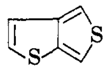
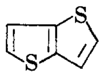

I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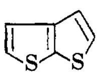
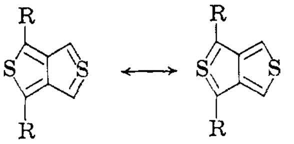
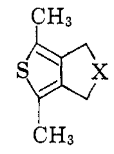

III

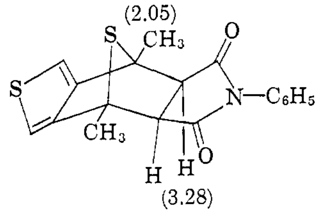

V



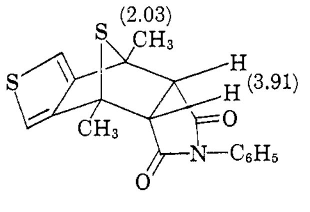
IV, R = H
X, R = CH_3



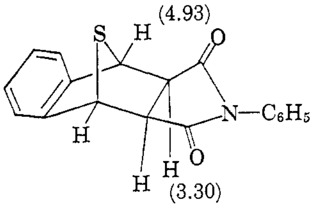
VI, X = S
VII, X = SO



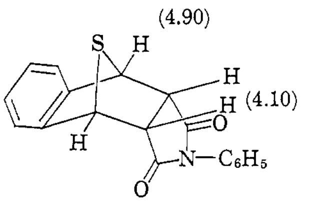
VIII



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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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.

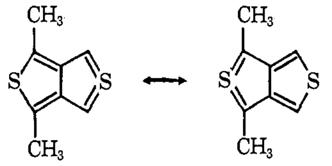
[8] J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 16 (1967).

Reactive Tetravalent Sulfur Intermediates. 2-Thiaphenalene[1]

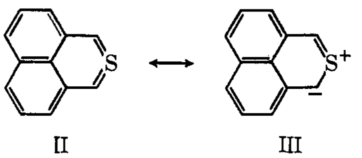
Sir:

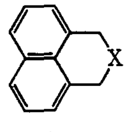
In our previous communication we described the generation of 1,3-dimethylthieno[3,4-*c*]thiophene (I), a thiophthene in which both heteroatoms must have partial tetravalent sulfur character.[2] We report now the generation of naphtho[1,8-*cd*]thiapyran (II, 2-thiaphenalene), a molecule for which, in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

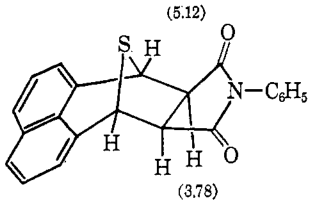
Periodate oxidation of 1,3-dihydro-2-thiaphenalene (IV)[3] in aqueous ethanol afforded, in 83% yield, the corresponding sulfoxide (V),[4] mp 236–241° dec.



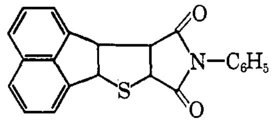
I


II III

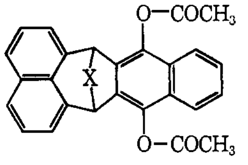

IV, X = S
V, X = SO



VI



VII



VIII, X = S
IX, X = SO_2

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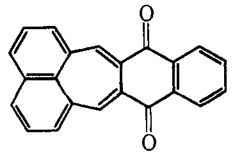
[1] During our study we learned that an independent study of the generation of 2-thiaphenalene was in progress in the laboratory of Professor R. H. Schlessinger. The preliminary results of both investigations are published simultaneously by mutual agreement.

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

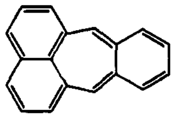
[3] Sulfide IV (mp 96–97°) was prepared according to P. M. Weintraub (unpublished experiments) by the reaction of 1,8-bis(hydroxymethyl)naphthalene [V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653 (1956)] with phosphorus pentasulfide in carbon disulfide.

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

Dehydration of V in refluxing acetic anhydride in the presence of N-phenylmaleimide afforded a single adduct (VI), mp 267–270°, in 55% yield. The nmr spectrum of VI was in agreement with the assigned structure. Thus, in addition to aromatic protons, the spectrum showed only two bridgehead protons at δ 5.12[5] and two protons α to the imide carbonyls at δ 3.78. The latter value supports the assigned *exo* configuration of adduct VI, since model compounds show the δ 3.78 value to be in better accord with a deshielding effect of the naphthalene ring than with the expected greater deshielding effect of a sulfur bridge.[6] It may be noted that the less likely adduct of general structure VII (stereochemistry unspecified) is ruled out by the nmr data, since VII would show aliphatic protons at four different positions.



X



XI

The trapping of 2-thiaphenalene (II) by appropriate dienophiles offers a simple new route to pleiadene derivatives. Using this approach we have succeeded in synthesizing the first example of a pleiadenequinone. Thus, the reaction of sulfoxide V with 1,4-naphthoquinone in a refluxing mixture of pyridine and acetic anhydride afforded, in 51% yield, adduct VIII, mp 289–293°. Peracetic acid oxidation of VIII afforded, in 82% yield, the corresponding sulfone IX, mp 250° dec. Hydrolysis of IX at room temperature in a mixture of tetrahydrofuran and aqueous potassium hydroxide in the presence of air afforded directly, in 32% yield, chocolate brown needles of benzo[*l*]pleiadene-8,13-quinone (X), mp 247–249°. Quinone X appears to be a compound of unusual stability, in contrast to the great instability of pleiadene (XI)[7] and related hydrocarbons.[8,9]

The synthesis and transformations of other adducts of II is under investigation and will form the subject of subsequent reports.

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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obtained for all new compounds reported. Nmr spectra were determined in $CDCl_3$. Mass spectra obtained for VIII, IX, and X were in agreement with the assigned structures. The ultraviolet–visible spectrum of X shows the following bands: $\lambda_{max}^{dioxane}$ 239 mμ (log ε 4.38), 268 (4.68), 430 sh (4.03), 449 (4.07), 530 sh (3.06), 570 sh (2.75), and 625 sh (2.03).

(5) See ref 2 for nmr values of similar bridgehead protons.

(6) The corresponding pair of protons in the pleiadene–N-phenylmaleimide adduct, which are in an almost identical environment, appear at δ 3.85: M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965). Similar protons appear at fields below δ 3.9 when deshielded by a sulfur bridge: see ref 2.

(7) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965).

(8) M. P. Cava and R. H. Schlessinger, *ibid.*, **21**, 3051 (1965).

(9) M. P. Cava and R. H. Schlessinger, *ibid.*, **21**, 3065 (1965).

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Received April 24, 1967

Reactive Aromatic Heterocycles Containing "Tetravalent Sulfur"[1]

Sir:

We wish to report the generation of naphtho[1,8-*cd*]thiapyran (I, 2-thiaphenalene) and its acenaphthene analog acenaphtho[5,6-*cd*]thiapyran (II, 2-thiaacephenalene), two highly reactive heterocycles derived from the aromatic hydrocarbon *peri*-cycloheptanaphthalene (III)[2] by substitution of a tetracovalent sulfur atom for two sp^2 carbon atoms.[3]

Recently an elegant application of the Pummerer reaction[4] to the synthesis of unusual thiophenes from 2,5-dihydrothiophene sulfoxides has been reported.[5] We have found this transformation also to occur with certain cyclic 2,6-dihydrosulfoxides.[6]

Reaction of 1,8-bis(hydroxymethyl)naphthalene (IV)[2] with phosphorus pentasulfide in carbon disulfide[7] gave in 85% yield sulfide V, mp 102°. Oxidation of V using sodium periodate in aqueous methanol[8] afforded the corresponding sulfoxide VI, mp 230° dec, in 90% yield.[9] Decomposition of VI in refluxing acetic anhydride was found to occur readily, accompanied by the formation of a complicated mixture of products.[10] In contrast, the reaction of N-phenylmaleimide with sulfoxide VI in refluxing acetic anhydride afforded a single highly crystalline adduct VII, mp 278–285°, in 70% yield.

The gross structure of adduct VII was provided by its mass spectrum which, in addition to the parent ion at *m/e* 357, gave rise to a retro-Diels–Alder-type fragmentation pattern with peaks at *m/e* 184 (heterocycle I)[11] and 173 (N-phenylmaleimide) accompanied by a metastable peak at *m/e* 94.84. That the peak at *m/e* 184 represents the parent ion of I is substantiated by the occurrence of a strong peak at *m/e* 152 (parent ion of acenaphthylene; extrusion of sulfur from I) accompanied by a metastable peak at *m/e* 125.57. The *exo* geometry for the adduct VII was indicated by its nmr spectrum which shows the two protons α to the imide carbonyls at δ 3.75, a position similar to that (δ 3.85) of the corresponding protons of the N-phenylmaleimide–

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[1] During this investigation we learned of similar efforts in the laboratory of Professor M. P. Cava. Our results are published simultaneously through mutual agreement.

[2] V. Boekelheide and G. K. Vick, *J. Am. Chem. Soc.*, **78**, 653 (1956).

[3] R. Zahradnik and C. Parkanye, *Collection Czech. Chem. Commun.*, 30, 3016 (1965).

[4] For recent studies of the Pummerer reaction see (a) L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959); (b) S. Oae, T. Kitaa, S. Kawamura, and Y. Kilaoka, *Tetrahedron*, **19**, 817 (1963).

[5] (a) M. P. Cava and N. M. Pollack, *J. Am. Chem. Soc.*, **88**, 4112 (1966); (b) H. Wynberg and D. J. Zwanenburg, *Tetrahedron Letters*, 761 (1967).

[6] All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds reported. Nmr spectra were determined in $CDCl_3$; mass spectra were taken at 70 ev.

[7] M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965).

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

[9] The structure of VI is confirmed by an infrared band at 1040 cm^{-1}, characteristic of sulfoxides, and by its nmr spectrum which shows six aromatic protons in the δ 7.25–7.92 region and four methylene protons as a singlet at δ 4.4.

[10] Spectral examination (infrared and nmr) of the crude reaction mixture indicates that products containing carbonyl functions do not appear to be present. All attempts to isolate crystalline materials from this mixture have met thus far with no success.

[11] Peaks at 357 and 184 cm^{-1} showed correct ^{34}S isotopic abundance.