr_2O_7$; KM = $K_3Mo(CN)_8$.

System, named as oxidant	Solvent	Titrated with	Normal potential, E_0 (av.), v.
4,7-Thionaphthenequinone (XIII)	A (HCl)	KD	0.540
	B	TB	.559
α-Naphthoquinone	A (HCl)		.470[16]
	B		.484[17]
Pot. 4,5-Thionaphthenequinone-7-sulfonate (VII)	A (*p*H 4.9, *p*H 6.2)	KM	.705
Pot. 1,2-Naphthoquinone-4-sulfonate	A		.630[1a]
4,5-Thionaphthenequinone-4-imine	C	KM	.700[18]
1,2-Naphthoquinone-1-imine	C	KM	.622[18]

Various comparisons between the heterocyclic and the carbocyclic systems can be made and the results are all concordant. The para quinone derived from thionaphthene has a potential in aqueous solution 70 mv. higher than that of α-naphthoquinone, and in alcoholic solution the difference is 75 mv. The heterocyclic ortho quinone sulfonate is 75 mv. higher in potential than the naphthalene derivative. The β-thionaphthenequinone itself is not available, but a comparison is possible between the ortho quinone-imines of the thionaphthene and the naphthalene series, even though these substances are extremely unstable, and the difference in this case amounts to 78 mv. Clearly the ΔE_0 value for substances of quite different structural types is an essentially constant quantity.

As judged by the criterion of these oxido-reduction potentials, the thiophene ring is distinctly less aromatic than benzene. The effect of fusing a benzene ring to ortho or para benzoquinone is to lower the potential by 231 mv.[19] The average effect of the thiophene ring is 156

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(13) Krollpfeiffer and Schäfer, *Ber.*, **56**, 623 (1923); Anschütz and Wenger, *Ann.*, **482**, 32 (1930).

(14) Stadnikoff and Goldfarb, *Ber.*, **61**, 2341 (1928).

(15) Fieser and Fieser, THIS JOURNAL, **57**, 782 (1935).

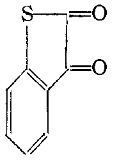
(16) La Mer and Baker, THIS JOURNAL, **44**, 1960 (1922).

(17) Fieser and Fieser, *ibid.*, **56**, 1565 (1934).

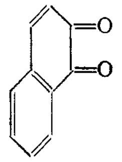
(18) Determined by the method of discontinuous titration (*ibid.*, **52**, 4915 (1930)). The figure reported is in each case the average of seven determinations agreeing within 1 mv. The values for the constant *C* were 0.97 and 1.23, respectively; the initial rates of change at the mid-point were 3.5 mv. per minute and 1.4 mv. per minute.

(19) Average of: 229, 239 (aqueous solutions); 231, 224 (alcoholic solutions).

mv., and if the relative aromaticity is the only factor involved it is given by the ratio of these two figures. The previous comparison[1b] of 2,3-thionaphthenequinone with β-naphthoquinone points in the same direction, but the difference is greatly magnified.



E_0 = 0.264 v.



E_0 = 0.555 v.

The free energy of reduction is considerably lower in the case of the heterocyclic quinone, which means that the dihydrothiophene ring has much less tendency than a dihydrobenzene ring to assume the aromatic structure which it acquires on conversion to the hydroquinone. This is a very direct and reliable measure of the relative aromaticities, and the fact that a much greater difference between thiophene and benzene is indicated by the direct than by the indirect method of comparison affords grounds for questioning the validity of the indirect method in which a heterocyclic ring is characterized by observing its effect upon a quinonoid nucleus. In the light of the direct comparison, the potential of 4,7-thionaphthenequinone (XIII) appears to be lower than would be expected if the aromaticity of the heterocycle were the only factor determining the effect of this ring. It was pointed out in the first paper of the series[1a] that the hetero atom may exert an influence independent of the stability of the ring system by functioning as the key atom of a substituent group. Since the effect of a group containing bivalent sulfur would be in the observed direction, that is, to lower the potential, it appears possible that this complicating factor indeed is involved. This point will be discussed further in the sixth paper of the series.

Experimental Part

1. Synthesis of 5-Hydroxythionaphthene (VI)

Redistilled *o*-chlorobenzaldehyde (70 g.) was nitrated according to Erdmann[20] and the crude precipitate was washed free of acid with sodium carbonate solution and crystallized from a mixture of 650 cc. of glacial acetic acid and 1300 cc. of water; yield, 75 g. (81%); m. p. 72–77°. This material was converted in quantities as large as 260 g. into 5-nitrothionaphthene-2-carboxylic acid by Hemmecke's method,[5] purification being accomplished by crystallization of the sodium salt from 2.5% alkali. Very satisfactory material (m. p. 239–241°) was obtained in 26% yield.

5-Nitrothionaphthene (V).—An intimate mixture of 50 g. of 5-nitrothionaphthene-2-carboxylic acid, 260 cc. of quinoline, and 13 g. of copper powder (Naturkupfer C) was heated under nitrogen with shaking and the bath temperature was soon brought to 180–190°. Decarboxylation proceeded vigorously and was complete in one-half hour. The cooled mixture was extracted with ether and the quinoline removed by extraction with 10% hydrochloric acid. After drying the ethereal solution and removing the solvent, the brown residue (m. p. 147–149°) was crystallized from dilute acetic acid, giving practically pure material; yield, 28 g. (69%).

The nitro compound is only moderately soluble in alcohol and more readily soluble in benzene. It forms pale yellow, feathery needles melting at 149–150°, and it has a pleasant, cinnamon-like odor.

Anal. Calcd. for $C_8H_5O_2NS$: S, 17.90. Found: S, 17.74.

5-Aminothionaphthene was obtained by adding the finely powdered nitro compound (25 g.) to a well-stirred solution of 150 g. of stannous chloride crystals in 150 cc. of concentrated hydrochloric acid at 50° (at 100° there was some chlorination). After two hours the material was largely converted to colorless crystals of the tin double salt of the amine. This was collected after cooling and dissolved in 3 liters of water; 2 g. of unchanged nitro compound was recovered on filtering the solution, and the amine separated as a flocculent precipitate on adding alkali in excess. Without drying, the amine (m. p. 70.5–72°) was dissolved in a solution of 20 g. of sulfuric acid in 1.5 liters of water at the boiling point; on cooling 18 g. (65%) of the pure amine sulfate separated.

The conversion of the amine sulfate to 5-hydroxythionaphthene was accomplished according to Hemmecke[5] except that the hydrolysis of the diazonium salt was conducted at 88° under nitrogen (thirty minutes) and with double the volume of solution specified. The crude material (m. p. 91–98°, 68% yield) was purified by treatment with Norite in alkaline solution; on acidification 5-hydroxythionaphthene separated as colorless plates, m. p. 103–104° (51% yield).

2. The Ortho Quinone Series

4-Amino-5-hydroxythionaphthene[5] was obtained in the form of the hydrochloride in 54% yield by the procedure used in the naphthalene series.[21] Using stannous chloride as antioxidant in the crystallizations, the substance was obtained as completely colorless needles.

4-Amino-5-hydroxythionaphthene-7-sulfonic Acid.—To a boiling solution of 3.1 g. of 5-hydroxythionaphthene and 2.3 g. of fused zinc chloride in 22 cc. of alcohol there was added a solution of 1.5 g. of sodium nitrite in 4 cc. of water. The zinc salt of 4-nitroso-5-hydroxythionaphthene soon separated as a red precipitate, and after one hour it was collected and suspended in a solution of 4.8 g. of sodium hydroxide in 54 cc. of water. Conversion to the sodium salt was brought to completion by warming at 60°, and after cooling the brown sodium salt was washed with a little water and triturated with a solution of 8.2 g. of

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[20] Erdmann, *Ann.*, **272**, 153 (1893).

[21] Fieser and Fieser, THIS JOURNAL, **57**, 491 (1935).

sodium bisulfite in 53 cc. of water and 4 cc. of 6% sodium hydroxide solution. The material was brought into solution rapidly and the filtered solution, diluted to 95 cc., was treated with 5.4 cc. of concentrated sulfuric acid. After standing for eight hours in the dark, the somewhat green, crystalline material which separated was washed with water, alcohol and ether; yield 2.6 g. (51%). Crystallization from water, in which it is only sparingly soluble, gave small, colorless needles of the pure material.

Anal. Calcd. for $C_8H_7O_4NS_2$: S, 26.15. Found: S, 25.96.

Potassium 4,5-thionaphthenequinone-7-sulfonate (VII) was best prepared on a small scale, 0.29 g. of 4-amino-5-hydroxythionaphthene-7-sulfonic acid being stirred into 0.42 cc. of 33% nitric acid at 30°. The mixture became red, with frothing, and the ammonium salt of the quinone separated as a red paste. Potassium chloride solution was added and the solid was collected, dissolved in water at 45°, and salted out with potassium chloride. After two recrystallizations, avoiding a temperature above 45°, the quinone was obtained as crimson needles of the monohydrate (0.1 g.). The substance responds to the usual tests for *o*-quinone sulfonates.

Anal. Calcd. for $C_8H_3O_5S_2K\cdot H_2O$: S, 21.36. Found: S, 21.20.

5 - Methoxy - 4,7 - thionaphthenequinone (VIII).—On warming a paste made from 0.6 g. of the *o*-quinone sulfonate and 20 cc. of methyl alcohol containing five drops of concentrated sulfuric acid, the red solution soon became yellow and yellow needles of the nearly pure methoxy quinone (0.15 g.) separated on cooling. Crystallized from methyl alcohol the compound formed yellow needles, m. p. 205–206°.

Anal. Calcd. for $C_9H_6O_2S$: S, 16.52. Found: S, 16.76.

3. Synthesis of 4-Hydroxythionaphthene

β-(α-Thenoyl)-propionic Acid (IX).—Aluminum chloride (288 g.) was added in one hour to a stirred mixture at 0–5° of 98 g. of succinic anhydride, 80 g. of thiophene, and 880 cc. of nitrobenzene. After stirring for four hours longer the mixture was worked up in the usual way, the crude product precipitated from a soda solution being a dark, oily solid. Most of the dark tar was separated by dissolving the crude acid in 1.4 liters of boiling water, decanting and filtering the solution. After clarification with Norite the acid separated as nearly colorless plates on cooling; yield, 95 g. (54%); m. p. 118–120°. Using carbon bisulfide as the solvent the yield was 21%. The pure keto acid forms large colorless plates, m. p. 119–120° from water, in which it is only slightly soluble in the cold.

Anal. Calcd. for $C_8H_8O_3S$: S, 17.41. Found: S, 17.21, 17.25.

γ-(α-Thienyl)-butyric Acid (X).—In a flask immersed in a large water-bath at 25° 500 g. of zinc turnings, which had been amalgamated by immersion for one hour in 1.4 liters of 5% mercuric chloride solution, was covered with 900 cc. of 1:1 hydrochloric acid and 50 g. of powdered β-(α-thenoyl)-propionic acid was added. The mixture was allowed to stand with occasional shaking for fifty hours, 500 cc. of 1:1 acid being added at intervals during this period. The solid keto acid became oily and formed a film over the zinc. To complete the reaction the mixture was refluxed for thirty-five minutes. After cooling, the reaction product was extracted with ether, dried and distilled in vacuum. The desired fraction distilled at 130–134° at 1.5 mm. and solidified on being cooled to a crystalline solid melting at 13.5–15°; yield, 33.5 g. (72%).

Anal. Calcd. for $C_8H_{10}O_2S$: S, 18.84. Found: S, 18.61.

4 - Keto - 4,5,6,7 - tetrahydrothionaphthene (XI).—The acid chloride was prepared by boiling gently for five hours a solution of 67 g. of γ-(α-thienyl)-butyric acid, 39 cc. of thionyl chloride, and twelve drops of pyridine in 90 cc. of absolute ether. After removal of the solvent and the excess reagent, the acid chloride was distilled in vacuum: b. p. 104–110° at 2 mm.; yield, 67 g. (90%).

A solution of 50 g. of the acid chloride in 150 cc. of carbon bisulfide was added during twenty minutes to a stirred solution at 0° of 78.5 g. of anhydrous stannic chloride in 400 cc. of carbon bisulfide. A yellow addition compound separated, and on heating to the boiling point and refluxing the mixture for two hours this became orange and pasty. After cooling and adding ice, the mixture was steam distilled. Following the elimination of the solvent, the cyclic ketone came over in about 3 liters of distillate as an oil. It was extracted with ether, dried, and distilled in vacuum, b. p. 102–110° at 2 mm. The distillate crystallized on cooling to a colorless solid melting at 35.5–37°; yield, 36 g. (90%). The odor is similar to that of α-tetralone.

Anal. Calcd. for C_8H_8OS: S, 21.08. Found: S, 20.94.

4-Hydroxythionaphthene (XII).—A mixture of 33.9 g. of the above ketone and 7.2 g. of sulfur contained in a small distilling flask with a sealed-on receiving bulb was heated in a metal bath at 235–245° for four and one-half hours, when the evolution of hydrogen sulfide had largely ceased. The product was distilled in vacuum from a tarry residue, and the semi-solid distillate was taken up in ether. The phenolic fraction was extracted with alkali, a neutral oil (thionaphthene?) being retained by the ether. On acidifying the alkaline solution, extracting with ether, drying and distilling in vacuum, 4-hydroxythionaphthene (b. p. about 120° at 1.5 mm.) was obtained as a solid melting at 76–78°; yield, 15.3 g. (46%). The substance has a phenolic odor, it is sparingly soluble in water, and it crystallizes from ligroin as long, slender, colorless needles melting at 80–81°. Biedermann[9] gives the melting point of his sample, presumably of the same substance, as 72°.

On heating the phenol with monochloroacetic acid and alkali in the usual way[22] **4-thionaphthoxylacetic acid** was obtained as fern-like clusters of small needles (from water), m. p. 152–153°.

Anal. Calcd. for $C_{10}H_8O_3S$: C, 57.67; H, 3.87. Found: C, 57.51; H, 3.98.

4. The Para Quinone Series

7-Amino-4-hydroxythionaphthene hydrochloride was prepared through the *p*-sulfobenzeneazo compound by the usual procedure,[21] modified in accordance with the greater solubility of 4-hydroxythionaphthene in water as com-

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[22] Koelsch, This Journal, **53**, 304 (1931).

pared with α-naphthol. The hydrochloride crystallized in the presence of a trace of stannous chloride as quite colorless needles; yield, 66%.

Anal. Calcd. for C_8H_8ONSCl: S, 15.90. Found: S, 15.76.

4,7-Thionaphthenequinone (XIII).—A solution of 10.8 g. of the amine hydrochloride in 300 cc. of water was treated with 51 cc. of concentrated sulfuric acid, heated to 95°, and poured rapidly with shaking into a solution of 10.5 g. of potassium dichromate in 150 cc. of water at 25°. The quinone separated at once as a mass of brown-yellow needles, m. p. 126–129° (7.9 g.). Crystallized from ether with the liberal use of Norite, it formed clear yellow needles, m. p. 130–131°; yield, 6.4 g. (73%). The quinone volatilizes easily and has an odor similar to that of *p*-benzoquinone. It is very sparingly soluble in water and readily soluble in alcohol or ether. The solution in concentrated sulfuric acid has a wine-red color which rapidly darkens.

Anal. Calcd. for $C_8H_4O_2S$: S, 19.54. Found: S, 19.40.

4,5,7-Trihydroxythionaphthene Triacetate (XIV).—4,7-Thionaphthenequinone (1.9 g.) was stirred into 3.5 cc. of acetic anhydride containing five drops of concentrated sulfuric acid at 40°. The triacetate soon separated on cooling to give a thick paste. It was collected and washed free of the dark-colored mother liquor with alcohol and ether, giving a nearly white powder melting at 147–150°; yield, 1.2 g. (33%). The substance crystallizes from alcohol as colorless plates, m. p. 151–153°.

Anal. Calcd. for $C_{14}H_{12}O_6S$: S, 10.40. Found: S, 10.37.

The triacetate was hydrolyzed with alcoholic alkali under nitrogen, the solution was diluted with water, acidified and treated with ferric chloride. 5-Hydroxy-4,7-thionaphthenequinone separated as small crystals on cooling the solution, and it was identified by conversion to the methyl ether with methyl alcohol and sulfuric acid. Yellow needles, m. p. 204–205°, were obtained on crystallization, and the substance (VIII) was identical with that described above.

4,7-Thionaphthenequinone monosemicarbazone was obtained from the quinone and semicarbazide hydrochloride in boiling alcohol. Brown-yellow crystals separated in a few minutes in 74% yield. Crystallized from alcohol (sparingly soluble), the substance forms yellow needles melting with decomposition at about 235°.

Anal. Calcd. for $C_9H_7O_2N_3S$: S, 14.50. Found: S, 14.56.

In the hope of determining which carbonyl group is involved in the semicarbazone formation, the substance was heated with sodium ethylate in alcohol in a sealed tube for five hours at 140°, following the method of cleavage of Thiele and Barlow[23] and of Wolff.[24] The material was largely converted into a black tar, but there was isolated a small quantity of a phenolic substance which, after purification with alkali, distillation, and crystallization from water, formed colorless plates melting at 70–70.5°. The substance has the composition and properties of an hydroxythionaphthene (calcd. for C_8H_6OS: S, 21.36. Found: S, 20.98). A mixture with an equal part of 4-hydroxythionaphthene (m. p. 80–81°) melted at 69–70°. The carboxymethyl ether melted at 158–159°, and a mixture with the 4-derivative (m. p. 152–153°) melted at 151–152°. Although these results are not decisive, we are inclined to regard the hydroxythionaphthene obtained in this way as a mixture of the 4 and 7 derivatives. Semicarbazide probably attacks both of the carbonyl groups of the quinone to some extent.

Summary

Quinones having a thiophene ring in place of the benzene ring of ortho and para naphthoquinones are about 75 mv. higher in reduction potential than the naphthoquinones of corresponding structure. This indicates a lower degree of aromaticity for thiophene as compared with benzene.

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(23) Thiele and Barlow, *Ann.*, **302**, 311 (1898).

(24) Wolff, *ibid.*, **394**, 86 (1912).

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RECEIVED JULY 1, 1935

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Paraffins with Olefins[1]

BY VLADIMIR N. IPATIEFF AND ARISTID V. GROSSE

We have found that different classes of hydrocarbons, *i. e.*, paraffins, naphthenes, aromatics and olefins, in the presence of specific catalysts, react among themselves with much greater ease than has been considered possible heretofore. As catalysts metallic halides (of Al, B, Be, Ti, Zr, Hf, Th, Cb and Ta) proved effective in these reactions.

So far practically the only known reaction between hydrocarbons, which went smoothly and quantitatively, was M. Balsohn's[2] alkylation of aromatic hydrocarbons with olefins, with aluminum chloride as a catalyst. We started to investigate this reaction some time ago and in so doing have discovered the above-mentioned reactions which will be described in a series of papers. This paper will deal only with the reaction of paraffins with olefins.

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(1) Presented before the Organic Division, American Chemical Society, New York meeting, April 22–23, 1935.

(2) M. Balsohn, *Bull. soc. chim.*, [2] **31**, 539 (1879).