

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).

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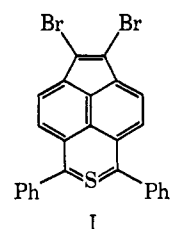
A One-Step Synthesis of a Stable "Tetravalent Sulfur" Heterocycle

Sir:

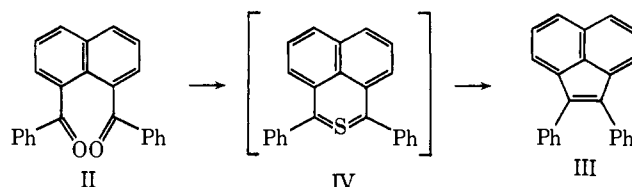
A ten-step synthesis (3% over-all yield) of the stable tetravalent sulfur heterocycle, 6,7-dibromo-1,3-diphenylacenaphtho[5,6-*cd*]thiopyran (**I**), was described recently.¹ Extended experimental examination into

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

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**.



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-diketooacenaphthylene 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-diphenyl-naphtho[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

Heterocycle **VI** showed absorption maxima at $\lambda_{\max}^{\text{CH}_2\text{Cl}_2}$: 256 $m\mu$ (ϵ 26,400), 273 (25,300), 301 (20,200), 415 (71,800), 565 (3930), 610 (3450), and 665 (2330) with tailing to 775 $m\mu$. 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 ($J_{\text{AB}} = 8.6$ cps). The stability of **VI** is reflected by its mass spectrum (75 eV) which shows major peaks at

(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.

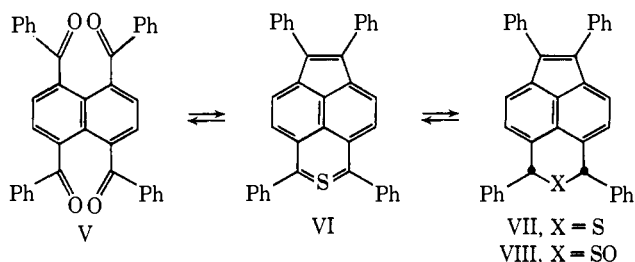
(6) R. H. Schlessinger and A. G. Schultz, *J. Am. Chem. Soc.*, **90**, 1676 (1968).

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

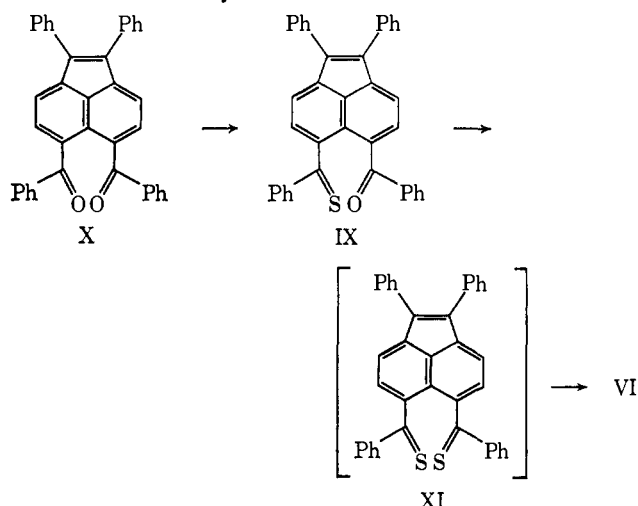
(8) All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds. Nmr spectra were determined in CDCl_3 . Mass spectra were determined on a Hitachi RMU-6E.

m/e 512 (100%, parent ion of VI) and 480 (22%, ion of 1,2,5,6-tetraphenylpyracylene).

Oxidative degradation of heterocycle VI using sodium dichromate⁹ gives rise to the tetraketone V in 71% yield. Catalytic reduction (palladium on carbon) of VI occurs sluggishly (100 hr) to give the *cis*-sulfide VII. Conversion of VII into its corresponding sulfoxide VIII followed by dehydration of VIII regenerates heterocycle VI in good over-all yield.¹⁰



A remarkable reaction occurs on oxidation of VI with Sarett's reagent.¹¹ Brief treatment of VI with chromium trioxide in pyridine gives rise to a mixture of the brown monothiodiketone IX (68%, mp 235–238°)¹² and the red diketone X (32%, mp 296–297°). Prolonged oxidation of either VI or IX under these conditions affords diketone X as the sole reaction product. Both IX and X along with heterocycle VI are formed when the reaction of tetraketone V with phosphorus pentasulfide is carried out over brief periods (100°, 10 min). Treatment of either IX or X with the phosphorus pentasulfide-pyridine mixture gives VI in high yield. However, no reaction occurs on treatment of IX with pyridine alone (100°, 6 hr). These results suggest that the formation of VI from X probably occurs by stepwise conversion of the diketone *via* the monothiodiketone into the dithiodiketone XI followed by collapse of XI into the heterocycle.



An interesting series of interconversions between the monothiodiketone IX and compounds VI and X have been found. Compound IX smoothly gives heterocycle VI on treatment with gaseous hydrogen chloride in freshly distilled ether solvents. In addition, either *p*-toluenesulfonyl chloride or triphenylphosphine in

(9) The oxidation procedure used was similar to that described by H. C. Brown and C. P. Carg, *J. Am. Chem. Soc.*, 83, 2952 (1961).

(10) For examples of similar transformations, see ref 1 and 6.

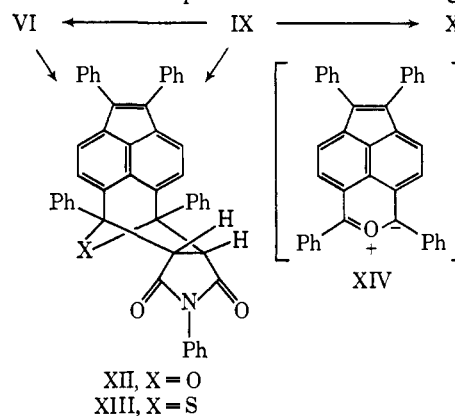
(11) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, 75, 422 (1953).

(12) Unlike most thioketones, the monothiodiketone IX is remarkably stable and presents no problems with respect to isolation and purification.

degassed xylene solution (110°) converts IX into VI in high yield. However, when these reactions are carried out in the presence of dissolved oxygen, diketone X is the predominate product and only small amounts of heterocycle VI are formed. The dramatic influence of oxygen on the course of these reactions is not yet clearly understood.

Upon heating above its melting point (240°), the monothiodiketone IX suffered extensive decomposition. The only isolable product from this reaction was heterocycle VI (27%). Surprisingly, thermolysis of IX at 240° in the presence of *N*-phenylmaleimide gave a mixture of the oxide adduct XII (70%, mp 320–322°) and the sulfide adduct XIII (10%, mp >360°). A 94% yield of adduct XIII was obtained by reaction of heterocycle VI with the dienophile. Adducts XII and XIII show ultraviolet and visible absorption typical of diphenylacenaphthylene derivatives. The nmr spectra of XII and XIII exhibit resonance for the two protons α to the imide carbonyls at δ 4.55 and 5.10, respectively, a position compatible with *exo* geometry. Both adducts undergo *retro*-Diels-Alder fragmentation on electron impact. Adduct XII (75 eV) shows peaks at *m/e* 669 (35%, parent ion of XII) and 496 (100%, ion of pyran XIV) while adduct XIII shows peaks at 685 (25%, parent ion of XIII) and 512 (100%, ion of heterocycle VI). It is not yet known whether the oxygen heterocycle XIV is involved in the formation of adduct XII from IX.

A thorough examination of the manifold chemical and physical properties of heterocycle VI hopefully will allow a detailed description of this interesting system.



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The Carbon-13 Nuclear Magnetic Resonance Spectrum of the Stable Nonclassical Norbornyl Cation. Incompatibility with the Equilibrating Classical Ion Conception and Further Proof for the Protonated Nortricyclene Structure¹

Sir:

The stable norbornyl cation has been shown by Raman spectroscopy² to be closely related to nortricy-

(1) Stable Carbonium Ions. LXXXVI. Part LXXXV: G. A. Olah, A. Commeyras, J. R. DeMember, and J. L. Bribes, *J. Amer. Chem. Soc.*, in press.