trum: m/e (rel intensity) 664 ($M^+ + 2$, 7), 662 (M^+, 2), 241 (44), 201 (57), 200 (65), 81 (44), 69 (100). *Anal.* Found: C, 83.1; H, 9.3.

The ir, uv,[18] and nmr[19] spectra of chlorobiumquinone, *cis,trans*-**1**, and *trans*-**2** were very similar. The mass spectra of chlorobiumquinone and *trans*-**2** were superimposable, whereas that of *cis,trans*-**1** was distinctly different, possessing a molecular ion at m/e 634. Tlc confirmed the dissimilarity of chlorobiumquinone and *cis,trans*-**1** while *trans*-**2** was coincident with the natural material. Therefore, chlorobiumquinone is *all-trans*-1′-oxomenaquinone-7 (**2**).

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[18] Although the uv spectra of chlorobiumquinone and 1′-oxomenaquinone-7 are qualitatively identical, a quantitative disparity exists; that is, we find an extinction coefficient at 250 nm of 32,000 *vs.* a reported value of 16,000.[1] A possible explanation is that this quinone series is particularly photolabile and exposure of spectrophotometric solutions to laboratory light even briefly before measurement could effect such a diminution.

[19] Whereas the nmr spectrum of *trans*-2 and that reported[1] for chlorobiumquinone are identical, there is a discrepancy with the assignments reported in ref 2, where the ring methyl and conjugated vinyl methyl absorptions have been reversed. These assignments will be discussed in detail in our full paper.

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William E. Bondinell,[20] Clinton D. Snyder,[20] Henry Rapoport[21]
Department of Chemistry, University of California
Berkeley, California 94720
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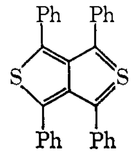
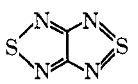
The Synthesis of Two Nonclassical Thienothiadiazoles

Sir:

Recently, syntheses of the stable nonclassical ten-π-electron heterocycles tetraphenylthieno[3,4-*c*]thiophene (**1**)[1] and 1,2,5-thiadiazolo[3,4-*c*]-1,2,5-thiadiazole (**2**)[2] have been described. These compounds are of considerable interest because of the unusual tetracovalent sulfur bonding found in them. In this regard, we wish to describe the preparation of 2,5-diphenylthieno[3,4-*c*]-1,2,5-thiadiazole (**3**) and the generation of 2,5-diphenylthieno[3,4-*e*]-2,1,3-benzothiadiazole (**4**), two novel sulfur-containing heterocyclic systems which are electronically similar to both thiophene **1** and thiadiazole **2**.



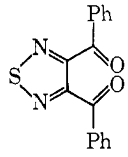
1



2

Treatment of 3,4-dibenzoyl-1,2,5-thiadiazole (**5**)[3] with phosphorus pentasulfide in dioxane solution at 110° for 5 hr gave heterocycle **3** as brilliant purple needles (mp 146°, 78% yield).[4] Heterocycle **3** shows ultraviolet and visible absorption maxima at $\lambda_{\max}^{\mathrm{CH_2Cl_2}}$ 275 nm (ϵ 16,700), 312 (21,600), 330 (19,900), and 558 (8650). The nmr spectrum of **3** closely resembles that of diketone **5** with proton resonance appearing as two complex multiplets centered at δ 7.5 (3 H) and 8.2 (2 H), suggesting that the phenyl substituents lie in the plane of the thienothiadiazole ring system. An extremely simple mass spectrum of the heterocycle was obtained with peaks at m/e 294 (100%, parent ion of **3**) and 121 (30%, ion of C_7H_5S).

Heterocycle **3** undergoes a sluggish Diels–Alder reaction at 140° with N-phenylmaleimide giving rise in 71% yield to a 2:1 mixture of the adducts **6** and **7**, respectively. The *exo* adduct **6**, mp 217°, shows a sharp singlet resonance for the two protons α to the imide carbonyl groups at δ 4.8, while the *endo* adduct **7**, mp 213°, exhibits singlet resonance for these protons at δ 3.8.[5] Both **6** and **7** undergo retro-Diels–Alder fragmentation on electron impact.



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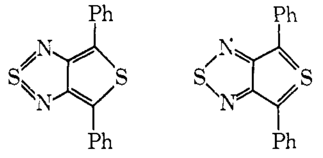

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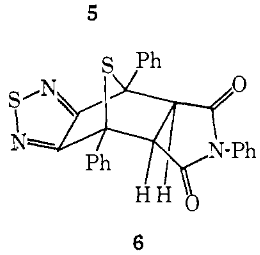

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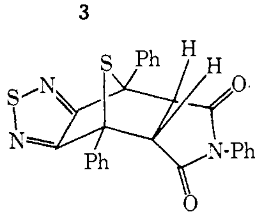

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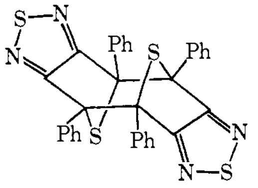

8

Irradiation of 0.1 *M* solutions of the heterocycle in rigorously degassed methylene chloride gave the insoluble white crystalline dimer, **8**, mp 100° dec (30% yield), along with unreacted **3** (68% yield). This result is in marked contrast to other stable tetracovalent sulfur systems which have been found to be photochemically inert under these conditions.[6] The ultraviolet and infrared spectra of the dimer show only the presence of a thiadiazole ring system. Compound **8** gives the correct parent ion (m/e 588) in the mass spectrum with the major fragment representing retrodimerization into heterocycle **3**.[7] In addition, thermal cracking of the dimer readily occurs in a variety of organic solvents when gently warmed.

Heterocycle **4** has been prepared starting from the readily available 5,6-dimethyl-2,1,3-benzothiadiazole (**9**).[8] Bromination of **9** with N-bromosuccinimide in

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[1] M. P. Cava and G. E. M. Husbands, *J. Amer. Chem. Soc.*, **91**, 3952 (1969).

[2] M. Carmack, R. W. Street, and R. Y. Wen, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-54.

[3] L. M. Weinstock and P. I. Pollak, *Advan. Heterocyclic Chem.*, **9**, 136 (1968).

[4] All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds.

[5] For a detailed discussion relating the chemical shifts of these protons to conformation in similar adduct systems, see ref 1.

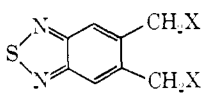
[6] For examples, see I. S. Ponticello and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **90**, 4190 (1968).

[7] The geometric assignment given to the dimer (head to tail) must be considered tentative.

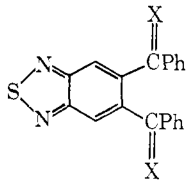
[8] V. G. Pesin, V. A. Sergeev, and A. M. Khaletskii, *J. Gen. Chem. USSR*, **34**, 1261 (1962).

carbon tetrachloride gave the dibromide **10**, mp 109°, in 90% yield. Reaction of **10** with a slurry of aluminum chloride and benzene gave rise (80% yield) to the dibenzylthiadiazole **11**, mp 108°, which in turn was oxidized with sodium dichromate in acetic acid into the diketone **12** (mp 178°, 92% yield). Although attempts to convert this diketone directly into **4** have been unsuccessful, the heterocycle has been generated as a transient species by dehydration of its corresponding dihydrosulfoxide **13**. Sulfoxide **13** was prepared from the diketone **12** by sodium borohydride reduction of the latter. The resultant diol, **14**, was then converted with phosphorus pentasulfide into the sulfide **15** (mp 212°, 50% overall yield from **12**). Oxidation of **15** with *m*-chloroperbenzoic acid in chloroform solution gave the sulfoxide **13**, mp 250° dec, in 71% yield.

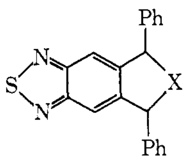
Upon heating 10^{-3} *M* solutions of sulfoxide **13** in acetic anhydride at 140°, a light blue color slowly formed. The visible spectrum of these solutions showed absorption at 645 nm, but all attempts to isolate heterocycle **4** from these reactions have resulted only in the high yield formation of an insoluble crystalline dimer, **16**. The infrared and ultraviolet spectra of **16**, mp >300°, show only the presence of a thiadiazole and thiophene ring system, indicating that dimerization of the heterocycle has occurred at the benzene ring and not at the thiophene ring.[7]



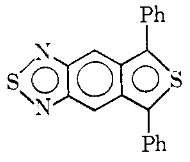
9, X = H
10, X = Br
11, X = Ph



12, X = O
14, X = HOH



13, X = SO
15, X = S



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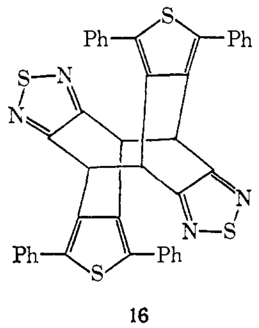
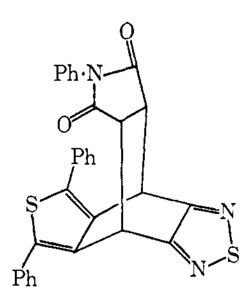


16

On the other hand, solutions of heterocycle **4** react with N-phenylmaleimide at both the benzene and thiophene rings, giving rise to adducts **17** (42% yield), **18** (24%), **19** (25%), and **20** (8%). Adducts **17** and **18** give absorption in the ultraviolet typical of thiadiazole and thiophene ring systems, while adducts **19** and **20** give absorption clearly indicating the presence of a benzothiadiazole residue. The assignment of *exo* geometry to **19** and *endo* geometry to **20** follows from the chemical shifts found for the protons α to the imide carbonyl groups in these adducts. Thus, singlet resonance at δ 5.1 was observed for adduct **19** while adduct **20** exhibited resonance at δ 4.15.[5] The nmr spectra of adduct **17**, mp 270°, and adduct **18**, mp 320°, are quite similar, and the configurational assignment indicated for these adducts must be considered uncertain.[9]



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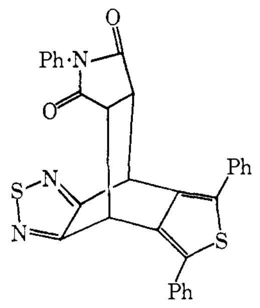

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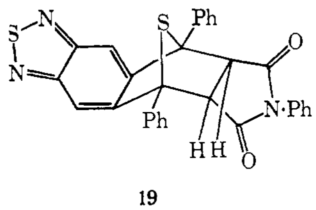

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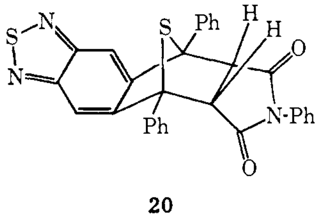

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Further work on the preparation of a stable analog **4** along with a detailed chemical and theoretical investigation of these heterocyclic systems is in progress.

Acknowledgment. We wish to thank the National Science Foundation for funds to purchase the Hitachi mass spectrometer.

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[9] Both adducts **17** and **18** show resonance for the protons α to the imide carbonyl groups at δ 3.7 and resonance for the bridgehead protons at δ 5.6.

J. D. Bower, R. H. Schlessinger
Department of Chemistry, University of Rochester
Rochester, New York 14627

Received September 30, 1969

The Stereochemistry of the Methylene Iodide–Zinc–Copper Couple Methylenation of Cyclic Allylic Alcohols[1]

Sir:

The reaction developed by Simmons and Smith[2] for methylene addition to double bonds has found wide application in organic synthesis. One of the more valuable aspects of this reaction is the stereochemical control exerted on the developing cyclopropane ring by a properly oriented hydroxyl group. First discovered by Winstein and coworkers[3] and later verified in a wide variety of simple systems,[4] the ability of a hydroxyl group to control the steric course of methylene addition has been successfully employed in several synthetic sequences.[5] Complex formation between the oxygen atom and the

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958).

[3] (a) S. Winstein, J. Sonnenberg, and L. de Vries, *ibid.*, **81**, 6523 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).

[4] (a) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963); (b) E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963); (c) A. C. Cope, S. Moon, and C. H. Park, *ibid.*, **84**, 4843 (1962); (d) J. J. Sims, *J. Org. Chem.*, **32**, 1751 (1967); (e) J. H. Chan and B. Rickborn, *J. Am. Chem. Soc.*, **90**, 6406 (1968).

[5] (a) W. G. Dauben and A. C. Ashcraft, *ibid.*, **85**, 3673 (1963); (b) P. Radlick and S. Winstein, *ibid.*, **86**, 1866 (1964); (c) R. Ginsig and A. D. Cross, *ibid.*, **87**, 4629 (1965); (d) M. Gasic, D. Whalen, B. Johnson, and S. Winstein, *ibid.*, **89**, 6382 (1967); (e) D. Whalen, M. Gasic, B. Johnson, H. Jones, and S. Winstein, *ibid.*, **89**, 6384 (1967).