Nonclassical Heterocycles. II. The Thieno[3,4-*c*]pyrazole System[1]

K. T. Potts* and D. McKeough

Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181. *Received November 9, 1973*

Abstract: Reaction of 3,4-dibenzoylpyrazoles, readily prepared from *N*-substituted *N*-nitrosoglycine derivatives, dibenzoylacetylene and Ac_2O, with P_4S_{10}–pyridine was a convenient route to the thieno[3,4-*c*]pyrazole system, a 10π-electron heterocycle containing "tetravalent" sulfur. Cycloaddition with olefinic and acetylenic dipolarophiles always occurred across the thiocarbonyl ylide. With acetylenes sulfur was lost forming the 2*H*-indazole system; with olefins 1:1 primary cycloadducts were obtained together with secondary products formed by the elimination of H_2S. 5,6-Dibenzoyl-2,4,7-triphenyl-2*H*-indazole with P_4S_{10}–pyridine gave 2,4,5,7,8-pentaphenylthieno[3,4-*f*]-2*H*-indazole, a 14π-electron heterocycle which also gave a 1:1 cycloadduct across the thiocarbonyl ylide with *N*-phenylmaleimide.

In part I of this series[2] it was shown that in the thieno[3,4-*c*]pyrrole system the azomethine ylide was more reactive than the thiocarbonyl ylide. Addition of olefinic dipolarophiles occurred across the former in a kinetically controlled process and across the latter in a thermodynamically controlled one. It was of particular interest to introduce a second nitrogen atom into the pyrrole ring so that the reactivity of the azomethine imine ylide could be compared with that of the thiocarbonyl ylide.

Variation of the synthetic procedure used previously provided a convenient route to 2,4,6-triphenylthieno[3,4-*c*]pyrazole.[1d] *N*-Phenylsydnone[3] (**1**; R = Ph; R^1 = H), or *N*-phenyl-*N*-nitrosoglycine (**2**; R = Ph; R^1 = H) in the presence of acetic anhydride,[4] underwent ready 1,3-dipolar cycloaddition with dibenzoylacetylene to give good yields of 3,4-dibenzoyl-1-phenylpyrazole (**4**; R = Ph; R^1 = H), presumably by way of the primary 1:1 cycloadduct **3** (R = Ph; R^1 = H) which undergoes ready loss of CO_2.

Phosphorus pentasulfide treatment of **4** (R = Ph; R^1 = H) resulted in its conversion into 2,4,6-triphenylthieno[3,4-*c*]pyrazole (**5**; R = Ph; R^1 = H), obtained as brick red needles in 85% yield. This system exhibited absorption maxima at 298, 276, and 250 nm in the ultraviolet and 497 nm in the visible. The resonance signal of the proton at the 3 position was observed as a singlet at τ 1.68 with two aromatic multiplets constituting the remainder of the nmr spectrum, τ 2.92–2.20 (11 protons) and 2.12–1.75 (four protons). As expected, the mass spectrum was relatively simple, being dominated by an intense molecular ion, *m/e* 352, the only other significant ion observed being the doubly charged molecular ion, *m/e* 176. In solution, **5** (R = Ph, R^1 = H) was slowly oxidized to 3,4-dibenzoyl-1-phenylpyrazole (**4**; R = Ph; R^1 = H) on exposure to light, but in the solid state, it was stable indefinitely.

As was observed in the case of the thieno[3,4-*c*]pyrrole system, the substituent pattern in the dibenzoyl precursor compounds can sometimes have a profound effect on the course of the phosphorus pentasulfide reaction. In order to determine if formation of the thieno[3,4-*c*]pyrazole system was also sensitive to substituent changes, the synthesis of two other derivatives was attempted.

Precursors 3,4-dibenzoyl-1-methylpyrazole (**4**; R = CH_3; R^1 = H) and 3,4-dibenzoyl-5-methyl-1-phenylpyrazole (**4**; R = Ph; R^1 = CH_3) were prepared as before, either by direct treatment of the appropriately substituted sydnone with dibenzoylacetylene or by *in situ* generation of the mesoionic compound in the presence of dibenzoylacetylene. These pyrazoles could also be readily converted into their corresponding fused thiophene systems. Thus, 4,6-diphenyl-2-methylthieno[3,4-*c*]pyrazole (**5**; R = CH_3; R^1 = H), mp 133–135°, was isolated in 76% yield as orange prisms upon phosphorus pentasulfide treatment of **4** (R = CH_3; R^1 = H) (Scheme I), whereas **4** (R = Ph; R^1 = CH_3) afforded 3-methyl-2,4,6-triphenylthieno[3,4-*c*]pyrazole (**5**; R = Ph; R^1 = CH_3), mp 189–191°, as lustrous, brown plates in 64% yield. The spectral properties of these systems (Experimental Section) were similar to those of **5** (R = Ph; R^1 = H) described above.

2,4,6-Triphenylthieno[3,4-*c*]pyrazole can be represented as a hybrid of "tetravalent" and dipolar contributors and behavior as both a thiocarbonyl ylide and azomethine imine ylide might be anticipated in Diels–Alder type reactions. With *N*-phenylmaleimide in refluxing benzene two products were isolated and in both cases analytical data confirmed formation of 1:1 primary cycloadducts. In the nmr spectra of both, the resonance signal in the aliphatic region corresponded to only two protons. As such, both of these compounds must be formed by the addition of *N*-phenylmaleimide across the thiocarbonyl ylide of **5a** (R^1 = H) and thus represent *exo*-**6** and *endo*-**7** adducts.[5] Addition across the azomethine imine ylide to give adduct **8** or its endo analog would result in the observation of three protons in the aliphatic region of the nmr spectrum.

Structural assignments are based on the chemical shift of the protons α to the imide carbonyl groups con-

(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, 1973; (c) Sterling-Winthrop Fellow, 1971–1973; (d) preliminary communication: K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **94**, 6215 (1972).

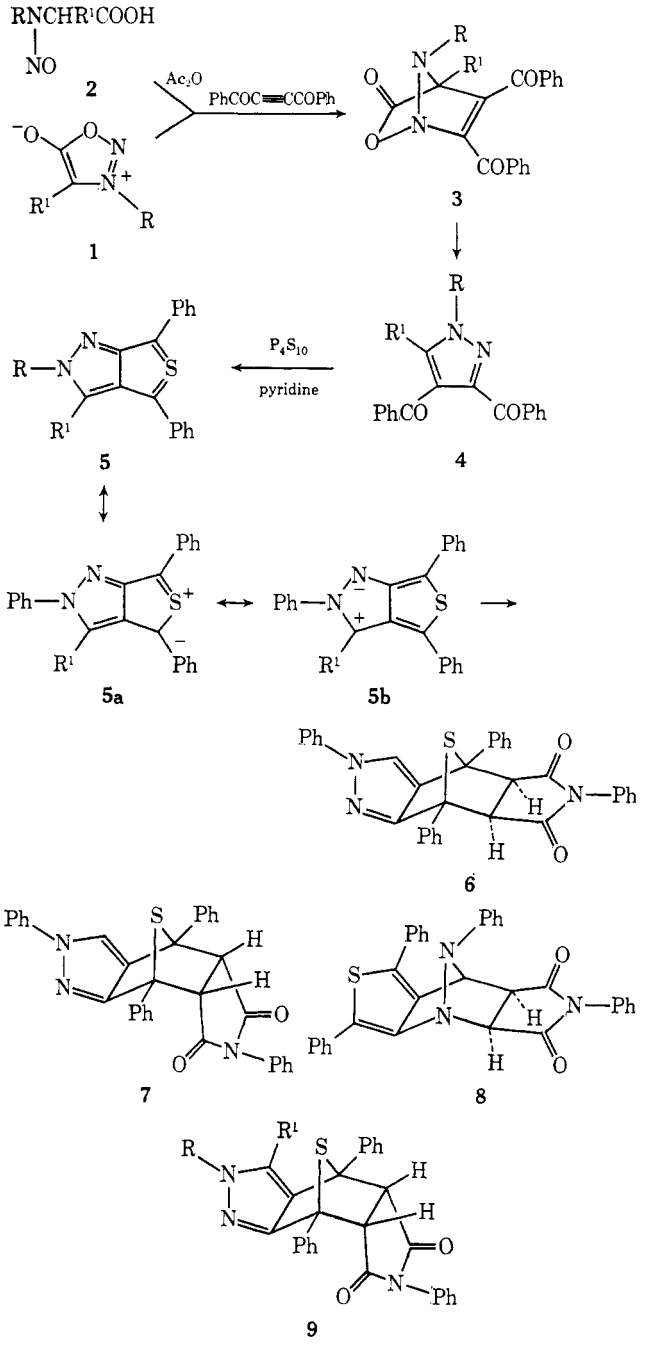
(2) K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **96**, 4268 (1974).

(3) *E.g.*, see R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, **101**, 536 (1968); M. Ohta and H. Kato in "Non-Benzenoid Aromatics," J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, Chapter 4.

(4) K. T. Potts and U. P. Singh, *Chem. Commun.*, 66 (1969).

(5) Exo/endo nomenclature refers to the orientation of substituents with respect to the sulfur bridge.

Scheme I



sidering the effect of the bridge sulfur atom.[6] Thus, in the case of *exo*-4,5,6,7-tetrahydro-*N*,2,4,7-tetraphenyl-4,7-epithio-2*H*-indazole-5,6-dicarboximide (**6**), the resonance signal for these protons was noted at τ 5.76 while the analogous protons of *endo*-4,5,6,7-tetrahydro-*N*,2,4,7-tetraphenyl-4,7-epithio-2*H*-indazole-5,6-dicarboximide (**7**) were deshielded and exhibited a signal at τ 5.18.[7]

The isomer ratio in this reaction is temperature dependent. A value of 18:1 favoring the endo adduct was found when the reaction was carried out in refluxing benzene. This reduced to 9:1 when refluxing toluene was used as solvent.

In contrast to the above reaction **5** (R = CH_3; R^1 = H) and **5** (R = Ph; R^1 = CH_3) gave rise to only one primary 1:1 cycloadduct **9** (R = CH_3; R^1 = H) and **9** (R = Ph; R^1 = CH_3) resulting from addition across the thiocarbonyl ylide. Assignment of the endo structures was based on the chemical shift of the protons α to the imide carbonyls at τ 5.23 and 5.08, respectively.

The reaction of 2,4,6-triphenylthieno[3,4-*c*]pyrazole and fumaronitrile in refluxing benzene gave two products: a thermally unstable primary 1:1 cycloadduct of uncertain stereochemistry (**10** or **11**) and 5,6-dicyano-2,-4,7-triphenyl-2*H*-indazole (**12**). In the nmr spectrum of the initial cycloadduct, the resonance signals in the aliphatic region integrated for only two protons indicating that the addition of fumaronitrile occurred across the thiocarbonyl ylide of the thieno[3,4-*c*]pyrazole system. Also the observed coupling constant of 4.0 Hz for the protons α to the nitrile groups confirmed that the stereochemistry of the dienophile was maintained throughout the addition. When refluxing xylene was used as solvent, addition of fumaronitrile still took place across the thiocarbonyl ylide; however, the yield of the 2*H*-indazole system was increased apparently at the expense of the primary cycloadduct. As before, the transformation of the primary cycloadduct to the 2*H*-indazole system could be effected in a base-catalyzed process.

Once again, cycloaddition reactions of **5** with olefinic dienophiles such as dimethyl fumarate, dimethyl maleate, and diphenylcyclopropenone were not successful under a variety of conditions. Heterocumulenes such as phenyl isocyanate and phenyl isothiocyanate were also unreactive.

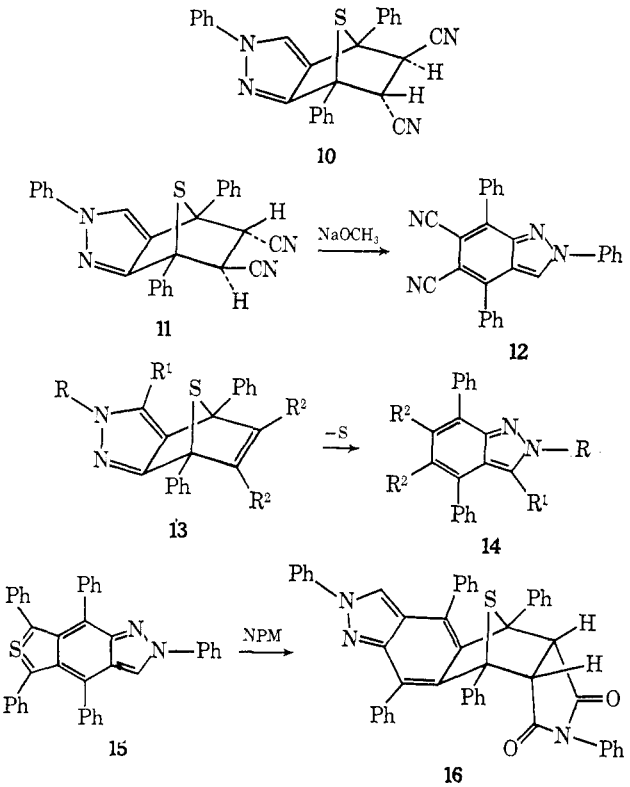
The reactions of the thieno[3,4-*c*]pyrazole systems with acetylenic dienophiles were also investigated and, regardless of reaction conditions, addition occurred across the thiocarbonyl ylide. As noted with the thieno[3,4-*c*]thiophene system, the initially formed cycloadducts **13** in these reactions were unstable and readily eliminated elemental sulfur. Thus, 5,6-bis-(methoxycarbonyl)-2*H*-indazole derivatives (**14**; R^2 = CO_2CH_3) were formed upon treatment of **5** (R = Ph, R^1 = H; R = CH_3, R^1 = H; R = Ph, R^1 = CH_3) with dimethyl acetylenedicarboxylate.

Reaction of **5** (R = Ph; R^1 = H) with dibenzoylacetylene afforded 5,6-dibenzoyl-2,4,7-triphenyl-2*H*-indazole (**14**; R = Ph; R^1 = H; R^2 = COPh), mp 196–198°, which provided the necessary precursor to the thieno[3,4-*f*]-2*H*-indazole system. Phosphorus pentasulfide treatment of **14** (R = Ph; R^1 = H; R^2 = COPh) afforded 2,4,5,7,8-pentaphenylthieno[3,4-*f*]-2*H*-indazole (**15**) in 90% yield. This compound, isolated as blue, matted needles, is only the second known example of a stable, tricyclic, 14π-electron, nonclassical thiophene. It exhibited absorption maxima at 303, 252, and 231 nm in the ultraviolet and 602 nm in the visible. Its mass spectrum was dominated by an intense molecular ion, *m/e* 554, and the doubly charged analog, *m/e* 227. Diels–Alder reaction of **15** with *N*-phenylmaleimide afforded a single product, mp 362–364° dec, whose analytical data confirmed formation of a 1:1 primary cycloadduct (Scheme II). There are three possible sites of addition; across the 1 and 3 positions

(6) M. P. Cava, M. Behforouz, G. E. M. Husbands, and M. Srinivasan, *J. Amer. Chem. Soc.*, **95**, 2561 (1973).

(7) In our preliminary communication, the reversed assignments of configuration were made for adducts **6**, **7**, and **16** on the basis of the possible deshielding of the protons α to the carbonyl groups in the exo adduct by the bridgehead phenyl groups. Recent data on similar exo–endo adducts of 1,3-diphenylisobenzofuran indicate that this deshielding was not as significant as originally thought.[6]

Scheme II



or azomethine imine ylide of **15**, across the 4 and 8 positions, or across the 5 and 7 positions or thiocarbonyl ylide.

Addition across the azomethine imine ylide is discounted based on the observation of a resonance signal corresponding to only two protons in the aliphatic region of the nmr spectrum (*vide supra*). Of the remaining two choices, that resulting from addition across the thiocarbonyl ylide seems favored as the ultraviolet absorption spectrum indicates the presence of a 2*H*-indazole residue. Assignment of the endo configuration to *endo*-*N*,2,4,5,8,9-hexaphenyl-5,6,7,8-tetrahydro-5,8-epithionaphtho[2,3-*c*]pyrazole-6,7-dicarboximide (**16**) was made on the basis of the chemical shift of the protons α to the imide carbonyl groups. This is observed at τ 5.02 and is consistent with the chemical shifts of exo protons in similar thiocarbonyl ylide adducts described above.[6]

These results show that, in this ring system, the thiocarbonyl ylide function was more reactive than the azomethine imine ylide system.

Experimental Section[8]

The following procedures are representative of those used for the preparation of 3,4-dibenzoylpyrazole derivatives.

3,4-Dibenzoyl-1-phenylpyrazole (4; R = Ph; R¹ = H). A. Anhydro-5-hydroxy-3-phenyl-1,2,3-oxadiazolium hydroxide[9] (2.20 g, 13.60 mmol), dibenzoylacetylene (3.20 g, 13.60 mmol), and benzene (40 ml) were refluxed for 36 hr. The solvent was removed under vacuum; the residue was triturated with ethanol and finally recrystallized from ethanol affording colorless irregular prisms: 4.06 g (85%), mp 103–105°; ir (KBr) 3150, 3090, 3080 (CH), 1670, 1650 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 277 nm sh (log ϵ 4.45), 254 (4.64); nmr ($CDCl_3$) τ 2.88–2.40 (m, 9, aromatic), 2.37–2.08 (m, 4, aromatic), 2.00–1.80 (m, 2, aromatic), 1.70 (s, 1, H_5); $M\cdot^+$ 352 (55).

Anal. Calcd for $C_{23}H_{16}N_2O_2$: C, 78.39; H, 4.58; N, 7.95. Found: C, 78.23; H, 4.44; N, 7.85.

B. *N*-Nitroso-*N*-phenylglycine[9] (1.00 g, 5.55 mmol), dibenzoylacetylene (1.30 g, 5.55 mmol), and acetic anhydride (20 ml) were heated at 120° for 4 hr. Upon cooling the solution, water (30 ml) was added and the mixture 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 prisms, 1.23 g (63%).

3,4-Dibenzoyl-5-methyl-1-phenylpyrazole (4; R = Ph; R¹ = CH_3) crystallized from ethanol as cream, matted needles: yield 82% (method A), 32% (method B); mp 113–115°; ir (KBr) 3070 (CH), 1670, 1650 (CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 255 nm (log ϵ 4.38); nmr ($CDCl_3$) τ 7.58 (s, 3, 5-CH_3), 2.88–2.13 (m, 13, aromatic), 2.04–1.78 (m, 2, aromatic); $M\cdot^+$ 366 (97).

Anal. Calcd for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.73; H, 4.83; N, 7.65.

3,4-Dibenzoyl-1-methylpyrazole (4; R = CH_3; R¹ = H) was obtained as a viscous yellow oil which decomposed on attempted vacuum distillation: yield 69% (method A), 43% (method B); ir (7% solution in $CHCl_3$) 3050, 3000, 2950 (CH), 1660 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 253 nm (log ϵ 4.36); nmr ($CDCl_3$) τ 6.10 (s, 3, NCH_3), 2.90–2.43 (m, 6, aromatic), 2.38–1.87 (m, 5, aromatic); $M\cdot^+$ 290 (61).

This system was further characterized by its conversion into 4,6-diphenyl-2-methylthieno[3,4-*c*]pyrazole.

2,4,6-Triphenylthieno[3,4-*c*]pyrazole (5; R = Ph; R¹ = H). 3,4-Dibenzoyl-1-phenylpyrazole (1.00 g, 2.84 mmol), phosphorus pentasulfide (0.63 g, 2.84 mmol), and dry pyridine (20 ml) were refluxed for 5 hr. Upon cooling, the reaction mixture was poured into ice–water. A red solid separated which was co lected, washed with water, and air dried. Recrystallization from acetic anhydride gave lustrous brick red needles: 0.85 g (85%), mp 200–202°; ir (KBr) 3090 and 3025 (CH) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 497 nm (log ϵ 4.06), 298 (4.18), 276 (4.21), 250 (4.12); nmr ($CDCl_3$) τ 2.92–2.20 (m, 11, aromatic), 2.12–1.75 (m, 4, aromatic), 1.68 (s, 1, H_3); $M\cdot^+$ 352 (100), M^{2+} 176 (13).

Anal. Calcd for $C_{23}H_{16}N_2S$: C, 78.38; H, 4.58; N, 7.95. Found: C, 78.08; H, 4.52; N, 7.89.

4,6-Diphenyl-2-methylthieno[3,4-*c*]pyrazole (5; R = CH_3; R¹ = H). 3,4-Dibenzoyl-1-methylpyrazole (1.50 g, 5.16 mmol), phosphorus pentasulfide (1.15 g, 5.16 mmol), and dry pyridine (20 ml) were refluxed for 5 hr. Upon cooling, the reaction mixture was poured into ice–water. An orange solid separated which was collected, washed with water, and air dried. Chromatography on silica gel (benzene–ethyl acetate, 15:2) followed by recrystallization from acetonitrile afforded orange prisms: 1.14 g (76%), mp 133–135°; ir (KBr) 3025 (CH) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 465 nm (log ϵ 4.44), 455 sh (4.41), 313 sh (3.70), 264 (4.40); nmr ($CDCl_3$) τ 5.87 (s, 3, NCH_3), 2.91–2.38 (m, 8, aromatic), 2.29 (s, 1, H_3), 2.08–1.83 (m, 2, aromatic); $M\cdot^+$ 290 (100), M^{2+} 145 (3).

Anal. Calcd for $C_{18}H_{14}N_2S$: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.38; H, 4.96; N, 9.67.

3-Methyl-2,4,6-triphenylthieno[3,4-*c*]pyrazole (5; R = Ph; R¹ = CH_3). 3,4-Dibenzoyl-5-methyl-1-phenylpyrazole (2.00 g, 5.45 mmol), phosphorus pentasulfide (1.22 g, 5.45 mmol), and dry pyridine (30 ml) were refluxed for 7 hr. Upon cooling the reaction mixture was poured into ice–water. A brown solid separated which was collected, washed with water, and air dried. Chromatography on silica gel (benzene) followed by recrystallization from acetonitrile gave lustrous brown plates: 1.28 g (64%) mp 189–191°; ir (KBr) 3050 (CH) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 478 nm (log ϵ, 4.33), 322 sh (3.79), 289 (4.33); nmr ($CDCl_3$) τ 7.42 (s, 3, 3-CH_3), 2.92–2.16 (m, 13, aromatic), 1.98–1.75 (m, 2, aromatic); $M\cdot^+$ 366 (100), M^{2+} 183 (23).

Anal. Calcd for $C_{24}H_{18}N_2S$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.80; H, 5.18; N, 7.59.

Reaction of 2,4,6-Triphenylthieno[3,4-*c*]pyrazole (5; R = Ph; R¹ = H) with *N*-Phenylmaleimide. 2,4,6-Triphenylthieno[3,4-*c*]-pyrazole (2.00 g, 5.68 mmol), *N*-phenylmaleimide (0.99 g, 5.68 mmol), and benzene (50 ml) were refluxed for 14 hr. The solvent was removed under vacuum and the residue chromatographed on

(8) 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; 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.

(9) J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, 899 (1935).

Florisil (benzene followed by benzene–ethyl acetate, 25:1). The first fraction, after recrystallization from ethanol, gave colorless irregular prisms of *endo*-4,5,6,7-tetrahydro-*N*,2,4,7-tetraphenyl-4,7-epithio-2*H*-indazole-5,6-dicarboximide (**7**): 2.03 g (68%), mp 138–140° dec; ir (KBr) 3060 (CH) and 1730 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 273 nm (log ϵ 4.29); nmr ($CDCl_3$) τ 5.18 (AB qt, 2, $H_{5\text{-exo}}$, $H_{6\text{-exo}}$, $J_{5\text{-exo},6\text{-exo}}$ = 8.5 Hz; AB calcd ν_A τ 5.13, ν_B 5.24), 3.45–3.15 (m, 2, aromatic), 3.07–2.45 (m, 14, aromatic), 2.37 (s, 1, H_3), 2.30–1.75 (m, 4, aromatic); $M\cdot^+$ 525 (1).

Anal. Calcd for $C_{33}H_{23}N_3O_2S$: C, 75.41; H, 4.41; N, 8.00. Found: C, 75.01; H, 4.27; N, 7.92.

The second fraction crystallized from acetonitrile as colorless fibrous needles of *exo*-4,5,6,7-tetrahydro-*N*,2,4,7-tetraphenyl-4,7-epithio-2*H*-indazole-5,6-dicarboximide (**6**): 0.11 g (3.8%), mp 231–233° dec; ir (KBr) 3050 (CH), 1730 (CO) cm^{-1}, $\lambda_{max}^{CH_3OH}$ 274 nm (log ϵ 4.36); nmr (DMSO-d_6) τ 5.76 (s, 2, $H_{5\text{-endo}}$, $H_{6\text{-endo}}$), 3.02–2.05 (m, 20, aromatic), 1.68 (s, 1, H_3); $M\cdot^+$ 525 (2).

Anal. Calcd for $C_{33}H_{23}N_3O_2S$: C, 75.41; H, 4.41; N, 8.00. Found: C, 75.28; H, 4.39; N, 7.96.

When the same reaction was carried out in refluxing toluene (50 ml) for 6 hr, the yield of endo adduct was 64% whereas the yield of exo adduct was 7%.

***endo*-2-Methyl-4,5,6,7-tetrahydro-*N*,4,7-triphenyl-4,7-epithio-2*H*-indazole-5,6-dicarboximide (9; R = CH_3; R^1 = H).** 4,6-Diphenyl-2-methylthieno[3,4-*c*]pyrazole (1.35 g, 4.65 mmol), *N*-phenylmaleimide (0.81 g, 4.65 mmol), and toluene (35 ml) were refluxed for 16 hr. Upon cooling the solution, a white solid separated which crystallized as colorless needles from acetonitrile: 1.66 g (77%), mp 234–236° dec; ir (KBr) 3060, 3030, 2935 (CH), 1710 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 221 nm (log ϵ 4.41) and 217 sh (4.45); nmr ($CDCl_3$) τ 6.18 (s, 3, NCH_3), 5.23 (s, 2, $H_{5\text{-exo}}$, $H_{6\text{-exo}}$), 3.29–3.03 (m, 2, aromatic), 2.90 (s, 1, H_3), 2.77–2.42 (m, 9, aromatic), 2.26–1.76 (m, 4, aromatic); $M\cdot^+$ 463 (3).

Anal. Calcd for $C_{28}H_{21}N_3O_2S$: C, 72.56; H, 4.57; N, 9.07. Found: C, 72.45; H, 4.68; N, 8.98.

***endo*-3-Methyl-4,5,6,7-tetrahydro-*N*,2,4,7-tetraphenyl-4,7-epithio-2*H*-indazole-5,6-dicarboximide (9; R = Ph; R^1 = CH_3).** 3-Methyl-2,4,6-triphenylthieno[3,4-*c*]pyrazole (1.00 g, 2.73 mmol), *N*-phenylmaleimide (0.47 g, 2.73 mmol), and toluene (20 ml) were refluxed for 12 hr. Upon cooling the solution, a white solid separated which crystallized from acetonitrile as colorless prisms: 0.93 g (63%), mp 246–247° dec; ir (KBr) 3055, 3025, 2960 (CH), 1715 (CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 257 nm (log ϵ 4.12); nmr ($CDCl_3$) τ 8.20 (s, 3, 3-CH_3), 5.08 (AB qt, 2, $H_{5\text{-exo}}$, $H_{6\text{-exo}}$, $J_{5\text{-exo},6\text{-exo}}$ = 8.0 Hz; AB calcd ν_A τ 4.95, ν_B 5.23), 3.27–2.97 (m, 2, aromatic), 2.88–2.32 (m, 14, aromatic), 2.10–1.72 (m, 4, aromatic); $M\cdot^+$ 539 (5).

Anal. Calcd for $C_{34}H_{25}N_3O_2S$: C, 75.68; H, 4.67; N, 7.79. Found: C, 75.64; H, 4.62; N, 7.81.

Reaction of 2,4,6-Triphenylthieno[3,4-*c*]pyrazole (5; R = Ph; R^1 = H) with Fumaronitrile. 2,4,6-Triphenylthieno[3,4-*c*]pyrazole (2.00 g, 5.68 mmol), fumaronitrile (0.45 g, 5.68 mmol), and benzene (50 ml) were refluxed for 30 hr. The solvent was removed under vacuum and the residue chromatographed on silica gel (benzene). The first fraction, after low-temperature recrystallization from chloroform–petroleum ether, gave colorless irregular prisms of 5-*endo*(*exo*)-6-*exo*(*endo*)-dicyano-4,5,6,7-tetrahydro-2,4,7-triphenyl-4,7-epithio-2*H*-indazole (**10**, **11**): 1.08 g (44%), mp 186–187° dec; ir (KBr) 3142, 3077, 3047, 2957, 2947 (CH), 2255 (CN) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 270 nm (log ϵ 4.18); nmr ($CDCl_3$) τ 6.17 (d, 1, $H_{6\text{-endo}}$, $J_{6\text{-endo},\ 5\text{-exo}}$ = 4.0 Hz), 5.52 (d, 1, $H_{5\text{-exo}}$), 2.84–2.08 (m, 16, aromatic); $M\cdot^+$ 430 (0.5).

This adduct retained chloroform as solvent of crystallization. Attempts to effect drying by exposure to vacuum at room temperature resulted in a retro-Diels–Alder reaction. As a result, a sample suitable for analysis could not be prepared. This system was further characterized, however, by its conversion into 5,6-dicyano-2,4,7-triphenyl-2*H*-indazole (**12**).

Anal. Calcd for $C_{27}H_{18}N_4S$: C, 75.33; H, 4.22; N, 13.02. Found: C, 73.68; H, 4.13; N, 13.61.

The second fraction crystallized from acetonitrile as colorless matted needles of 5,6-dicyano-2,4,7-triphenyl-2*H*-indazole (**12**): 0.56 g (25%), mp 315–316°; ir (KBr) 3075 3035 (CH), 2240 (CN) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 342 nm (log ϵ 4.15), 277 (4.60); nmr ($CDCl_3$) τ 2.48–1.91 (m, 15, aromatic), 1.47 (s, 1, H_3); $M\cdot^+$ 396 (100), M^{2+} 198 (6).

Anal. Calcd for $C_{27}H_{16}N_4$: C, 81.80; H, 4.07; N, 14.13. Found: C, 82.03; H, 3.97; N, 14.23.

When this reaction was repeated in refluxing xylene (40 ml) for 24 hr, the yield of 5,6-dicyano-2,4,7-triphenyl-2*H*-indazole was increased to 63%, accompanied by a decrease in the yield of primary adduct to 7%.

5,6-Dicyano-2,4,7-triphenyl-2*H*-indazole (12) (0.82 g, 89%) was formed when 5-*endo*-6-*exo*-dicyano-4,5,6,7-tetrahydro-2,4,7-triphenyl-4,7-epithio-2*H*-indazole (1.00 g, 2.32 mmol) was stirred with 10% methanolic sodium methoxide (30 ml) at room temperature for 2 hr.

5,6-Bis(methoxycarbonyl)-2,4,7-triphenyl-2*H*-indazole (14; R = Ph; R^1 = H; R^2 = $COOCH_3$). 2,4,6-Triphenylthieno[3,4-*c*]-pyrazole (3.00 g, 8.60 mmol), dimethyl acetylenedicarboxylate (1.21 g, 8.60 mmol), and benzene (50 ml) were refluxed for 30 hr. The solvent was evaporated under vacuum and the residue chromatographed on silica gel (benzene followed by benzene–ethyl acetate, 25:1). Recrystallization from ethanol afforded colorless needles: 3.00 g (76%), mp 192–194°; ir (KBr) 3137, 3062, 2997, 2947 (CH), 1735 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 319 nm (log ϵ 4.24), 260 (4.59), 218 (4.46); nmr ($CDCl_3$) τ 6.42 (s, 3, CO_2CH_3), 6.39 (s, 3, CO_2CH_3), 2.82–2.04 (m, 15, aromatic), 1.68 (s, 1, H_3); $M\cdot^+$ 462 (100), M^{2+} 231 (14).

Anal. Calcd for $C_{29}H_{22}N_2O_4$: C, 75.31; H, 4.80; N, 6.06. Found: C, 74.93; H, 4.74; N, 6.13.

5,6-Bis(methoxycarbonyl)-4,7-diphenyl-2-methyl-2*H*-indazole (14; R = CH_3; R^1 = H; R^2 = $COOCH_3$). 4,6-Diphenyl-2-methylthieno[3,4-*c*]pyrazole (1.00 g, 3.45 mmol), dimethyl acetylenedicarboxylate (0.48 g, 3.45 mmol), and benzene (25 ml) were refluxed for 40 hr. Upon cooling the solution, a white solid separated which crystallized from acetonitrile as colorless matted needles: 0.85 g (62%), mp 222–223°; ir (KBr) 3135, 3040, 2950 (CH), 1735 1720 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 323 nm (log ϵ 4.05) and 244 (4.52); nmr ($CDCl_3$) τ 6.42 (s, 6, CO_2CH_3), 5.88 (s, 3, NCH_3), 2.80–2.34 (m, 10, aromatic), 2.21 (s, 1, H_3); $M\cdot^+$ 400 (100), M^{2+} 200 (8).

Anal. Calcd for $C_{24}H_{20}N_2O_4$: C, 71.98; H, 5.03; N, 7.00. Found: C, 71.82; H, 5.10; N, 6.82.

5,6-Bis(methoxycarbonyl)-3-methyl-2,4,7-triphenyl-2*H*-indazole (14; R = Ph; R^1 = CH_3; R^2 = $COOCH_3$). 3-Methyl-2,4,6-triphenylthieno[3,4-*c*]pyrazole (1.00 g, 2.73 mmol), dimethyl acetylenedicarboxylate (0.39 g, 2.73 mmol), and benzene (20 ml) were refluxed for 15 hr. Addition of petroleum ether (3 ml) resulted in separation of a light organge solid which crystallized from acetonitrile as colorless prisms: 0.87 g (67%), mp 225–227°; ir (KBr) 3040, 3025, 2940 (CH), 1715 (CO) cm^{-1}; $\lambda_{max}^{CHCl_3}$ 337 nm (log ϵ 3.93) and 256 (4.56); nmr ($CDCl_3$) τ 8.08 (s, 3, 3-CH_3), 6.48 (s, 3, CO_2CH_3), 6.42 (s, 3, CO_2CH_3), 2.81–2.26 (m, 15, aromatic); $M\cdot^+$ 476 (100).

Anal. Calcd for $C_{30}H_{24}N_2O_4$: C, 75.61; H, 5.08; N, 5.88. Found: C, 75.46; H, 5.10; N, 5.77.

5,6-Dibenzoyl-2,4,7-triphenyl-2*H*-indazole (14; R = Ph; R^1 = H; R^2 = COPh). 2,4,6-Triphenylthieno[3,4-*c*]pyrazole (1.00 g, 2.84 mmol), dibenzoylacetylene (0.66 g, 2.84 mmol), and xylene (20 ml) were heated at 120° for 36 hr. The solvent was removed under vacuum and the residue chromatographed on Florisil using benzene as eluent. Recrystallization from ethanol gave colorless, fibrous needles: 0.96 g (61%), mp 196–198°; ir (KBr) 3085, 3050, 2950 (CH), 1670 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 342 nm sh (log ϵ 4.02), 296 (4.44), 253 (4.62), 208 sh (4.64); nmr ($CDCl_3$) τ 3.05–1.95 (m, 25, aromatic), 1.60 (s, 1, H_3); $M\cdot^+$ 554 (69), M^{2+} 277 (5).

Anal. Calcd for $C_{39}H_{26}N_2O_2$: C, 84.44; H, 4.73; N, 5.05. Found: C, 84.03; H, 4.60; N, 5.38.

2,4,5,7,8-Pentaphenylthieno[3,4-*f*]-2*H*-indazole (15). 5,6-Dibenzoyl-2,4,7-triphenyl-2*H*-indazole (1.00 g, 1.81 mmol), phosphorus pentasulfide (0.40 g, 1.81 mmol), and dry pyridine (25 ml) were refluxed for 5 hr. Upon cooling, the reaction mixture was poured into ice–water. A blue solid separated which was collected, washed with water, and air dried. Chromatography on silica gel (benzene) followed by recrystallization from acetonitrile afforded blue, matted needles: 0.90 g (90%), mp 238–240°; ir (KBr) 3077, 3057, 3027 cm^{-1}; $\lambda_{max}^{CH_3OH}$ 602 nm (log ϵ 4.11), 303 (4.42), 252 (4.43), 231 (4.51); nmr ($CDCl_3$) τ 3.16–2.25 (m, 24, aromatic), 2.07–1.80 (m, 2, aromatic); $M\cdot^+$ 554 (100), M^{2+} 277 (17).

Anal. Calcd for $C_{39}H_{26}N_2S$: C, 84.44; H, 4.73; N, 5.05. Found: C, 84.58; H, 4.82; N, 4.97.

***endo*-*N*,2,4,5,8,9-Hexaphenyl-5,6,7,8-tetrahydro-5,8-epithionaphtho[2,3-*c*]pyrazole-5,6-dicarboximide (16).** 2,4,5,7,8-Pentaphenylthieno[3,4-*f*]-2*H*-indazole (1.00 g, 1.81 mmol), *N*-phenylmaleimide (0.31 g, 1.81 mmol), and benzene (30 ml) were refluxed for 6 hr. Upon cooling the solution, a white solid separated which crystallized from acetonitrile as colorless needles: 0.80 g (61%), mp 362–364° dec; ir (KBr) 3070, 3040 (CH), 1715 (CO) cm^{-1}; $\lambda_{max}^{CH_3OH}$ 317 nm (log ϵ 4.15) and 270 (4.30); nmr ($CDCl_3$) τ 5.02 (s, 2, $H_{6\text{-exo}}$, $H_{7\text{-exo}}$), 3.28–1.95 (m, 31, aromatic).

Anal. Calcd for $C_{49}H_{33}N_3O_2S$: C, 80.86; H, 4.57; N, 5.77. Found: C, 80.69; H, 4.45; N, 5.55.