therefrom. In agreement with this it was found that the reaction of **1** in methanol with 0.05 *M* NaOPh in the presence of an increased concentration of phenol (0.5 *M*) gave **5** (93%), $PhCH_2COCH(OPh)CH_3$ (6%), and $PhCH(OPh)COCH_2CH_3$ (1%) to the exclusion of ester **9**.

The enol solvolysis mechanism is probably responsible for the formation of α-alkoxy ketone by-products from Favorskii rearragements carried out with *dilute* sodium alkoxides and alcohols in a number of other systems.[1,2c,3,6,11] This side reaction is avoided in aprotic media and at high alkoxide concentrations in protic media. This is no doubt at least part of the reason that better yields of Favorskii rearrangement products are obtained at high alkoxide than at low alkoxide concentrations.[12]

Acknowledgment. This work was supported by the National Science Foundation (GP 7065).

(11) J. G. Strong, Ph.D. Dissertation, Northwestern University, 1968, found that the yield of α-methoxy ketone increased markedly at the expense of Favorskii ester when low methoxide concentrations were used with α-chlorocyclohexanone and a number of its derivatives. R. G. Scamehorn, Ph.D. Dissertation, Northwestern University, 1968, found that 2-chloro- or 2-bromo-3,3-diphenylcyclopentanone reacted with 0.1 *M* NaOMe in MeOH at 0° to give an essentially quantitative yield of α-methoxy ketone.

(12) G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **82**, 4307 (1960).

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Tetraphenylthieno[3,4-*c*]thiophene. A Stable Nonclassical Thiophene

Sir:

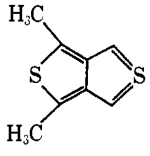
We have reported previously evidence for the transient existence of 1,3-dimethylthieno[3,4-*c*]thiophene (**1**), a derivative of a 10π-electron aromatic system for which the only uncharged resonance contributors are structures containing tetravalent sulfur.[1] We now report the synthesis of tetraphenylthieno[3,4-*c*]thiophene (**2**), an isolable and remarkably stable derivative of this same unusual aromatic system.

The reaction of tetrabenzoylethane[2] (**3**) with phosphorus pentasulfide in refluxing xylene afforded, in 46% yield, 1,3-dihydro-1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene (**4**), mp 195–196°. The nmr spectrum of **4** showed two benzylic protons as a singlet at δ 5.74 and the four phenyls as a 20-proton multiplet in the range of δ 6.9–7.3. The mass spectrum of **4** showed the molecular ion as the base peak at 446, the only other significant higher mass peak appearing at 369 ($M - C_6H_5^+$, 20%).[3]

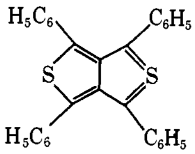
Periodate oxidation[4] of **4** gave in 96% yield the corresponding sulfoxide **5**, mp 234–235° dec, molecular weight 462 by mass spectrometry. The infrared spectrum of **5** showed a band at 9.6 μ characteristic of sulfoxides, while its nmr spectrum showed two protons α to the sulfoxide group at δ 5.37 and a 20-proton aromatic multiplet at δ 7–7.5.

Dehydration of sulfoxide **5** with refluxing in acetic anhydride[5] (N_2, 4 hr) afforded in 87% yield tetraphenylthieno[3,4-*c*]thiophene (**2**), mp 245–248°, as glistening purple needles, $\lambda_{\max}^{C_2H_4Cl_2}$ 255 mμ (ε 17,000), 296 (20,000), and 553 (13,000). The nmr spectrum of **2** consists of a single sharp band at δ 7.12 suggesting that the phenyl groups lie considerably out of the plane of the thienothiophene system.[6] The mass spectrum indicates a very stable molecule showing a base peak for the molecular ion at 444, the next strongest peak above mass 130 being the M^{2+} peak (11%) at 222.

The thienothiophene **2** could also be obtained in a single operation (3% yield) by the direct reaction of tetrabenzoylethylene[7] (**6**) with phosphorus pentasulfide



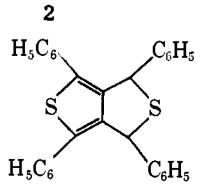
1



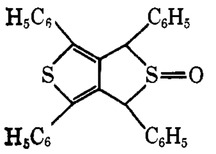
2

$(C_6H_5CO)_2CHCH(COC_6H_5)_2$

3



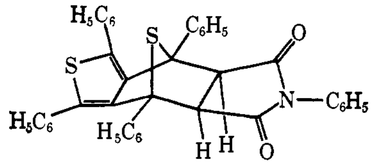
4



5

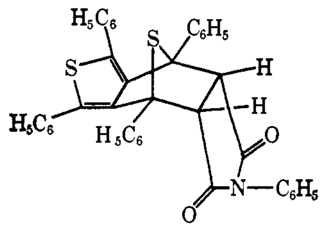
$(C_6H_5CO)_2C{=}C(COC_6H_5)_2$

6



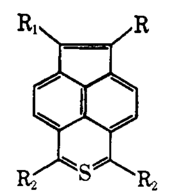
exo

7



endo

8



9, $R_1 = Br; R_2 = C_6H_5$

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

[2] R. D. Abell, *J. Chem. Soc. Transactions*, **101**, 997 (1912).

[3] Nmr spectra were determined in $CDCl_3$. All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds. Mass spectra were recorded on an Atlas CH4 spectrometer.

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

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

[6] An analogous system occurs in 1,8-diphenylnaphthalene; see H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).

[7] A. Andres, Dissertation, Strassburg, 1911.

in refluxing xylene, along with a 30% yield of its dihydro derivative, sulfide **4**.

The reaction of **2** with N-phenylmaleimide in boiling acetic anhydride gave a mixture of two adducts, A and B, in a 3:1 ratio. The total yield was 88% and the adducts were separated by preparative tlc. Adduct A, mp 310–313° dec, was assigned the *exo* structure **7**, and adduct B, mp 274–275°, the *endo* structure **8**, on the basis of their nmr spectra which were dominated by the effects of the bridgehead phenyl groups. Thus in the *exo* adduct, the protons α to the imide carbonyls are greatly deshielded by the bridgehead phenyls and appear at δ 5.16, whereas the *ortho* protons of the bridgehead phenyls are appreciably deshielded and appear as a clear four-proton multiplet at δ 7.6–7.8. The *endo* adduct shows no deshielded aromatic protons but only a broad aromatic multiplet in the region of δ 6.8–7.5 where the remaining aromatic protons of the *exo* adduct also occur. The two protons α to the imide carbonyls of the *endo* adduct appear at the much less deshielded position of δ 4.27. The mass spectrum of the *exo* adduct showed a molecular ion at 617 which was 20% of the base peak at 444.

The thienothiophene **2** appears to be stable indefinitely in the solid state although dilute solutions are slowly bleached by light. The compound appears to be relatively nonpolar as evidenced by its ready elution from grade I neutral alumina by benzene in which it is very soluble. If the phenyl substituents are indeed considerably twisted out of the plane of the thienothiophene nucleus as suggested by the nmr data, the basic ring system would appear to have considerably more delocalization energy than one would expect from the results of recent molecular orbital calculations in which d-orbital participation by sulfur was discounted.[8] Further reactions of **2** as well as a complete X-ray crystallographic analysis of its structure will be reported shortly.

The only previously reported isolable heterocycle containing tetravalent sulfur bonded only to carbon is a derivative (**9**) of acenaphtho[5,6-*cd*]thiapyran,[9] a system which unlike that of **2** may be partially stabilized by divalent sulfur contributors.

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

(8) D. T. Clark, *Tetrahedron*, **24**, 2567 (1968).

(9) I. S. Ponticello and R. H. Schlessinger, *J. Am. Chem. Soc.*, **90**, 4190 (1968).

(10) To whom correspondence should be addressed at the Department of Chemistry, University of Pennsylvania, Philadelphia, Pa. 19104.

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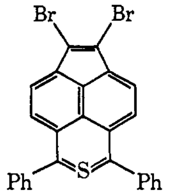
A One-Step Synthesis of a Stable "Tetravalent Sulfur" Heterocycle

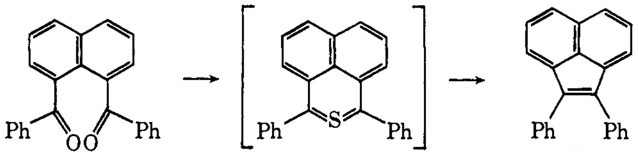
Sir:

A ten-step synthesis (3% over-all yield) of the stable tetravalent sulfur heterocycle, 6,7-dibromo-1,3-diphenylacenaphtho[5,6-*cd*]thiopyran (I), was described recently.[1] Extended experimental examination into the unusual sulfur bonding found in I was precluded by the very small quantities of the heterocycle which were available. To circumvent this problem, we have developed a novel, high-yield, one-step synthesis of an analog of I.



I

A classic method of synthesizing thiophenes is the reaction of 1,4-dicarbonyl compounds with inorganic sulfides.[2] It occurred to us that stable heterocycles like I might be formed in this manner starting from 5,6-diketoacenaphthylene derivatives. Unfortunately, simple and efficient methods of preparing these compounds are not available. However, it was known that the *peri*-substituted diketone, 1,8-dibenzoylnaphthalene (II),[3] when treated with phosphorus pentasulfide gave rise to 1,2-diphenylacenaphthylene (III)[4] in high yield.[5] The latter reaction was thought to proceed through the reactive tetravalent sulfur heterocycle 1,3-diphenylnaphtho[1,8-*cd*]thiopyran (IV) which is known to undergo facile thermal extrusion of sulfur to give hydrocarbon III.[6] A similar extrusion reaction from heterocycle I does not occur.[1] These observations suggested that *peri*-substituted tetraketonaphthalene derivatives could be directly converted into stable tetravalent sulfur heterocycles. This supposition has proven to be correct, for when 1,4,5,8-tetrabenzoylnaphthalene (V),[7] a trivial transformation product of pyrene, is treated with a mixture of phosphorus pentasulfide in pyridine (100°, 2 hr), there is formed in 85% yield the highly crystalline blue-black heterocycle 1,3,6,7-tetraphenylacenaphtho[5,6-*cd*]thiopyran (VI), mp 280–282°.[8]



II IV III

Heterocycle VI showed absorption maxima at $\lambda_{max}^{CH_2Cl_2}$ 256 mμ (ϵ 26,400), 273 (25,300), 301 (20,200), 415 (71,800), 565 (3930), 610 (3450), and 665 (2330) with tailing to 775 mμ. The nmr spectrum of VI gave resonance for the phenyl protons as a broad multiplet centered at δ 7.59 and the naphthalene protons as a well-defined AB quartet centered at δ 8.04 and 8.60 (J_{AB} = 8.6 cps). The stability of VI is reflected by its mass spectrum (75 eV) which shows major peaks at

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(1) R. H. Schlessinger and I. S. Ponticello, *J. Am. Chem. Soc.*, **90**, 4190 (1968).

(2) M. H. Palmer, "The Structure and Reactions of Heterocyclic Compounds," Edward Arnold Ltd., London, 1967, p 259.

(3) W. Schlenk and J. Holtz, *Ber.*, **50**, 268 (1917).

(4) G. Wittig, M. Leo, and W. Wiemer, *ibid.*, **64**, 2405 (1931).

(5) Private communication from A. G. Schultz.

(6) R. H. Schlessinger and A. G. Schultz, *J. Am. Chem. Soc.*, **90**, 1676 (1968).

(7) H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Ann.*, **531**, 1 (1937).

(8) All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds. Nmr spectra were determined in $CDCl_3$. Mass spectra were determined on a Hitachi RMU-6E.