DMF with three volumes of water. Most of the benzene was removed and the residue placed on the chromatography column as described.

Great care was necessary to prevent conversion of the free base porphyrins to their metallochelates, particularly in those cases where very small amounts of petroporphyrin were available. The chromatographic reagents were of the highest purity available; all glassware and equipment were acid washed, rinsed with deionized water, and dried in a dust-free area prior to use. Even with these precautions, occasional contamination was noted, as in the case of Rozel Point petroporphyrin (Figure 1b). The peaks at masses 529 and 537 are almost certainly the result of some contamination by copper.

Mass Spectrometry of Petroporphyrins. The mass spectra were obtained on an AEI MS-9 mass spectrometer equipped with a solid sample probe. The indicated temperature of the probe for a typical run was 260° and the indicated beam energy was 12 ev. These parameters were selected as being the most suitable for the particular kinds of mixtures under investigation on the following basis.

A suitable temperature range for obtaining mass spectra of these mixtures was arrived at in the following way. A series of five samples of Boscan petroporphyrin was introduced to the spectrometer at temperatures ranging from 195 to 280°. In Table VII are shown the mean mass of the Boscan petroporphyrin as a function of the indicated temperature of the probe. It is seen that the center of the porphyrin envelope moves up as a function of temperature until about 230° and then remains relatively constant, thus setting a lower level on the probe temperature. It was also known that at temperatures somewhat above 300° pure alkylporphyrin begins to produce thermal fragment peaks. Thus, a probe temperature of *ca.* 260° was selected.

Since in analysis of mixtures one wishes to observe insofar as possible only parent molecular ions without the complications of fragment ions, it is necessary to select an appropriate beam energy. To be certain that only parent ions were observed, the energy of the beam would have to be somewhat above the ionization potential of the molecule and below the appearance potential of the first fragment ion. Practically, such a selection is not possible because the appearance potentials of the parent ions and fragments for the components of the mixture are not known and indeed may overlap. Furthermore, the spectrometer tends to lose regulation at very low beam energies, and the over-all intensity of the spectrum suffers. Taking all of these factors into consideration, a compromise value of 12 ev was selected.

Table VII. Temperature Dependence of Mass Spectra of Boscan Petroporphyrin

Temp, °C	Mean mass of etio series of Boscan petroporphyrin[a]	Height of largest peaks in the spectrum[b]
195	459	8.5
213	463	28
233	468	34.5
259	468	81
265	468	107

[a] Calculated according to $\Sigma IM/\Sigma I$. [b] Peak heights measured in mm on the X10 scale. The noise level was roughly constant at 0.75 mm.

At this beam energy, the greatest fragment peak is probably not greater than 1% of the parent, less than the noise and impurity level. Using these selected instrument parameters, quadruplicate analyses of petroporphyrin from Boscan asphaltene gave an average standard deviation (σ) of 5.7% on the 15 largest peaks in the spectrum. The accuracy of the mass spectra was further checked in the case of Wilmington petroporphyrin by comparison with the data of Morandi and Jensen.[26] Very good agreement was found. The average difference was 5.8% in the normalized intensities of 14 major peaks.

Acknowledgment. This work was sponsored by the Gulf Research & Development Company as part of the research program of the Multiple Fellowship on Petroleum.

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(26) J. R. Morandi and H. B. Jensen, *J. Chem. Eng. Data*, **11**, 81 (1966).

Communications to the Editor

Reactive Tetravalent Sulfur Intermediates. A Nonclassical Thiophthene

Sir:

We have previously reported a convenient synthesis of benzo[*c*]thiophenes by dehydration of the sulfoxides of the corresponding dihydrothiophenes.[1] The utilization of this method in the synthesis of thieno[3,4-*b*]thiophene (I), the last of the three classical thiophthene isomers (I–III), was described recently.[2]

We now report evidence for the transient existence of a derivative of thieno[3,4-*c*]thiophene (IV), a fourth thiophthene for which the only uncharged resonance contributors are structures containing tetravalent sulfur. An analogous structure (V) has been long suggested as an appreciable contributor to the thiophene molecule.[3]

The reaction of 3,4-bis(chloromethyl)-2,5-dimethylthiophene[4] with aqueous ethanolic sodium sulfide afforded, in 35% yield, 1H,3H-dihydro-4,6-dimethylthieno[3,4-*c*]thiophene (VI),[5] mp 65–71°. Periodate oxidation[6] of VI in aqueous methanol gave the corresponding sulfoxide, VII, mp 115–119°, in 91% yield. Attempted pyrolysis of VII in the presence of neutral alumina[1] afforded only polymeric material. On the other hand, when a solution of VII and N-phenylmaleimide was refluxed for 4 hr in acetic anhydride,

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(1) M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **88**, 4112 (1966).

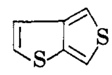
(2) (a) H. Wynberg and D. J. Zwanenburg, *Tetrahedron Letters*, 761 (1967); (b) for the first syntheses of the 1H,3H-thienothiophenes, see: H. Wynberg and D. J. Zwanenburg, *J. Org. Chem.*, **29**, 1919 (1964).

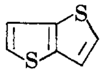
(3) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939); C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press, New York, N. Y., 1962, p 29; S. Gronowitz, *Advan. Heterocyclic Chem.* **1**, 3 (1963).

(4) K. Dimroth, G. Pohl, and H. Follmann, *Chem. Ber.*, **99**, 634 (1966).

(5) All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds reported. Nmr spectra were determined in $CDCl_3$.

(6) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).


I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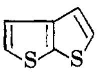
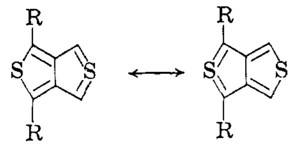
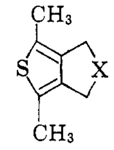

III

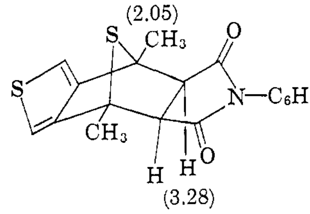

V



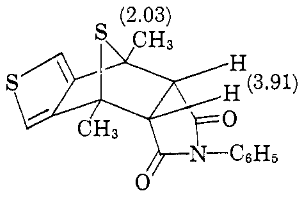
IV, R = H
X, R = CH_3



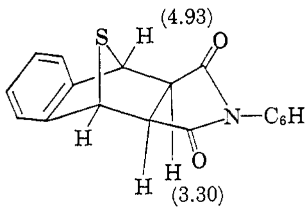
VI, X = S
VII, X = SO



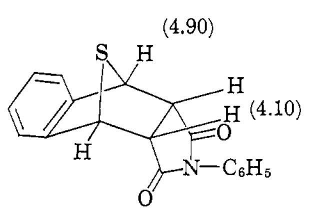
VIII



IX



XI



XII

two adducts (VIII, mp 227–229°, and IX, mp 180–182°) were isolated in 24 and 10% yield, respectively.[7] The structures of VIII and IX were assigned on the basis of their nmr spectra. Both VIII and IX show, in addition to five phenyl protons in the δ 7.0–7.5 region, two aromatic thiophene protons at δ 6.76 and six unsplit methyl protons at δ 2.05 and 2.03, respectively. By analogy with the two isothianaphthene-N-phenylmaleimide adducts XI and XII, VIII is assigned the *exo* configuration and IX is assigned the *endo* configuration. Thus, the protons α to the imide carbonyls in adduct VIII appear at δ 3.28, a position similar to that (δ 3.30) of the corresponding protons of the *exo*-isothianaphthene adduct XI. In adduct IX, the protons α to the carbonyls (δ 3.91) show the same deshielding effect of the sulfur bridge as the corresponding protons (δ 4.10) in the *endo*-isothianaphthene adduct XII. Significantly, neither VIII nor IX shows protons in the δ 4.9 region, characteristic of the bridgehead protons of XI and XII.[1]

The preferential addition of N-phenylmaleimide to the methyl-substituted ring of the dehydration product of sulfoxide VII lends support to a highly delocalized structure for the intermediary 1,3-dimethylthieno[3,4-*c*]thiophene (X). The enhanced activity of the methylated 1,3 positions of X toward N-phenylmaleimide parallels the activating effect toward dienophiles of methyl groups in the 9,10 positions of anthracene.[8]

The generation of various functionally substituted thieno[3,4-*c*]thiophenes is under investigation, with the ultimate objective of synthesizing a stable derivative of this novel heterocycle.

Acknowledgment. We thank the U. S. Army Research Office (Durham) for Grant DA-ARD-D-31-124-G850 in support of this work.

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Detroit, Michigan
Received April 24, 1967

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[7] In fact, preparative thin layer chromatography of the reaction residues afforded a third adduct, mp 270–285°, in less than 1% yield. Characterization of this compound is as yet incomplete, due to lack of material.

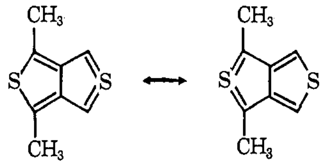
[8] J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 16 (1967).

Reactive Tetravalent Sulfur Intermediates. 2-Thiaphenalene[1]

Sir:

In our previous communication we described the generation of 1,3-dimethylthieno[3,4-*c*]thiophene (I), a thiophthene in which both heteroatoms must have partial tetravalent sulfur character.[2] We report now the generation of naphtho[1,8-*cd*]thiapyran (II, 2-thiaphenalene), a molecule for which, in addition to dipolar contributors (*e.g.*, III), only a single tetracovalent sulfur structure can be written.

Periodate oxidation of 1,3-dihydro-2-thiaphenalene (IV)[3] in aqueous ethanol afforded, in 83% yield, the corresponding sulfoxide (V),[4] mp 236–241° dec.



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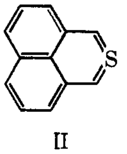
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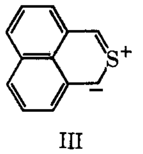
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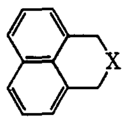
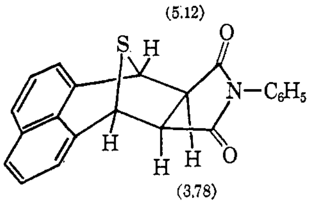
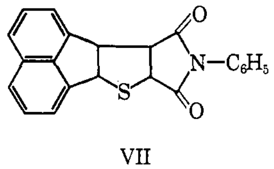
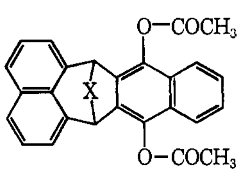

IV, X = S
V, X = SO



VI



VII



VIII, X = S
IX, X = SO_2

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[1] During our study we learned that an independent study of the generation of 2-thiaphenalene was in progress in the laboratory of Professor R. H. Schlessinger. The preliminary results of both investigations are published simultaneously by mutual agreement.

[2] M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **89**, 3639 (1967).

[3] Sulfide IV (mp 96–97°) was prepared according to P. M. Weintraub (unpublished experiments) by the reaction of 1,8-bis(hydroxymethyl)naphthalene [V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653 (1956)] with phosphorus pentasulfide in carbon disulfide.

[4] All melting points are uncorrected. Satisfactory analyses were