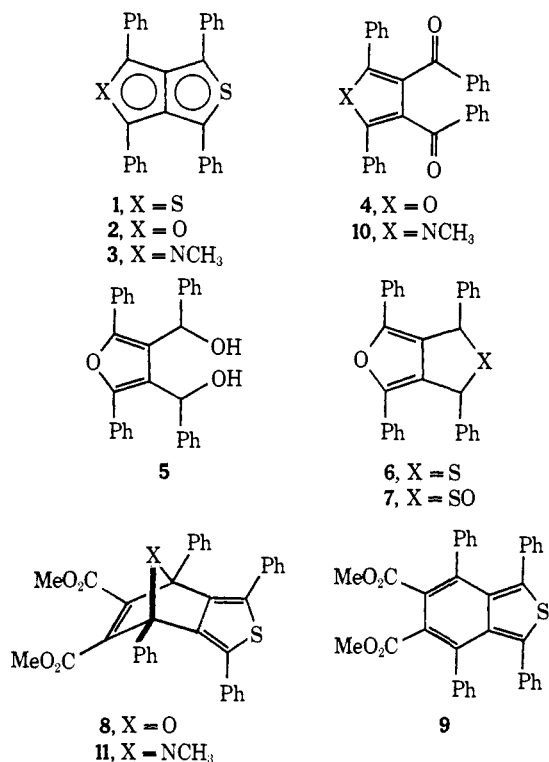


phorus pentasulfide in carbon disulfide³ gave, after alumina chromatography, the cis sulfide **6**, mp 246–248°, in 19% yield.⁴ Periodate oxidation⁵ of **6** gave (92%) the corresponding sulfoxide **7**, mp 241–243° dec.

When **7** was refluxed in acetic anhydride under nitrogen, a pale violet color appeared; attempted work-up (tlc) indicated the formation of a complex mixture which has not yet been resolved. However, when the same dehydration of **7** was carried out in the presence of dimethyl acetylenedicarboxylate, adduct **8**, mp 228–230°, was readily isolated in 70% yield, indicating the intermediary formation of the thienofuran **2**. The assigned structure **8** was supported by the presence of a strong (33%) M – 16 peak in its mass spectrum, and was confirmed by the deoxygenation of **8** by hot triethyl phosphite to give the isothianaphthene diester **9**.⁶



The reaction of tetrabenzoylthane with methylamine in acetic acid afforded (90%) 1-methyl-2,5-diphenyl-3,4-dibenzoylpyrrole (**10**), mp 198–200°. Treatment of diketone **10** with phosphorus pentasulfide in refluxing toluene (1.5 hr), followed by evaporation of the solvent, gave an amorphous brown solid. Digestion of this solid with hot 10% aqueous sodium hydroxide afforded a bright red powder, which is stable to air for weeks in the dry state. This material, which shows a strong peak at *m/e* 441 and a strong absorption maximum in benzene at 526 nm, consists primarily of thienopyrrole **3**, as shown by its rapid reaction with dimethyl acetylenedicarboxylate in chloroform to give (>85%) adduct **11**, mp 247–248°. The structure of adduct **11** was supported by the shielded value (δ 1.72) of its *N*-methyl group, and confirmed by its conversion

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

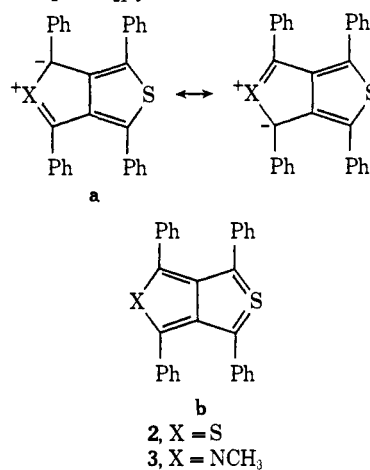
(4) Satisfactory analyses were obtained for all new compounds reported with melting points. Nmr and mass spectra were found to be consistent with assigned structures.

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

(6) We thank Dr. M. Behforouz for an authentic sample of **9** prepared from the reaction of **1** with dimethyl acetylenedicarboxylate (unpublished results).

(98% yield) to isothianaphthene **9** by oxidation with *m*-chloroperbenzoic acid.⁷

Heterocycles **2** and **3** may be viewed electronically as hybrids of 1,3-dipolar (**2a** and **3a**) and tetravalent thiophene contributors (**2b** and **3b**). The greater stability of **3** relative to **2** is not unexpected in view of the greater electronegativity of oxygen as compared to nitrogen. Although we cannot rule out the possibility of a triplet ground state for the transient thienofuran **2**, we have observed that benzene solutions of the more stable thienopyrrole **3** give no esr signal, thereby indicating a singlet ground state. In this regard, it may be noted that recent SCF-MO calculations, assuming no sulfur d orbital participation, have predicted a triplet ground state for thieno[3,4-*c*]pyrrole.⁸



Acknowledgment. We thank the National Institutes of Health (for a Predoctoral Fellowship to M. A. Sprecker) and the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

(7) This reaction undoubtedly proceeds by formation of the *N*-oxide of **11** followed by a facile elimination of nitrosomethane. For a closely related decomposition of an aziridine *N*-oxide to an olefin, see J. E. Baldwin, A. K. Bhatnager, Se Chun Choi, and T. J. Shorridge, *J. Amer. Chem. Soc.*, **93**, 4082 (1971).

(8) L. Klasinc and N. Trinajstić, *Tetrahedron*, **27**, 4045 (1971).

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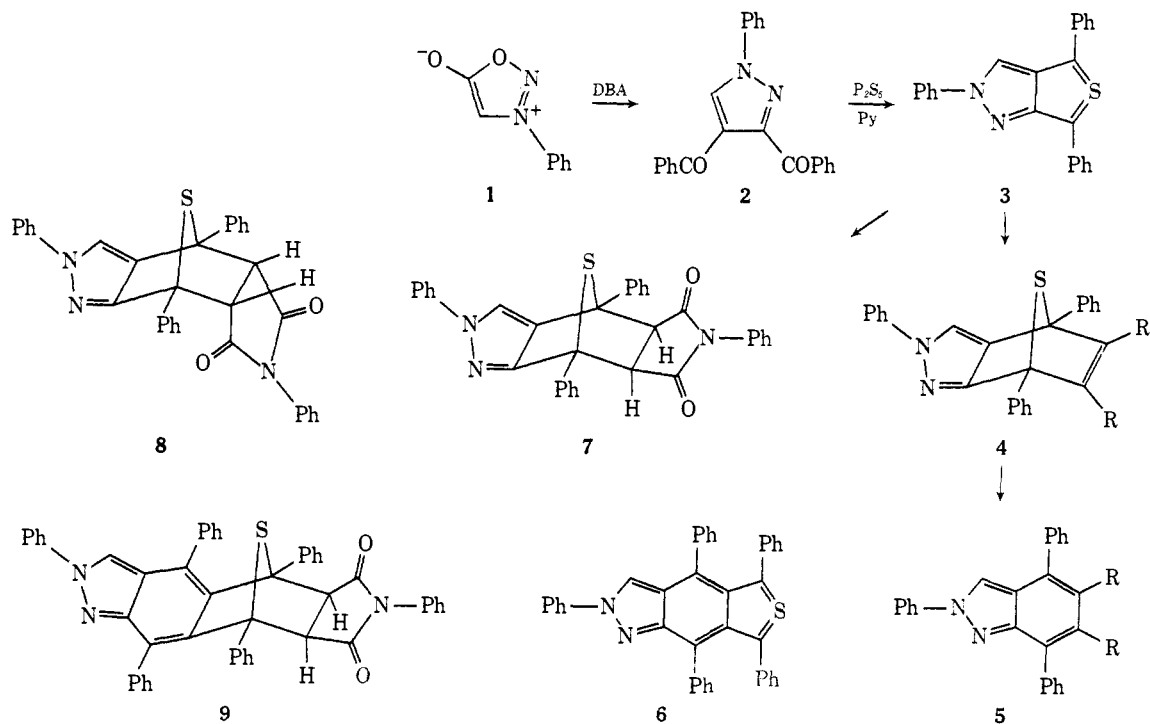
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The Synthesis of Stable "Tetravalent Sulfur" Heterocycles

Sir:

Syntheses of several stable, nonclassical 10 π -electron heterocycles have been reported¹ recently in the literature, these compounds being of particular interest because of the tetravalent environment of the sulfur. We now wish to describe a simple synthetic route to the thieno[3,4-*c*]pyrrole system (**3**). Yields of the order of 85% in each of two steps makes this unusual aromatic system available in sufficient quantity for detailed chemical studies.

(1) (a) M. P. Cava and G. E. M. Husbands, *J. Amer. Chem. Soc.*, **91**, 3952 (1969); (b) J. M. Hoffman and R. H. Schlessinger, *ibid.*, **91**, 3953 (1969); J. D. Bower and R. H. Schlessinger, *ibid.*, **91**, 6891 (1969); (c) F. H. M. Deckers, W. N. Speckamp, and H. O. Huisman, *Chem. Commun.*, 1521 (1970); (d) D. W. H. MacDowell, A. T. Jeffries, and M. B. Meyers, *J. Org. Chem.*, **36**, 1416 (1971).



Utilizing the ability of mesoionic ring systems to act as 1,3 dipoles² in cycloaddition reactions (and also the precursors to these systems to undergo the same reactions³), we have condensed *N*-phenylsydnone (1) with dibenzoylacetylene (DBA) to form 3,4-dibenzoyl-1-phenylpyrazole (2) in 85% yield.⁴ Reaction of 2 with phosphorus pentasulfide in refluxing pyridine,⁵ followed by quenching the reaction in ice-water, gave 2,4,6-triphenylthieno[3,4-*c*]pyrazole (3) as brick-red needles (85%) from Ac₂O: mp 200–202°; $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 497 nm (ϵ 11,500), 298 (15,300), 276 (16,000), 250 (13,300), 202 (28,300). The nmr spectrum (CDCl₃) of 3 consisted of a sharp singlet at τ 1.68 (3-H) and two aromatic multiplets at 2.92–2.20 (11 protons) and 2.12–1.75 (four protons). As was found with other tetravalent sulfur compounds,¹ the mass spectrum indicated a very stable molecule with the molecular ion at *m/e* 352 being the base peak and a strong ion at *m/e* 176 (13%) corresponding to the M²⁺ ion.

Cycloaddition reactions of 3 with acetylenic and olefinic dipolarophiles occur readily. With dimethyl acetylenedicarboxylate in refluxing benzene a 76% yield of 2,4,7-triphenyl-5,6-dicarbomethoxybenzo[*c*]pyrazole (5, R = COOCH₃), colorless needles, mp 192–194°, was obtained. This ready elimination of sulfur from the primary 1:1 cycloadduct 4 is characteristic of bridged-sulfur systems of this type⁶ and provides a ready route to many heteroaromatic ring systems. Thus, reaction of 3 with dibenzoylacetylene gave the corresponding 6,7-dibenzoyl-2,4,7-triphenylbenzo[*c*]pyrazole (5, R = COPh) as colorless, fibrous needles

(61%), mp 196–198°. Application of the phosphorus pentasulfide–pyridine procedure to 5 (R = COPh) gave the tricyclic, tetravalent sulfur heterocycle 6 as blue-black needles (90%) from acetonitrile: mp 238–240°; $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 602 nm (ϵ 12,820), 303 (26,500), 252 (26,850), 231 (32,300). In the mass spectrum the molecular ion at *m/e* 554 was the base peak with the next most intense ion being the M²⁺ ion at *m/e* 277 (17%), again reflecting the stability of these tetravalent sulfur systems.

N-Phenylmaleimide and 3 readily gave a mixture (65%) of exo and endo cycloadducts which was temperature dependent. In refluxing benzene, the exo:endo ratio was 18:1, whereas in boiling toluene this ratio was reduced to 9:1. The exo adduct 7 formed colorless, irregular prisms from 95% ethanol [mp 138–140° dec; nmr (CDCl₃) τ 5.17 (AB q, 2), 3.45–3.15 (m, 2), 3.07–2.45 (m, 14), 2.37 (s, 1, 5 H of pyrazole), 2.30–1.75 (m, 4)] whereas the endo adduct 8 was obtained as colorless, fibrous needles from acetonitrile [mp 231–233° dec; nmr (DMSO-*d*₆) τ 5.76 (s, 2), 3.02–2.05 (m, 20), 1.68 (s, 1, 5 H of pyrazole)]. These nmr data clearly establish the structures as shown.

Similarly 6 and *N*-phenylmaleimide gave a 1:1 adduct (61%) which was assigned the exo configuration 9 on the basis of the nmr data for the C-2 and C-3 protons of the bicyclo[2.2.1]heptane system [τ 5.02 (s, 2)].

This present reaction sequence offers considerable scope for variation of the heterocycle fused to the thio-phen nucleus and for the introduction of alkyl and aryl substituents. These aspects together with a study of the Diels–Alder type characteristics of these ring systems are currently under investigation in this laboratory.

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(2) E.g., see R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, **101**, 536 (1968); K. T. Potts and D. N. Roy, *Chem. Commun.*, 1061, 1062 (1968).

(3) K. T. Potts and U. P. Singh, *ibid.*, 66 (1969).

(4) All compounds were characterized by satisfactory analytical data, mass spectra, and nmr spectra.

(5) R. H. Schlessinger and J. M. Hoffman, *J. Amer. Chem. Soc.*, **91**, 3953 (1969).

(6) K. T. Potts, E. Houghton, and U. P. Singh, *Chem. Commun.*, 1129 (1969); R. Helder and H. Wynberg, *Tetrahedron Lett.*, 605 (1972); D. D. Callender, P. L. Coe, and J. C. Tatlow, *Chem. Commun.*, 143 (1966).