[Contribution from Research and Development Laboratory of Socony Mobil Oil Co., Inc.]

The Isolation of Thianaphthene (Benzo(B)thiophene) from a Crude Petroleum

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The isolation of a condensed thiophene from a crude oil (Santa Maria Valley) is reported for the first time. The procedure involves the concentration of sulfur compounds in the thianaphthene boiling range by chromatographic separation of a selected distillate fraction. The thianaphthene was further concentrated as its picrate. Its isolation was facilitated by the discovery that naphthalene picrate coprecipitates thianaphthene picrate essentially completely from an ethanol solution. The crude thianaphthene was purified through its diacetoxymercuri derivative. The identity of the regenerated thianaphthene was confirmed by its melting point, mixed melting point with an authentic sample and ultraviolet spectrum. A minimum concentration of 0.0006% thianaphthene was found in the crude.

The influence of sulfur compounds in petroleum on processing methods and product quality is well-recognized. Even more intriguing is the potential bearing that a better knowledge of the structures of these compounds may have upon speculations concerning the evolution of petroleum. In the present paper the isolation of a condensed thiophene from a crude oil is reported for the first time. Since the thiophene nucleus and its benzo derivatives are rarely found in nature, it is quite likely that the thianaphthene found in Santa Maria Valley crude did not originate in the source material. It must have been formed, then, sometime during the evolution of the petroleum.

Although the occurrence of thiophene compounds in pyrolytic products derived from petroleum is widespread,[1] it was not until recently that they were identified in crude petroleum. Thompson, Coleman, Rall and Smith[2] (American Petroleum Institute Research Project 48A) have reported the identification of thiophene systems in Wasson crude by mass spectrometer analysis of selected chromatographic fractions. Some evidence for the presence of condensed thiophenes in Middle East gas oils has been presented by Hoog.[3]

A chemical procedure for the separation of sulfur compounds has been devised by Birch.[4] His application of this procedure[5] to the "tar oil" obtained by treating a kerosine from a Persian crude with sulfuric acid led to the isolation of several polyalkylated thiophenes. However, no thianaphthene was isolated.

Thianaphthene has been found in shale oils.[6,7] Since these oils are pyrolytic products, this evidence has no bearing on the origin of the thiophene derivative.

In the present study a concentrate of sulfur compounds in the thianaphthene boiling range was prepared by chromatographic separation of a selected distillate fraction of Santa Maria Valley crude oil. The thianaphthene was further concentrated as its picrate and its isolation was simplified by the discovery that naphthalene picrate coprecipitates thianaphthene picrate essentially completely from an ethanol solution. The two picrates are isomorphous.

Crude thianaphthene was regenerated from the picrate and purified through its diacetoxymercuri derivative. This derivative was identified by analysis and infrared spectrum. The identity of the regenerated thianaphthene was confirmed by its melting point, mixed melting point with an authentic sample and ultraviolet spectrum.

Experimental

Preparation of Sulfur Concentrate (Fraction B).—Distillation of 156 kg. of crude (4.68% S) through a 9 ft. column yielded 5.4 kg. of a naphtha (fraction A, 3.5% of crude), b.p. 104–134° at 50 mm. The maximum liquid temperature in this distillation was about 250°. About 2.5 kg. of fraction A (1.66% S) was washed with 600 ml. of 2 *M* hydrochloric acid, 600 ml. of 2 *M* sodium hydroxide and 1200 cc. of water to remove polar materials. This fraction was then dried and percolated under nitrogen through 4.5 kg. of 28–200 mesh silica gel (Davison commercial grade), prewetted with *n*-pentane. After desorption with methyl alcohol, the eluate was salted out and extracted with pentane. Removal of the pentane yielded 351 g. of a concentrate (fraction B, 0.49% of crude) containing 10.27% S. This represents an 86% recovery of sulfur.

Preparation of Picrate Derivatives (Fraction D).—Fraction B (349 g.) was separated into a number of narrow boiling range cuts by distillation (50 mm.) through a 115 cm. column packed with glass helices. Portions of these fractions were treated with picric acid. Only cuts boiling between 115–132° (50 mm.) (fraction C, 116.6 g.) formed crystalline picrates. This fraction contains 11.39% S and amounts to 0.16% of the crude. The fraction (142 g.) boiling above thianaphthene was not treated with picric acid.

Treatment of 86 g. of fraction C in 170 ml. of ethanol with 0.6 *M* picric acid at 0° yielded crystalline picrate derivatives. After recrystallization from ethanol, the mixed picrates (fraction D, 11.15 g.) melted at 151.0–151.8°.

Thianaphthene picrate and naphthalene picrate are isomorphic and an equimolar mixture melts at 149°.[8] Mixed melting points of fraction D with authentic samples of thianaphthene picrate and naphthalene picrate produced no depressions, showing that the mixture was essentially pure thianaphthene and naphthalene picrate.

Since thianaphthene picrate contains 8.83% S, its concentration in fraction D (0.66% S) is 7.5%. This corresponds to 0.0006% unsubstituted thianaphthene based on crude. Separate studies with known thianaphthene–naphthalene mixtures showed that recoveries of thianaphthene and naphthalene from their picrates were about 90 and 18%, respectively.

Isolation of the Diacetoxymercuri Derivative.—Fraction D (10.5 g.) was added to excess 0.5 *M* sodium hydroxide and steam distilled. The crystalline precipitate, consisting of thianaphthene and naphthalene, was dissolved in 50 ml. of boiling methanol and treated dropwise with 3 g. of mercuric

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(3) H. Hoog, *Rec. trav. chim.*, **69**, 1289 (1950).

(4) S. F. Birch and D. T. McAllan, *J. Inst. Petroleum*, **37**, 443 (1951).

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(6) F. Challenger, J. Haslan, R. J. Bramball and J. Walkden, *J. Inst. Petroleum Tech.*, **12**, 106 (1926).

(7) I. W. Kinney, Jr., J. R. Smith and J. S. Ball, *Anal. Chem.*, **24**, 1749 (1952).

(8) R. Meyer and W. Meyer, *Ber.*, **52**, 1249 (1919).

acetate in 15 ml. of water, and 1 ml. of acetic acid. The mixture was heated for four hours. Cooling yielded 0.49 g. of the crystalline diacetoxymercurithianaphthene.[9] *Anal.* Calcd. for $C_{12}H_{10}O_4SHg_2$: S, 4.92. Found: S, 4.75.

Recovery of Thianaphthene.—The mercury derivative was steam distilled with excess 3 *M* hydrochloric acid. Crystalline thianaphthene, m.p. 29.5–30.0°, was obtained in the distillate. Pure thianaphthene melts at 31.34°.[10] A mixture of equal amounts of the recovered natural product and an authentic synthetic sample melted at 30.0–30.5°. The percentage recovery of pure thianaphthene from D was not determined in this particular case. However, from mixtures of known amounts of thianaphthene and naphthalene, which simulated the composition of fraction D, the recovery of pure thianaphthene was about 60%.

Discussion

Santa Maria Valley crude oil does not contain free sulfur and does not evolve significant quantities of hydrogen sulfide until a temperature plateau of 266° is reached.[11] Also, possible thianaphthene precursors are known to be thermally stable at even higher temperatures. On the basis of these facts and recent observations,[2] it seems that the thianaphthene isolated was present in the virgin crude and was not formed during the distillation.

The separation procedure depends upon the use of naphthalene picrate as a carrier for the isomorphic thianaphthene picrate. In separate experiments it was shown that coprecipitation of these picrates from ethanol, using a mixture of 1% thianaphthene with 99% naphthalene, gave a 90% yield of thianaphthene picrate but only an 18% yield of naphthalene picrate. The precipitation of thianaphthene picrate in the absence of naphthalene would have required thirty times as much thianaphthene. The greater solubility of naphthalene picrate in 95% ethanol (37 g. per l. at 30°) assists the preferential precipitation of the isomorphic thianaphthene picrate (13 g. per l. at 30°).

The fact that only the picrates of thianaphthene and naphthalene are formed in fraction D is somewhat surprising. However, a series of sulfur compounds (thiophenes, sulfides, cyclic sulfides) and alkyl aromatics, which are representative of materials that could be in fraction C, did not form crystalline picrates under the conditions used.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CANISIUS COLLEGE]

Complex Metal Hydride Reactions. I. Lithium Aluminum Hydride Reduction of Heterocyclic Nuclei[1]

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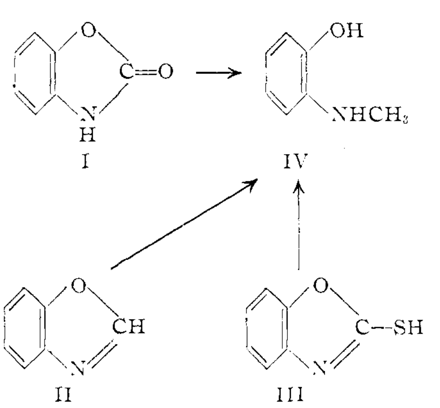
2-Benzoxazolinone and benzoxazole in ether solution and 2-benzoxazolethiol in tetrahydrofuran are reduced with lithium aluminum hydride to *o*-methylaminophenol, identified as the N-benzoyl derivative. 2-Benzimidazolethiol is not reduced in either ether or tetrahydrofuran solution. While the reduction of 2,5-diphenyloxazole in ether solution is unsuccessful, reduction in tetrahydrofuran gives 2-benzylamino-1-phenylethanol.

It has been reported[3] that an $-\overset{|}{N}\underset{|}{\overset{|}{C}}O-$ grouping and an $-\overset{|}{N}\underset{|}{\overset{|}{C}}S-$ grouping, normally not considered to be functional groups *per se*, are cleaved by lithium aluminum hydride (LAH) at the carbon–oxygen and carbon–sulfur bonds, respectively. The present investigation was undertaken to determine the applicability of this generalization to various heterocyclic nuclei.

The reduction of 2-benzoxazolinone (I) with LAH in ether solution gave *o*-methylaminophenol (IV), isolated in 57% yield as the N-benzoyl derivative V. The reduction of benzoxazole (II) in ether solution gave 59% of IV, isolated as V. The reduction of I with LAH involves initially the normal cleavage of the lactone group to yield a glycol. Subsequent cleavage of the $-\overset{|}{N}\underset{|}{\overset{|}{C}}O-$ group yields the N-methyl compound, analogous to the reduction of carbamates.[3] The reduction of II, on the other hand, initially involves the reduction of the carbon–nitrogen double bond, followed by cleavage of the $-\overset{|}{N}\underset{|}{\overset{|}{C}}O-$ grouping.



The reduction of 2-benzoxazolethiol (III) in ether

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(1) Presented before the Division of Organic Chemistry, 128th meeting of the American Chemical Society, Minneapolis, Minn., September, 1955.

(2) (a) Interchemical Corporation, The Research Laboratories, 432 West 45th Street, New York 36, N. Y.; (b) abstracted from the M.S. thesis of D. J. Kay, Canisius College, June, 1955.

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