data here presented strengthen the assumption that monomeric metaphosphorimidates can participate in the chemistry of phosphoramides.

Acknowledgments. The authors thank the National Science Foundation for financial support of this work under Grant No. GP 6465X, and the National Institutes of Health for a training grant for one of us (J. W.). We also express our appreciation to Professor S. Trippett and Dr. M. J. P. Harger, who made available to us details of their work prior to its publication, and to William Hull, who obtained Fourier transform nmr data for us. The XL-100 nmr spectrometer was purchased for this department through National Science Foundation Grant No. GP 32317.

Supplementary Material Available. A listing of the nmr data for compounds Ib, IIb, IIIb, Va, Vb, VIa, and VII will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-4262.

Synthesis of Nonclassical Thiophenes[1]

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Abstract: Phosphorus pentasulfide treatment of suitable vicinal dibenzoyl heterocycles has been established as a convenient pathway to three nonclassical thiophene systems: tetraphenylthieno[3,4-*c*]thiophene, 5-methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole, as well as hexaphenylthieno[3,4-*f*]isothianaphthene. 1,3-Dipolar cycloaddition reactions with dibenzoylacetylene, utilizing the "masked" 1,3-dipole of several mesoionic systems, readily provided the precursors to the 10π-electron heterocycles. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole formed 1:1 primary cycloadducts with activated olefins across both the 4 and 6 positions (azomethine ylide) and 1 and 3 positions (thiocarbonyl ylide), these additions being examples of kinetic and thermodynamic product control. In some cases, the thiocarbonyl ylide adducts underwent thermal elimination of the elements of hydrogen sulfide giving rise to bicyclic heteroaromatics. The addition of dibenzoylacetylene occurred only across the azomethine ylide affording a stable 1:1 adduct. Tetraphenylthieno[3,4-*c*]thiophene and dibenzoylacetylene formed an unstable 1:1 adduct which decomposed by the elimination of sulfur forming 5,6-dibenzoyl-1,3,4,7-tetraphenylisothianaphthene which, in turn, afforded hexaphenylthieno[3,4-*f*]isothianaphthene upon treatment with P_4S_{10}. This novel 14π-electron system underwent cycloaddition reactions with olefins across the 1 and 3 positions.

Nonclassical condensed thiophenes, because of their unusual electronic structure, have been the subject of several recent investigations.[2-4] Tetraphenylthieno[3,4-*c*]thiophene (**4**), initially reported[2e,c] in 1969, was the first stable example of a bicyclic heterocycle containing 10π electrons and a so-called "tetravalent sulfur" atom. Other representatives of this class of compound have since been described,[2a,b,d,f] and in several preliminary communications[1d] we have described an approach to the synthesis of nonclassical thiophenes based upon the cycloaddition reactions of mesoionic ring systems[5] with dibenzoylacetylene. The full details of this work are reported in this and the following publication.[6]

Tetraphenylthieno[3,4-*c*]thiophene (4). The synthesis of **4** was first effected by the acetic anhydride dehydration of *cis*-1,3,4,6-tetraphenyl-1*H*,3*H*-thieno[3,4-*c*]thiophene 2-oxide.[2c,e] It has now been prepared by P_4S_{10} treatment of 3,4-dibenzoyl-2,5-diphenylthiophene. This dibenzoylthiophene is readily available from anhydro-4-hydroxy-2,3,5-triphenylthiazolium hydroxide (**1**), itself formed by acetic anhydride cyclization of the acid formed from thiobenzanilide and α-bromophenylacetic acid.[5e] This system is generally represented as a hybrid of various charged separated structures (**1** and **1a**) though, in terms of the bonding concepts currently being discussed, contribution from a "tetravalent sulfur" structure (**1b**) must also be considered.[7] When **1** was treated with dibenzoylacetylene in refluxing benzene, 3,4-dibenzoyl-2,5-diphenylthiophene (**3**) was formed in 42% yield. This reaction presumably involves the initial addition of dibenzoylacetylene across the thiocarbonyl ylide (or 2 and 5 positions) of **1** affording the primary cycloadduct **2**, which then decomposes to **3** by the elimination of phenyl isocyanate. Analytical and spectral data (Experimental Section) clearly established the assigned structure.

When **3** was treated with phosphorus pentasulfide in

(1) (a) Support of this work by U. S. Public Health Service Research Grant CA 08495, National Cancer Institute is gratefully acknowledged; (b) abstracted from the Ph.D Thesis of D. McKeough, Rensselaer Polytechnic Institute, 1973; (c) Sterling-Winthrop Fellow, 1971–1973; (d) preliminary communications: K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **95**, 2749, 2750 (1973).

(2) (a) M. P. Cava and M. A. Sprecker, *J. Org. Chem.*, **38**, 3975 (1973); (b) M. P. Cava, N. M. Pollack, and G. A. Dieterle, *J. Amer. Chem. Soc.*, **95**, 2558 (1973); (c) M. P. Cava, M. Behforouz, G. E. M. Husbands, and M. Srinivasan, *ibid.*, **95**, 2561 (1973); (d) M. P. Cava and M. A. Sprecker, *ibid.*, **94**, 6214 (1972); (e) M. P. Cava and G. E. M. Husbands, *ibid.*, **91**, 3952 (1969); (f) J. D. Bower and R. H. Schlessinger, *ibid.*, **91**, 6891 (1969).

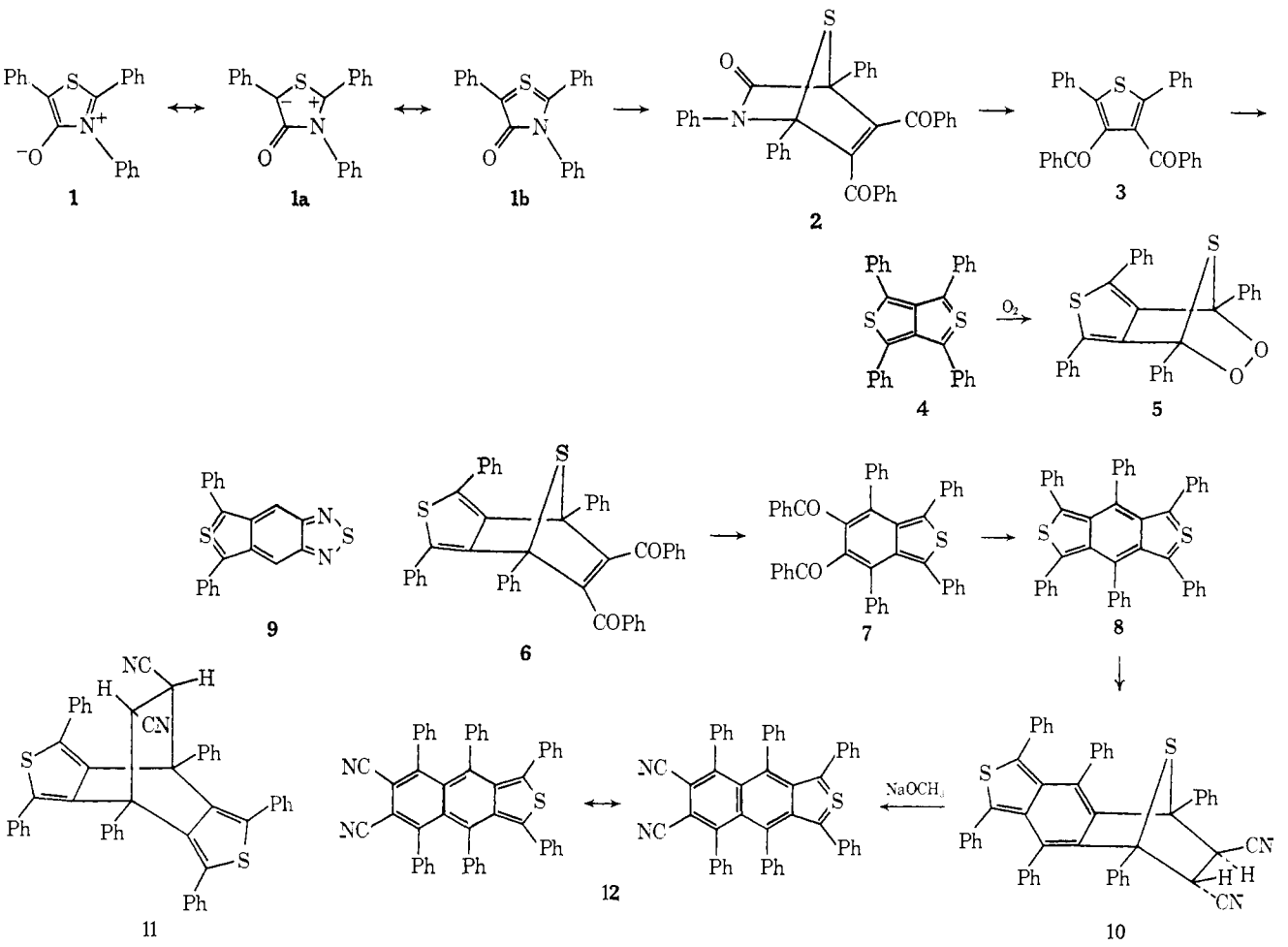
(3) M. D. Glick and R. E. Cook, *Acta Crystallogr., Sect. B*, **28**, 1336 (1972).

(4) M. O. Calculations on the thieno[3,4-*c*]thiophene system [D. T. Clark, *Tetrahedron*, **24**, 2567 (1968)] ignoring d orbital participation, predict a high energy for this system as well as a triplet ground state.

(5) *E.g.*, see (a) R. Huisgen, G. Gotthardt, and R. Grashey, *Chem. Ber.*, 101, 536 (1968); (b) K. T. Potts and D. N. Roy, *Chem. Commun.*, 1061, 1062 (1968); (c) K. T. Potts, E. Houghton, and U. P. Singh, *ibid.*, 1129 (1969).

(6) K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **96**, 4276 (1974).

(7) G. F. Duffin and J. D. Kendall, *J. Chem. Soc.*, 3189 (1956).



refluxing pyridine, tetraphenylthieno[3,4-*c*]thiophene (**4**) was isolated in 83% yield as glistening, purple needles, mp 245–247°. All of the spectral characteristics observed for this compound were consistent with those reported by Cava.[2c]

Recently[2c] the transformation of **3** into **4** was attempted in refluxing xylene using excess phosphorus pentasulfide. The product isolated from this experiment was not, however, the anticipated tetraphenylthieno[3,4-*c*]thiophene but rather its dihydro derivative. These results were interpreted[2c] in terms of the initial formation of **4** which, under the reaction conditions using excess phosphorus pentasulfide, underwent apparent reduction to the dihydro derivative. In support of this it was noted that **4** was reduced in 58% yield when subjected to P_4S_{10}–xylene treatment. Clearly the transformation of **3** into **4** by phosphorus pentasulfide is critically dependent on the reaction conditions.

As was noted previously,[2c] this ring system was stable indefinitely in the solid phase, but solutions of it were rapidly bleached upon exposure to light and significant amounts of 3,4-dibenzoyl-2,5-diphenylthiophene (**3**) were noted in the reaction mixture. These observations have been interpreted as a photochemically induced addition of oxygen, resulting in formation of the peroxide adduct **5** which collapses with elimination of sulfur to **3**. Similar type pathways have been proposed to account for the air oxidation in solution of 1,3-diphenyl-2-thiaphenylene[8c] and 6,7-dibromo-1,3-diphenylacenaphtho[5,6-*cd*]thiapyran[9c] to their corresponding dibenzoyl compounds, and has also been observed in the photochemical addition of oxygen to anhydro-3-hydroxy-2,4,6-triphenylpyrylium hydroxide.[10]

An indication of the ability of this ring system to undergo Diels–Alder type reactions was shown initially[2e] by the reaction of **4** and *N*-phenylmaleimide from which a stable exo–endo mixture of primary cycloadducts was obtained. Reaction of **4** with dimethyl acetylenedicarboxylate subsequently was shown[2c] to give an isothianaphthene derivative and in our study reaction of **4** with dibenzoylacetylene gave 5,6-dibenzoyl-1,3,4,7-tetraphenylisothianaphthene (**7**) in 61% yield as yellow needles, mp 299–300°.

This reaction presumably involves initial formation of unstable adduct **6**, which decomposes by the elimination of elemental sulfur giving rise to **7** whose spectral characteristics are described in the Experimental Section. An analogous type reaction was reported by Wittig, Knauss, and Niethammer,[11] who observed formation of 2,3-bis(methoxycarbonyl)-1,4-diphenylnaphthalene upon treatment of 1,3-diphenylisothianaphthene with dimethyl acetylenedicarboxylate. A similar

(8) (a) M. P. Cava, N. M. Pollack, and D. A. Repella, *J. Amer. Chem. Soc.*, **89**, 3640 (1967); (b) R. H. Schlessinger and I. S. Ponticello, *ibid.*, **89**, 3641 (1967); (c) R. H. Schlessinger and A. G. Schultz, *ibid.*, **90**, 1676 (1968).

(9) (a) R. H. Schlessinger and I. S. Ponticello, *Tetrahedron Lett.*, 4057 (1967); (b) R. H. Schlessinger and J. M. Hoffmann, *J. Amer. Chem. Soc.*, **91**, 3953 (1969); (c) I. S. Ponticello and R. H. Schlessinger, *ibid.*, **90**, 4190 (1968).

(10) H. H. Wasserman and D. L. Pavia, *Chem. Commun.*, 459 (1970).

(11) G. Wittig, E. Knauss, and K. Niethammer, *Justus Liebigs Ann. Chem.*, **630**, 10 (1960).

transient has been proposed[12] to rationalize the formation of 3,6-dimethylphthalonitrile from 2,5-dimethylthiophene and dicyanoacetylene.

Hexaphenylthieno[3,4-*f*]isothianaphthene (8). By an extension of these cycloaddition procedures described above, it is possible to prepare hexaphenylthieno[3,4-*f*]-isothianaphthene, a novel 14π-electron system containing a "tetravalent sulfur" in a five-membered ring. The only hitherto described[2f] example of such a ring system, 5,7-diphenylthieno[3,4-*f*]benzo[*c*][1,2,5]thiadiazole (**9**), was found to be unstable, being isolated as its 1:1 adduct with *N*-phenylmaleimide. Other examples are known, however, where the sulfur atom is in a six-membered ring, as in the naphtho[1,8-*cd*]thiapyran[8] and acenaphtho[5,6-*cd*]thiapyran[9] ring systems.

Phosphorus pentasulfide treatment of **7** in refluxing pyridine provided a convenient synthesis of hexaphenylthieno[3,4-*f*]isothianaphthene (**8**), isolated as finely matted blue needles, mp 348–350°. Absorption maxima were observed in the ultraviolet spectrum of **8** at 370 sh, 316, 259 sh, and 245 nm and in the visible at 877 and 793 nm. The most abundant ion in the mass spectrum corresponded to the molecular ion, *m/e* 646 with a less intense doubly charged molecular ion *m/e* 323 also being observed. In a recent publication[2a] the reaction of **7** with phosphorus pentasulfide in refluxing xylene was described. These reaction conditions resulted in reduction of **8** to the 3,4-dihydro derivative.

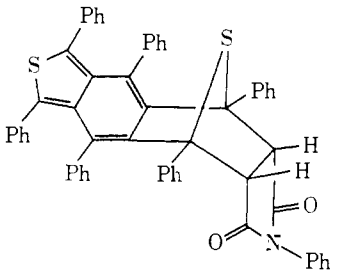
As was observed with tetraphenylthieno[3,4-*c*]thiophene, dilute solutions of **8** were rapidly bleached on exposure to light. Significant amounts of 5,6-dibenzoyl-1,3,4,7-tetraphenylisothianaphthene (**7**) were noted in these bleached solutions suggesting an oxidative process analogous to that discussed previously.

Treatment of **8** with fumaronitrile in refluxing xylene resulted in the formation of a single primary 1:1 cycloadduct, mp 293–295° dec, isolated as pale-yellow, matted needles. Two possible structures, **10** and **11**, were considered for this adduct as addition could occur across either the 1 and 3 positions or 4 and 8 positions.

The overall shape of the ultraviolet absorption spectrum of this product (λ_{max} 364, 280 nm) indicated the presence of an isothianaphthene chromophore. Consistent with this was the observation that the adduct fluoresced strongly when exposed to ultraviolet light, a property characteristic of isothianaphthenes. In addition, treatment with hot methanolic sodium methoxide resulted in its conversion into 6,7-dicyano-1,3,4,5,8,9-hexaphenylnaphtho[2,3-*c*]thiophene (**12**), mp 375–376°. This process, ultimately resulting in elimination of the elements of hydrogen sulfide, is probably initiated by methoxide ion abstraction of one of the protons α to a nitrile group.

All of these results indicate structure **10**, 6-*endo*-7-*exo*-dicyano-1,3,4,5,8,9-hexaphenyl-5,6,7,8-tetrahydro-5,8-epithionaphtho[2,3-*c*]thiophene, as the best representation for the 1:1 adduct. The exo/endo nomenclature, as used in this case, refers to the orientation of the substituents with respect to the sulfur bridge and this point of reference applies to all other bridged systems described below.

The reaction of hexaphenylthieno[3,4-*f*]isothianaphthene (**8**) with *N*-phenylmaleimide resulted in the formation of a single 1:1 adduct, mp 373–375° dec, for which three structures are possible: the endo or exo adducts **13** and **14** resulting from addition across the 1 and 3 positions or adduct **15** resulting from addition across the 4 and 8 positions. The overall similarities in the ultraviolet spectrum of this adduct to that of **10** eliminated structure **15** from further consideration. The chemical shift of the protons α to the imide carbonyl groups (τ 5.20), considering the deshielding



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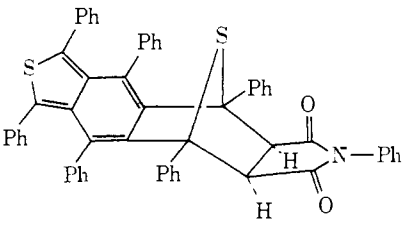

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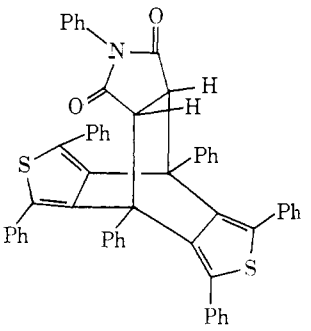

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effects of the bridgehead sulfur atom,[2c] indicates structure **13** as the best possible representation for this adduct.

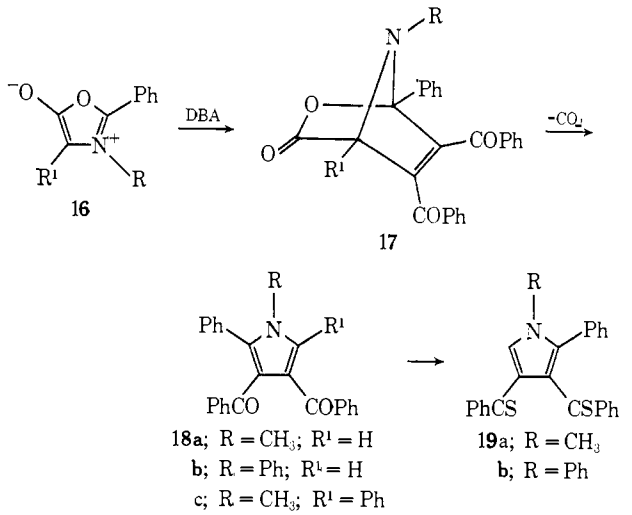
Thieno[3,4-*c*]pyrrole System (20). The introduction of a nitrogen atom into the second ring of a fused nonclassical thiophene system offers an opportunity to evaluate the relative reactivities of two ylides often encountered as the "masked 1,3-dipole" present in mesoionic ring systems.[5] The thieno[3,4-*c*]pyrrole system, unlike those previously investigated, can be represented by only one uncharged structure. However, dipolar forms undoubtedly make some contribution to its hybrid structure. Molecular orbital calculations, using a model neglecting d orbital participation, predicted this system to be extremely unstable,[13] and its synthesis was of considerable interest.

5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (**20**) has recently been prepared as a bright-red powder forming a 1:1 cycloadduct with dimethyl acetylenedicarboxylate in which addition had occurred across the azomethine ylide.[2d] Utilization of mesoionic ring systems in the synthesis of the 3,4-dibenzoylpyrrole precursor now provides a convenient route to this

(12) R. Helder and H. Wynberg, *Tetrahedron Lett.*, 605 (1972).

(13) L. Klasinc and N. Trinajstic, *Tetrahedron*, **28**, 4045 (1971).

system and enables the effect of substituents on the stability of the system to be studied. In addition to compound **20**, the synthesis of two other derivatives of this system was attempted, *viz.*, 5-methyl-1,3,4-triphenyl- and 1,3,4,5-tetraphenylthieno[3,4-*c*]pyrrole. In all cases the precursors were prepared by the addition of dibenzoylacetylene to derivatives of the anhydro-5-hydroxyoxazolium hydroxide system (**16**). The mesoionic compounds used in this investigation were not actually isolated, as most examples of **16**, because of their extreme reactivity, are unstable.[14] However, they can be generated *in situ* by acetic anhydride cyclization[15,16] of the corresponding *N*-benzoylglycine derivatives. When this was carried out in the presence of dibenzoylacetylene, 3,4-dibenzoylpyrrole derivatives (**18**) were isolated as products in good yields, presumably *via* the intermediate **17**.



Phosphorus pentasulfide treatment of those derivatives of **18** which contained a hydrogen at the 5 position resulted in formation of the corresponding dithiobenzoyl compounds **19**. Thus, 3,4-dithiobenzoyl-1-methyl-2-phenylpyrrole (**19a**) was formed from **18a** as yellow needles, and **18b** gave 1,2-diphenyl-3,4-dithiobenzoylpyrrole (**19b**) also as yellow needles. In both cases, the use of excess phosphorus pentasulfide did not alter the course of the reaction. Although the actual mechanism is not known, dithiobenzoyl compounds have been proposed as intermediates in processes whereby a dibenzoyl compound is converted into a fused thiophene system.[9b] Why the reaction apparently stops at this stage for the case of **18a** and **18b** is not immediately obvious but one possibility is that the fused thiophene systems which would result from collapse of **19a** and **19b** are unstable, high energy systems not attainable under the reaction conditions employed.

One other case has been reported in which a nonclassical, fused thiophene system could not be prepared directly from its corresponding dibenzoyl compound and involved phosphorus pentasulfide treatment of 5,6-dibenzoylbenzo[*c*][1,2,5]thiadiazole.[2f] It was subsequently shown by an alternative synthesis that this system could be generated and trapped *in situ* but was too unstable to be isolated.

Investigation of the Diels–Alder reactions of 5-methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole was initiated with fumaronitrile. In either refluxing toluene or xylene, two products were isolated and analytical data showed that only one of these was a primary cycloadduct. Two structures are possible for this adduct; **21** corresponding to the addition of fumaronitrile across the 1 and 3 positions or thiocarbonyl ylide of **20**, and **22** corresponding to addition across the 4 and 6 positions or azomethine ylide of **20**. The former was chosen, based on the observation that the chemical shift of the *N*-methyl group (τ 6.87) does not change significantly in going from starting material to adduct. Resonance signals for the protons α to the nitrile groups were observed as doublets at τ 5.88 and 5.42, consistent with the effect of the bridgehead sulfur atom. The observed coupling constant of 3.9 Hz indicated that the trans nature of the dienophile was maintained throughout the course of addition.

The second product isolated from the reaction mixture was identified as 5,6-dicyano-2-methyl-1,3,4,7-tetraphenylisoindole (**23**), obtained as yellow needles, mp 332–334°. The yields of both these products are dependent on the reaction conditions employed. In refluxing toluene, the yield of primary cycloadduct **21** was 67% with the yield of isoindole **23** being 5%. When refluxing xylene was used as solvent, the yield of the latter was increased to 53% apparently at the expense of the former, whose yield was decreased to 10%.

These results suggest that the isoindole is formed from the primary cycloadduct by thermal elimination of the elements of hydrogen sulfide. A possible mechanism that would account for this transformation would involve initial loss of a sulfur atom from the primary adduct to give a diradical species from which the sulfur atom could then abstract the hydrogen atoms α to the nitrile groups leading to the formation of **23** and hydrogen sulfide. The dehydrogenating ability of sulfur has previously been noted.[17]

It was found that adduct **21** could also be converted into isoindole **23** by a base-catalyzed process. Thus, treatment of **21** with methanolic sodium methoxide at room temperature afforded **23** in 93% yield.

In refluxing benzene, the reaction of 5-methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole and fumaronitrile, monitored by thin-layer chromatography, was complete within 1 hr. A product was isolated whose analytical data confirmed formation of a primary 1:1 cycloadduct. However, the properties of this compound differed markedly from those of adduct **21** above. Because of the symmetry of the "tetravalent" sulfur compound, the only possible structures for this new adduct is one resulting from the addition of fumaronitrile across the azomethine ylide of **20** to give **22**. Examination of the mother liquor from this reaction indicated that neither adduct **21** nor isoindole **23** was present.

It was thought that the resonance signal of the *N*-methyl group in **22** would be shifted upfield relative to its position in either adduct **21** or 5-methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (**20**). In both of these last two cases, the methyl group is influenced by the

(14) C. B. Greco, R. P. Gray, and V. G. Grosso, *J. Org. Chem.*, 32, 4101 (1967).
(15) K. T. Potts and U. P. Singh, *Chem. Commun.*, 66 (1969).
(16) H. O. Bayer, R. Huisgen, R. Knorr, and F. C. Schaefer, *Chem. Ber.*, 103, 2581 (1970).
(17) W. A. Pryor, "Mechanisms of Sulfur Reactions," McGraw-Hill, New York, N. Y., 1962, p 117.

diamagnetic ring current of the aromatic system to which it is attached. Contrary to expectations, the observed chemical shift of the *N*-methyl group of **22** was τ 7.07. However, due to solubility problems, the spectrum of **22** was determined in CF_3COOD, and apparently the bridgehead nitrogen was deuterated under the conditions of measurement. As a result, the resonance signal of the *N*-methyl group in **22** was fortuitously similar to the chemical shift of the *N*-methyl groups of **20** and **21**.

The major difference between the adducts resulting from azomethine ylide addition and thiocarbonyl ylide addition was thermal stability. On attempted dissolution in warm solvents, adduct **22** underwent a facile retro-Diels–Alder reaction. Conversely, adduct **21** was readily recrystallized from solvents such as ethanol and acetonitrile. In addition, **22** could not be heated under vacuum whereas **21** was stable to these conditions. When **22** was heated in refluxing xylene for 14 hr, 5,6-dicyano-2-methyl-1,3,4,7-tetraphenylisoindole (**23**) was formed in 60% yield and trace amounts of adduct **21** were detected in the reaction mixture. Adduct **22** had been completely consumed in this experiment. These results can be rationalized in terms of an initial retro-Diels–Alder reaction of adduct **22** affording 5-methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (**20**) and fumaronitrile. These last two compounds eventually recombine by a Diels–Alder reaction in which addition occurs across the thiocarbonyl ylide of **20** to give adduct **21**. Under conditions of refluxing xylene, **21** undergoes a thermally induced elimination of the elements of hydrogen sulfide affording **23**.

All of the observations encountered in the addition of fumaronitrile to 5-methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole suggest that this is a reaction which displays both kinetic and thermodynamic product control. Based on the above arguments, it appears that adduct **22**, resulting from azomethine ylide addition to fumaronitrile, is the kinetically controlled product whereas **21** resulting from thiocarbonyl ylide addition is the thermodynamically controlled product.

Similar modes of addition were observed using other olefinic dipolarophiles. In refluxing benzene solution, 5-methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole and *N*-phenylmaleimide formed a single 1:1 primary cycloadduct **25** in which addition had occurred across the azomethine ylide. When this reaction was repeated in refluxing xylene, addition of *N*-phenylmaleimide took place across the thiocarbonyl ylide. This adduct, **24**, however, did not undergo thermal elimination of the elements of hydrogen sulfide.

Acrylonitrile and ethyl acrylate both undergo addition across the azomethine ylide of **20** in refluxing benzene, giving **26** (R = CN and COOEt, respectively). When the solvent system was changed to refluxing toluene or xylene, isoindole derivatives **27** (R = CN and COOEt, respectively) were formed in addition to these azomethine ylide adducts. Cycloadducts resulting from thiocarbonyl ylide addition were never isolated. In these cases, as soon as addition occurred across the thiocarbonyl ylide the resulting adduct must immediately eliminate the elements of hydrogen sulfide giving rise to the isoindole systems. All of these results are summarized in Table I.

The Diels–Alder reactions of 5-methyl-1,3,4,6-tetra-

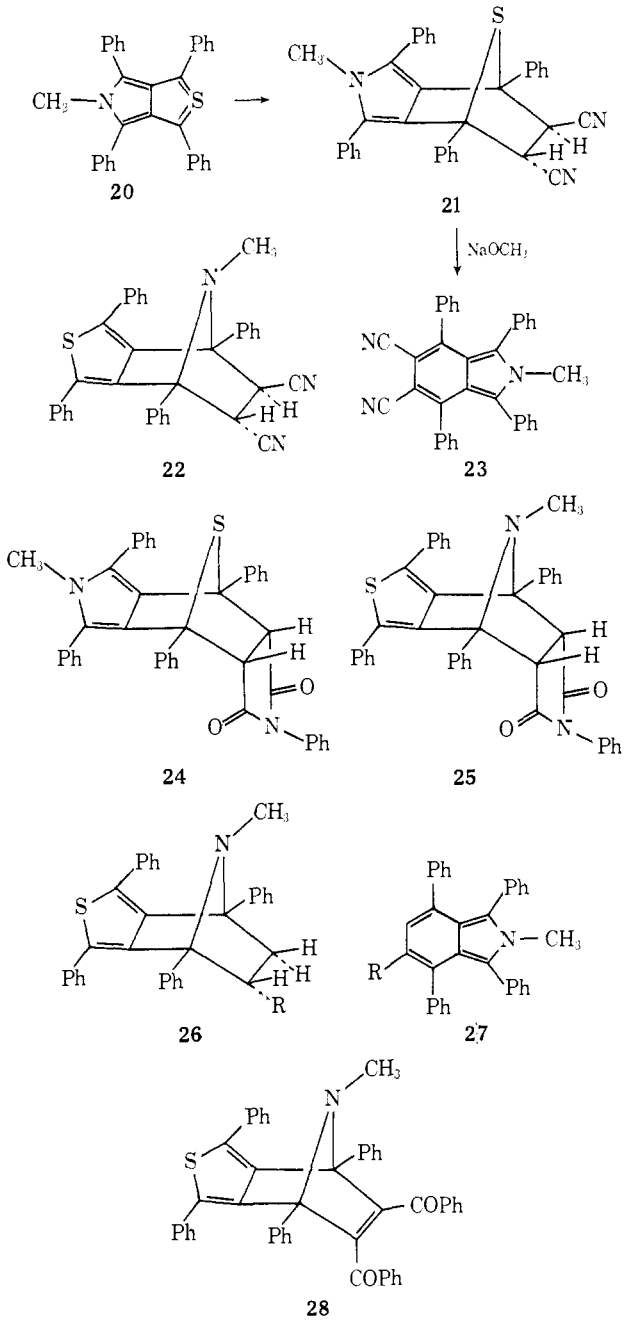


Table I. Product Distribution in the Cycloaddition Reactions of 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole with Olefinic Dipolarophiles

Dipolarophile	Solvent[a]	Time, hr	Yield %: Azomethine ylide adduct	Yield %: Thiocarbonyl ylide adduct	Yield %: Isoindole
Fumaronitrile	B	1	63		
Fumaronitrile	T	12		67	5
Fumaronitrile	X	12		10	53
N-Phenylmaleimide	B	0.5	68		
N-Phenylmaleimide	X	12		73	
Acrylonitrile	B	12	74		
Acrylonitrile	T	9	48		8
Acrylonitrile	X	24	4		55
Ethyl acrylate	B	15	68		
Ethyl acrylate	T	12	49		10
Ethyl acrylate	X	30	5		61

[a] All reactions carried out at the reflux temperature of the solvent: B = benzene; T = toluene; X = xylene.

phenylthieno[3,4-*c*]pyrrole and a variety of other olefinic systems could not be effected under conditions ranging from refluxing benzene to refluxing xylene. The dienophiles used included dimethyl fumarate, dimethyl maleate, norbornene, and diphenylcyclopropenone. The inactivity of these systems is probably due to unfavorable steric interactions and, similarly, heterocumulenes such as phenyl isocyanate, phenyl isothiocyanate, and benzoyl isocyanate also failed to undergo addition to **20**.

The reaction of 5-methyl-1,3,4,6-tetraphenylthieno-[3,4-*c*]pyrrole (**20**) with an acetylenic system was also investigated. With dibenzoylacetylene in refluxing benzene, a 1:1 adduct was formed in which addition occurred across the azomethine ylide to give 5,6-dibenzoyl-4,7-dihydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (**28**), mp 247–249° dec. As expected, the chemical shift of the *N*-methyl group (τ 7.98) is observed considerably upfield relative to its position in starting material.

Oxidation of **28** with *m*-chloroperoxybenzoic acid[2d] afforded 5,6-dibenzoyl-1,3,4,7-tetraphenylisothianaphthene (**7**), presumably through the intermediacy of the *N*-oxide. This was the same product formed upon treatment of tetraphenylthieno[3,4-*c*]thiophene with dibenzoylacetylene.

In an attempt to effect addition of dibenzoylacetylene across the thiocarbonyl ylide of **20**, the reaction was repeated in refluxing xylene for 48 hr. Once again, addition occurred across the azomethine ylide affording a 34% yield of adduct **28** together with a 17% yield of the isothianaphthene **7**. The latter is probably the result of a slow, air oxidation of **28** for, if the reaction takes place under a stream of nitrogen, formation of the isothianaphthene is inhibited. However, the predominant product in the reaction mixture is still the adduct resulting from azomethine ylide addition and, in no case, was an adduct isolated which resulted from thiocarbonyl ylide addition. These results indicate that the azomethine ylide adducts with acetylenes are thermally more stable than those with olefins.

The reactions described above clearly show that, in these ring systems, the azomethine ylide system is more reactive than the thiocarbonyl ylide system. This relationship has also been observed in mesoionic ring systems containing these ylide functions.

Experimental Section[18]

3,4-Dibenzoyl-2,5-diphenylthiophene (3). Anhydro-4-hydroxy-2,3,5-triphenylthiazolium hydroxide[5c] (2.00 g, 6.10 mmol), dibenzoylacetylene[19] (1.42 g, 6.10 mmol), and benzene (50 ml) were refluxed for 30 hr. The solvent was removed under vacuum and the residue chromatographed on Florisil using chloroform as eluent. The product separated as pale-yellow, irregular prisms from ethanol: 1.14 g (42%), mp 139–140° (lit.[2c] mp 142–143°); ir (KBr) 3050, 3025 (CH), 1660, 1640 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 262 nm (log ϵ 4.66); nmr ($CDCl_3$) τ 2.92–2.40 (m, 16, aromatic), 2.38–2.15 (m, 4, aromatic); $M\cdot^+$ 444 (100), M^{2+} 222 (3).

Anal. Calcd for $C_{30}H_{20}O_2S$: C, 81.06; H, 4.54. Found: C, 80.86; H, 4.49.

Tetraphenylthieno[3,4-*c*]thiophene (4). 3,4-Dibenzoyl-2,5-diphenylthiophene (1.00 g, 2.25 mmol), phosphorus pentasulfide (0.50 g, 2.25 mmol), and dry pyridine (25 ml) were refluxed for 90 min. Upon cooling, the reaction mixture was poured into ice–water. A purple solid separated which was collected, washed with water, and air dried. Recrystallization from acetic anhydride afforded glistening, purple needles: 0.83 g (83%), mp 245–247°; ir (KBr) 3085 and 3065 (CH) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 551 nm (log ϵ 3.92), 292 (4.15), 262 sh (4.27), 258 (4.30); nmr ($CDCl_3$) τ 2.85 (s, aromatic); $M\cdot^+$ 444 (100), M^{2+} 222 (10).

Anal. Calcd for $C_{30}H_{20}S_2$: C, 81.06; H, 4.54. Found: C, 80.82; H, 4.47.

5,6-Dibenzoyl-1,3,4,7-tetraphenylisothianaphthene (7). Tetraphenylthieno[3,4-*c*]thiophene (1.00 g, 2.25 mmol), dibenzoylacetylene (0.53 g, 2.25 mmol), and xylene (20 ml) were refluxed for 24 hr. The solvent was removed under vacuum and the residue chromatographed on silica gel, eluted initially with benzene followed by benzene–ethyl acetate (50:1). Recrystallization from acetic anhydride gave yellow needles: 0.89 g (61%), mp 299–300°; ir (KBr) 3070, 3040 (CH), 1670 (CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 411 nm (log ϵ 3.77), 260 (4.60); nmr ($CDCl_3$) τ 3.42–2.72 (m, 26, aromatic), 2.56–2.28 (m, 4, aromatic); $M\cdot^+$ 646 (100), M^{2+} 323 (2).

Anal. Calcd for $C_{46}H_{30}O_2S$: C, 85.42; H, 4.67. Found: C, 85.30; H, 4.61.

Hexaphenylthieno[3,4-*f*]isothianaphthene (8). 5,6-Dibenzoyl-1,3,-4,7-tetraphenylisothianaphthene (2.00 g, 3.10 mmol), phosphorus pentasulfide (0.69 g, 3.10 mmol), and dry pyridine (40 ml) were refluxed for 5 hr. Upon cooling, the reaction mixture was poured into 10% sodium hydroxide solution. A greenish-blue product separated which was filtered and washed with water. Digestion of this solid with hot dioxane afforded finely matted, blue needles: 1.48 g (74%), mp 348–350°; ir (KBr) 3070 and 3040 (CH) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 877 nm (log ϵ 3.25), 793 (4.06), 370 sh (3.48), 316 (4.38), 259 (4.50), 245 (4.59); $M\cdot^+$ 646 (100), M^{2+} 323 (18).

The poor solubility of this compound precluded both successful recrystallization and chromatography such that an analytically pure sample could not be obtained. However, it was further characterized by the formation of a stable 1:1 cycloadduct with *N*-phenylmaleimide.

6-*endo*-7-*exo*-Dicyano-1,3,4,5,8,9-hexaphenyl-5,6,7,8-tetrahydro-5,8-epithionaphtho[2,3-*c*]thiophene (10). Hexaphenylthieno[3,4-*f*]-isothianaphthene (1.00 g, 1.55 mmol), fumaronitrile (0.12 g, 1.55 mmol), and xylene (30 ml) were refluxed for 8 hr. A yellow solid separated upon cooling and crystallized from 1,2-dichloroethane as pale-yellow, matted needles: 0.85 g (76%), mp 293–295° dec; ir (KBr) 3050, 3020 (CH), 2245 (CN) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 364 nm (log ϵ 3.97) and 280 (4.46); nmr ($CDCl_3$ HA-100) τ 4.77 (AB qt, 2, $H_{6\text{-exo}}$, $H_{7\text{-endo}}$, $J_{6\text{-exo},7\text{-endo}}$ = 4.0 Hz; AB calcd ν_A τ 4.57, ν_B 4.78), 3.53–2.75 (m, 30, aromatic); $M\cdot^+$ 724 (18).

This adduct retained 1,2-dichloroethane as solvent of crystallization and could not be dried properly as heating under vacuum resulted in a thermally induced retro-Diels–Alder reaction. As a result, its analysis was low for carbon. The adduct was further characterized, however, by its conversion into 6,7-dicyano-1,3,4,-5,8,9-hexaphenylnaphtho[2,3-*c*]thiophene upon treatment with base.

Anal. Calcd for $C_{50}H_{32}N_2S_2$: C, 82.85; H, 4.45; N, 3.87. Found: C, 77.55; H, 4.47; N, 3.60.

6,7-Dicyano-1,3,4,5,8,9-hexaphenylnaphtho[2,3-*c*]thiophene (12). 6-*endo*-7-*exo*-Dicyano-1,3,4,5,8,9-hexaphenyl-5,6,7,8-tetrahydro-5,8-epithionaphtho[2,3-*c*]thiophene (1.00 g, 1.38 mmol) and 10% methanolic sodium methoxide (30 ml) were refluxed for 6 hr. A purple solid separated which was filtered and washed with water. Recrystallization from dioxane gave purple needles: 0.85 g, (89%), mp 375–376°; ir (KBr) 3045, 3020 (CH), 2210 (CN) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 567 nm (log ϵ 3.98), 406 sh (3.54), 324 (4.89), 266 sh (4.44), 244 (4.56); nmr ($CDCl_3$) τ 3.53–2.92 (m, aromatic).

Anal. Calcd for $C_{50}H_{30}N_2S$: C, 86.93; H, 4.38; N, 4.06. Found: C, 87.04; H, 4.40; N, 4.03.

***endo*-*N*,1,3,4,5,8,9-Heptaphenyl-5,6,7,8-tetrahydro-5,8-epithionaphtho[2,3-*c*]thiophene-6,7-dicarboximide (13).** Hexaphenylthieno[3,4-*f*]isothianaphthene (2.00 g, 3.10 mmol), *N*-phenylmaleimide (0.54 g, 3.10 mmol), and xylene (40 ml) were refluxed for 9 hr. Upon cooling the solution, a yellow solid separated which crystallized from chloroform–hexane as pale-yellow, irregular prisms: 2.10 g (83%), mp 373–375° dec; ir (KBr) 3045, 3020 (CH), 1710

(18) All melting points were determined in capillaries using a Thomas-Hoover capillary melting point apparatus or a Mel-Temp apparatus. Evaporations were carried out under reduced pressure using a Büchi rotavap apparatus. Spectral characteristics were determined on the following instrumentation: infrared spectra, Perkin-Elmer Model 337 spectrophotometer; ultraviolet spectra, Cary 14 spectrophotometer; nmr spectra, Varian T-60 and HA-100 spectrometers, using TMS as internal standard; mass spectra, Hitachi-Perkin-Elmer RMU-6E mass spectrometer, utilizing the direct inlet probe with a source temperature of *ca.* 150°. Microanalyses were performed by Instranal Laboratories, Inc., Rensselaer, N. Y., and Galbraith Laboratories, Inc., Knoxville, Tenn.

(19) J. D. White, M. E. Mann, H. D. Kirshbaum, and M. Mitra, *J. Org. Chem.*, **36**, 1048 (1971).

(CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 371 nm (log ϵ 4.03) and 287 (4.39); nmr ($CDCl_3$) τ 5.20 (s, 2, $H_{6\text{-exo}}$, $H_{7\text{-exo}}$), 3.71–2.97 (m, 33, aromatic), 2.81–2.52 (m, 2, aromatic).

Anal. Calcd for $C_{56}H_{37}NO_2S_2$: C, 82.01; H, 4.54; N, 1.70. Found: C, 81.96; H, 4.54; N, 1.76.

The following procedure is representative of those used for the preparation of 3,4-dibenzoylpyrrole derivatives.

3,4-Dibenzoyl-1-methyl-2-phenylpyrrole (18a). *N*-Benzoylsarcosine[16] (1.93 g, 10 mmol), dibenzoylacetylene (2.34 g, 10 mmol), and acetic anhydride (20 ml) were heated at 120° for 2 hr. The reaction mixture was poured into water and extracted in three portions with chloroform (40 ml total volume). The organic layer was washed with 10% sodium bicarbonate solution followed by water and dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the residue recrystallized from ethanol giving colorless needles: 2.48 g (65%), mp 186–188°; ir (KBr) 3080, 3070, 3050 (CH), 1650, 1640 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 287 nm sh (log ϵ 3.87), 248 (4.42); nmr ($CDCl_3$) τ 6.42 (s, 3, NCH_3), 2.92–2.49 (m, 11, aromatic), 2.47–2.20 (m, 5, aromatic); $M\cdot^+$ 365 (65), M^{2+} 182.5 (6).

Anal. Calcd for $C_{25}H_{19}NO_2$: C, 82.17; H, 5.24; N, 3.83. Found: C, 82.07; H, 5.23; N, 3.77.

3,4-Dibenzoyl-1,2-diphenylpyrrole (18b) crystallized from ethanol as colorless plates: yield 57%; mp 168–169°; ir (KBr) 3140, 3070 (CH), 1665, 1645 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 298 nm sh (log ϵ 3.85), 252 (4.47); nmr ($CDCl_3$) τ 2.97–2.46 (m, 17, aromatic), 2.36–2.07 (m, 4, aromatic); $M\cdot^+$ 427 (91), M^{2+} 213.5 (5).

Anal. Calcd for $C_{30}H_{21}NO_2$: C, 84.29; H, 4.95; N, 3.28. Found: C, 84.42; H, 4.94; N, 3.22.

3,4-Dibenzoyl-2,5-diphenyl-1-methylpyrrole (18c) crystallized from ethanol as colorless, matted needles: yield 63%, mp 200–202° (lit.[2d] mp 198–200°); ir (KBr) 3060, 3035 (CH), 1655, 1635 (CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 304 nm sh (log ϵ 3.97), 253 (4.66); nmr ($CDCl_3$) τ 6.62 (s, 3, NCH_3), 3.15–2.36 (m, 20, aromatic); $M\cdot^+$ 441 (55), M^{2+} 220.5 (3).

Anal. Calcd for $C_{31}H_{23}NO_2$: C, 84.33; H, 5.25; N, 3.17. Found: C, 84.58; H, 5.33; N, 3.22.

3,4-Dithiobenzoyl-1-methyl-2-phenylpyrrole (19a). 3,4-Dibenzoyl-1-methyl-2-phenylpyrrole (1.00 g, 2.74 mmol), phosphorus pentasulfide (0.61 g, 2.74 mmol), and dry pyridine (20 ml) were refluxed for 5 hr. Upon cooling, the reaction mixture was poured into ice–water. A yellow-gray solid separated which was purified by preparative thick-layer chromatography (silica gel, 1.00-mm plates) using benzene as developing solvent. Recrystallization from ethanol afforded yellow needles: 0.65 g (60%), mp 154–156°; ir (KBr) 3090, 3065, 3025, 2920 (CH), 1084, 1077 (CS) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 306 nm (log ϵ 3.92), 274 (4.04), 239 (3.82); nmr ($CDCl_3$) τ, 6.83 (s, 3, NCH_3), 4.45 (s, 1, H_5), 3.00–2.43 (m, 13, aromatic) 2.10–1.88 (m, 2, aromatic); $M\cdot^+$ 397 (100), M^{2+} 198.5 (6).

Anal. Calcd for $C_{25}H_{19}NS_2$: C, 75.55; H, 4.82; N, 3.52. Found: C, 75.40; H, 4.84; N, 3.49.

1,2-Diphenyl-3,4-dithiobenzoylpyrrole (19b). 3,4-Dibenzoyl-1,2-diphenylpyrrole (1.00 g, 2.34 mmol), phosphorus pentasulfide (0.52 g, 2.34 mmol), and dry pyridine (25 ml) were refluxed for 4 hr. After cooling, the reaction mixture was poured into ice–water. A yellow solid separated which was purified by preparative thick layer chromatography (silica gel, 1.00-mm plates) using benzene as developing solvent. Recrystallization from acetonitrile gave yellow needles: 0.74 g (67%), mp 227–229°; ir (KBr) 3100, 3075, 3045 (CH), 1079 (CS) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 323 nm sh (log ϵ 4.11), 278 (4.43), 227 sh (4.23); nmr ($CDCl_3$) τ 3.96 (s, 1, H_5), 3.10–2.42 (m, 18, aromatic), 2.14–1.84 (m, 2, aromatic); $M\cdot^+$ 459 (97), M^{2+} 229.5 (2).

Anal. Calcd for $C_{30}H_{21}NS_2$: C, 78.41; H, 4.61; N, 3.05. Found: C, 78.43; H, 4.57; N, 3.04.

5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (20). 3,4-Dibenzoyl-2,5-diphenyl-1-methylpyrrole (1.50 g, 3.40 mmol), phosphorus pentasulfide (0.75 g, 3.40 mmol), and dry pyridine (30 ml) were refluxed for 5 hr. Upon cooling, the reaction mixture was poured into 10% sodium hydroxide solution. Small red needles separated which were collected, washed with water, and air dried: 0.90 g (60%), mp 210–212°; ir (KBr) 3050, 3020 (CH) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 533 nm (log ϵ 3.15), 256 (4.41); nmr ($CDCl_3$) τ 6.93 (s, 3, NCH_3), 3.00–2.49 (m, 20, aromatic); $M\cdot^+$ 441 (100), M^{2+} 220.5 (21).

This system was readily oxidized on attempted recrystallization such that an analytically pure sample could not be obtained. However, it was further characterized by the formation of a variety of stable 1:1 cycloadducts.

Reaction of 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (20) and Fumaronitrile. A. Using Toluene as Solvent. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (2.00 g, 4.55 mmol), fumaronitrile (0.36 g, 4.55 mmol), and toluene (40 ml) were refluxed for 12 hr. The solvent was removed under vacuum and the residue chromatographed on silica gel (benzene followed by benzene–ethyl acetate, 50:1). The first fraction, after recrystallization from acetonitrile, gave colorless needles of 5-*endo*-6-*exo*-dicyano-2-methyl-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epithioisoindole (**21**): 1.58 g (67%), mp 244–245° dec; ir (KBr) 3075, 3045, 2970, 2945 (CH), 2250 (CN) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 278 nm (log ϵ 4.06); nmr ($CDCl_3$) τ 6.87 (s, 3, NCH_3), 5.88 (d, 1, $H_{6\text{-endo}}$, $J_{6\text{-endo},5\text{-exo}}$ = 3.9 Hz), 5.42 (d, 1, $H_{5\text{-exo}}$), 3.34–2.40 (m, 20, aromatic); $M\cdot^+$ 519 (2).

Anal. Calcd for $C_{35}H_{25}N_3S$: C, 80.90; H, 4.85; N, 8.09. Found: C, 81.02; H, 4.77; N, 7.99.

The second fraction, after recrystallization from acetonitrile, afforded 5,6-dicyano-2-methyl-1,3,4,7-tetraphenylisoindole (**23**) as yellow needles: 0.11 g (5%), mp 332–334°; ir (KBr) 3060 (CH), 2225 (CN) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 408 nm (log ϵ 3.31), 269 (4.51), 245 (4.58); nmr ($CDCl_3$) τ 6.54 (s, 3, NCH_3), 3.28–2.65 (m, 20, aromatic); $M\cdot^+$ 485 (100), M^{2+} 242.5 (13).

Anal. Calcd for $C_{35}H_{23}N_3$: C, 86.57; H, 4.77; N, 8.65. Found: C, 86.73; H, 4.80; N, 8.69.

B. Using Xylene as Solvent. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (2.00 g, 4.55 mmol), fumaronitrile (0.36 g, 4.55 mmol), and xylene (40 ml) were refluxed for 12 hr. The solvent was removed under vacuum and the residue chromatographed on silica gel (benzene followed by benzene–ethyl acetate, 50:1). 5-*endo*-6-*exo*-Dicyano-2-methyl-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epithioisoindole (**21**) (0.24 g, 10%) was isolated from the first fraction, while the second fraction afforded 1.17 g (53%) of 5,6-dicyano-2-methyl-1,3,4,7-tetraphenylisoindole (**23**).

C. Using Benzene as Solvent. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (1.30 g, 2.95 mmol), fumaronitrile (0.23 g, 2.95 mmol), and benzene (30 ml) were refluxed for 1 hr. The colorless solid that separated on cooling was collected, washed with ethanol, and air dried. Digestion of this solid with ethanol afforded irregular prisms of 5-*endo*-6-*exo*-dicyano-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (**22**): 0.96 g (63%), mp 231–234° dec; ir (KBr) 3060, 3030, 2955 (CH), 2245 (CN) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 288 nm, log ϵ 4.27; nmr (CF_3COOD) τ 7.07 (s, 3, NCH_3), 5.20 (d, 1, $H_{6\text{-endo}}$, $J_{6\text{-endo},5\text{-exo}}$ = 3.7 Hz), 4.53 (d, 1, $H_{5\text{-exo}}$), 3.17–2.27 (m, 20, aromatic).

Anal. Calcd for $C_{35}H_{25}N_3S$: C, 80.90; H, 4.85; N, 8.09. Found: C, 81.19; H, 5.11; N, 7.94.

5,6-Dicyano-2-methyl-1,3,4,7-tetraphenylisoindole (**23**) (0.87 g, 93%) was formed when 5-*endo*-6-*exo*-dicyano-2-methyl-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epithioisoindole (**21**) (1.00 g, 1.93 mmol) was stirred with 10% methanolic sodium methoxide (30 ml) at room temperature for 1 hr.

Thermolysis of 5-*endo*-6-*exo*-Dicyano-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (22). The above adduct (1.50 g, 2.89 mmol) and xylene (20 ml) were refluxed for 14 hr. Upon cooling the solution, 0.85 g (60%) of 5,6-dicyano-2-methyl-1,3,4,7-tetraphenylisoindole (**23**) separated as yellow needles. Analysis of the mother liquor by thin-layer chromatography indicated that trace amounts of 5-*endo*-6-*exo*-dicyano-2-methyl-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epithioisoindole (**21**) were present.

***endo*-2-Methyl-*N*,1,3,4,7-pentaphenyl-4,5,6,7-tetrahydro-4,7-epithioisoindole-5,6-dicarboximide (24).** 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (2.00 g, 4.55 mmol), *N*-phenylmaleimide (0.79 g, 4.55 mmol), and xylene (40 ml) were refluxed for 12 hr. Upon cooling the solution, a colorless solid separated which crystallized from acetonitrile as colorless matted needles: 2.04 g (73%), mp 228–230° dec; ir (KBr) 3070, 2970 (CH), 1710 (CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 303 nm sh (log ϵ 4.36), 297 (4.39), 247 sh (4.23); nmr ($CDCl_3$) τ 6.70 (s, 3, NCH_3), 4.85 (s, 2, $H_{5\text{-exo}}$, $H_{6\text{-exo}}$), 3.28–2.60 (m, 21, aromatic), 2.43–2.10 (m, 4, aromatic); $M\cdot^+$ 614 (1).

Anal. Calcd for $C_{41}H_{30}N_2O_2S$: C, 80.10; H, 4.91; N, 4.55. Found: C, 79.96; H, 4.95; N, 4.57.

***endo*-*N*,1,3,4,7-Pentaphenyl-4,5,6,7-tetrahydro-4,7-epi-*N*-methyliminoisothianaphthene-5,6-dicarboximide (25).** 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (1.30 g, 2.95 mmol), *N*-phenylmaleimide (0.51 g, 2.95 mmol), and benzene (25 ml) were refluxed for 30 min. Upon cooling the solution, a colorless solid separated which crystallized from acetonitrile as colorless prisms: 1.24 g (68%), mp 248–250° dec; ir (KBr) 3050, 3025, 2950 (CH), 1715 (CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 313 nm sh (log ϵ 4.08), 302 (4.27), 247 sh (4.19); nmr ($CDCl_3$) τ 8.11 (s, 3, NCH_3), 5.27 (s, 2, $H_{5\text{-exo}}$, $H_{6\text{-exo}}$), 3.12–2.52 (m, 21, aromatic), 2.40–2.03 (m, 4, aromatic); mass spectrum

m/e (rel intensity) 441 (100) ($M\cdot^+$ of 5-methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole), 173 (82) ($M\cdot^+$ of *N*-phenylmaleimide).

Anal. Calcd for $C_{41}H_{30}N_2O_2S$: C, 80.10; H, 4.91; N, 4.55. Found: C, 79.97; H, 5.06; N, 4.71.

Reaction of 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (20) and Acrylonitrile. A. Using Benzene as Solvent. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (2.70 g, 6.15 mmol), acrylonitrile (0.33 g, 6.15 mmol), and benzene were refluxed for 12 hr. Concentration of the reaction mixture resulted in separation of a colorless solid. Low-temperature recrystallization from chloroform–hexane afforded irregular prisms of 5-*endo*-cyano-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (**26**; R = CN): 2.24 g (74%), mp 208–210° dec; ir (KBr) 3050, 3025, 2950 (CH), 2240 (CN) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 298 nm (log ϵ 4.31), 246 sh (4.08); nmr ($CDCl_3$, HA-100) τ 8.31 (s, 3, NCH_3), 7.32 (dd, 1, $H_{6\text{-endo}}$, $J_{6\text{-endo},6\text{-exo}}$ = 12.3 Hz, $J_{6\text{-endo},5\text{-exo}}$ = 4.2 Hz), 6.67 (dd, 1, $H_{6\text{-exo}}$, $J_{6\text{-exo},5\text{-exo}}$ = 10.8 Hz), 6.05 (dd, 1, $H_{5\text{-exo}}$), 3.14–2.36 (m, 20, aromatic).

Anal. Calcd for $C_{34}H_{26}N_2S$: C, 82.57; H, 5.30; N, 5.66. Found: C, 82.45; H, 5.49; N, 5.59.

B. Using Toluene as Solvent. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (1.30 g, 2.95 mmol), acrylonitrile (0.16 g, 2.95 mmol), and toluene (25 ml) were refluxed for 9 hr. The solvent was removed under vacuum and the residue chromatographed on silica gel (benzene). The first fraction, after recrystallization from acetonitrile, gave 5-cyano-2-methyl-1,3,4,7-tetraphenylisoindole (**27**; R = CN) as yellow needles: 0.11 g (8%), mp 283–285°; ir (KBr) 3050, 3025 (CH), 2210 (CN) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 398 nm (log ϵ 4.03), 322 (4.01), 261 (4.65); nmr ($CDCl_3$) τ 6.48 (s, 3, NCH_3), 3.18–2.84 (m, 20, aromatic), 2.78 (s, 1, H_6); $M\cdot^+$ 460 (100), M^{2+} 230 (16).

Anal. Calcd for $C_{34}H_{24}N_2$: C, 88.66; H, 5.25; N, 6.08. Found: C, 88.50; H, 5.28; N, 6.19.

The second fraction afforded 0.70 g (48%) of 5-*endo*-cyano-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (**26**; R = CN).

C. Using Xylene as Solvent. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (1.75 g, 3.98 mmol), acrylonitrile (0.21 g, 3.98 mmol), and xylene (30 ml) were refluxed for 24 hr. The solvent was removed under vacuum and the residue chromatographed on silica gel (benzene). The first fraction afforded 5-cyano-2-methyl-1,3,4,7-tetraphenylisoindole (**27**; R = CN), 1.00 g (55%). 5-*endo*-Cyano-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (**26**; R = CN) was obtained from the second fraction, 0.08 g (4%).

Reaction of 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole with Ethyl Acrylate. A. Using Benzene as Solvent. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (1.70 g, 3.86 mmol), ethyl acrylate (0.39 g, 3.86 mmol), and benzene (30 ml) were refluxed for 15 hr. Concentration of the reaction mixture resulted in separation of a colorless solid which crystallized from chloroform–hexane (low temperature) as colorless, irregular prisms of 5-*endo*-ethoxycarbonyl-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (**26**; R = COOEt): 1.42 g (68%), mp 188–190° dec; ir (KBr) 3055, 3020, 2980, 2955 (CH), 1725 (CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 305 nm (log ϵ 4.43), 246 sh (4.16); nmr ($CDCl_3$) τ 8.96 (t 3, $CO_2CH_2CH_3$, J = 7.1 Hz), 8.31 (s, 3, NCH_3), 7.14 (dd, 1, $H_{6\text{-endo}}$, $J_{6\text{-endo},6\text{-exo}}$ = 12.2 Hz, $J_{6\text{-endo},5\text{-exo}}$ = 4.0 Hz), 6.87 (dd, 1, $H_{6\text{-exo}}$, $J_{6\text{-exo},5\text{-exo}}$ = 10.0 Hz), 6.08 (qt, 2, $CO_2CH_2CH_3$), 5.77 (dd, 1, $H_{5\text{-exo}}$), 3.02–2.75 (m, 16, aromatic), 2.68–2.50 (m, 2, aromatic), 2.38–2.18 (m, 2, aromatic).

Anal. Calcd for $C_{36}H_{31}NO_2S$: C, 79.83; H, 5.77; N, 2.59. Found: C, 79.64; H, 5.69; N, 2.57.

B. Using Toluene as Solvent. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (1.00 g, 2.27 mmol), ethyl acrylate (0.23 g, 2.27 mmol), and toluene (20 ml) were refluxed for 12 hr. The solvent was removed under vacuum and the residue chromatographed on silica gel (benzene–ethyl acetate, 75:1). The first fraction, after recrystallization from acetonitrile, gave 5-ethoxycarbonyl-2-methyl-1,3,4,7-tetraphenylisoindole (**27**; R = COOEt), as yellow irregular prisms: 0.12 g (10%), mp 205–206°; ir (KBr) 3050, 3020, 2975 (CH), 1700 (CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 388 nm (log ϵ 3.99), 320 (3.94) and 263 (4.50); nmr ($CDCl_3$) τ 9.14 (t, 3, $CO_2CH_2CH_3$, J = 7.0 Hz), 6.54 (s, 3, NCH_3), 6.07 (qt, 2, $CO_2CH_2CH_3$), 3.21–2.80 (m, 20, aromatic), 2.67 (s, 1, H_6); $M\cdot^+$ 507 (100), M^{2+} 253.5 (2).

Anal. Calcd for $C_{36}H_{29}NO_2$: C, 85.18; H, 5.76; N, 2.76. Found: C, 85.09; H, 5.67; N, 2.74.

The second fraction afforded 0.60 g (49%) of 5-*endo*-ethoxycarbonyl-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (**26**; R = COOEt).

C. Using Xylene as Solvent. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (1.50 g, 3.40 mmol), ethyl acrylate (0.34 g, 3.40 mmol), and xylene (30 ml) were refluxed for 30 hr. The solvent was removed under vacuum and the residue chromatographed on silica gel (benzene–ethyl acetate, 75:1). The first fraction afforded 5-ethoxycarbonyl-2-methyl-1,3,4,7-tetraphenylisoindole (**27**; R = COOEt), 1.05 g (61%). 5-*endo*-Ethoxycarbonyl-4,5,6,7-tetrahydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (**26**; R = COOEt) was obtained from the second fraction, 0.09 g (5%).

5,6-Dibenzoyl-4,7-dihydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (28). 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (2.00 g, 4.55 mmol), dibenzoylacetylene (1.06 g, 4.55 mmol), and benzene (40 ml) were refluxed for 15 hr. The solvent was removed under vacuum and the residue taken up in hot dioxane. Dropwise addition of water to this solution resulted in separation of a pale-yellow solid. Recrystallization from acetonitrile gave pale-yellow needles: 2.02 g (66%), mp 247–249° dec; ir (KBr) 3070, 2875 (CH), 1670, 1650 (CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 284 nm sh (log ϵ 4.45), 273 sh (4.48), 264 (4.54); nmr ($CDCl_3$) τ 7.98 (s, 3, NCH_3), 3.20–2.30 (m, 30, aromatic); $M\cdot^+$ 675 (1).

Anal. Calcd for $C_{47}H_{33}NO_2S$: C, 83.52; H, 4.92; N, 2.07. Found: C, 83.33; H, 4.83; N, 2.00.

5,6-Dibenzoyl-1,3,4,7-tetraphenylisothianaphthene (7). 5,6-Dibenzoyl-4,7-dihydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (2.00 g, 2.96 mmol), *m*-chloroperoxybenzoic acid (0.51 g, 2.96 mmol), and methylene chloride (35 ml) were refluxed for 2 hr. The reaction mixture was washed with 10% sodium bicarbonate solution followed by water and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum and the residue recrystallized from acetic anhydride as yellow needles, 1.72 g (90%), mp 299–301°.

Reaction of 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole with Dibenzoylacetylene Using Xylene as Solvent. 5-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (2.00 g, 4.55 mmol), dibenzoylacetylene (1.06 g, 4.55 mmol), and xylene (50 ml) were refluxed for 48 hr. The solvent was removed under vacuum and the residue chromatographed on silica gel (benzene–ethyl acetate, 50:1). The first fraction afforded 0.50 g (17%) of 5,6-dibenzoyl-1,3,4,7-tetraphenylisothianaphthene (**7**), while 1.06 g (34%) of 5,6-dibenzoyl-4,7-dihydro-1,3,4,7-tetraphenyl-4,7-epi-*N*-methyliminoisothianaphthene (**28**) was obtained from the second fraction.

The above adduct was also the major product when this reaction was repeated under a nitrogen atmosphere. In this case formation of the isothianaphthene was inhibited.