# Reaction of Diazoindenothiophenes with Acetylenic Esters and the Thermal Behavior of the Adducts[1]

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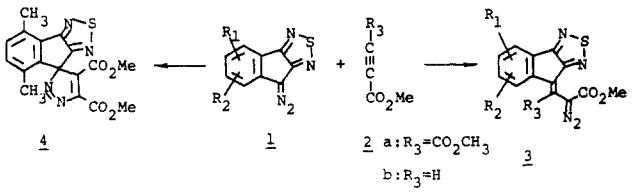
Reaction of three diazoindenothiophenes (**5a–c**) with dimethyl acetylenedicarboxylate (**2a**) and methyl propiolate (**2b**) was investigated. Reaction of **5a** and **5b** with **2a** gave thermally labile pyrazoles **7a** and **7b** which rearranged at 25 °C into the corresponding 3*H*-pyrazoles **13a** and **13b** via Van Alphen–Hüttel rearrangement and migration of an ester group. On thermolysis, **7a** afforded the cyclopropene **14a**, along with **13a**, while **7b** gave the unstable **14b** which afforded the lactone **15** during workup by hydrolysis and ring closure. The reaction of **5c** with **2a** gave a 2:1 adduct with a loss of nitrogen, **8**, which, on photolysis or thermolysis, gave butadiene derivative **9**. Reaction of **5a** with **2b** gave NH pyrazole **10a**, while, in the reaction of **5b** and **5c** with **2b**, the formation of the expected diazoalkenes **11a** and **11b** was detected spectroscopically; however, the isolation of **11** was unsuccessful. The steric effects of the thiophene ring on the above reactions are discussed.

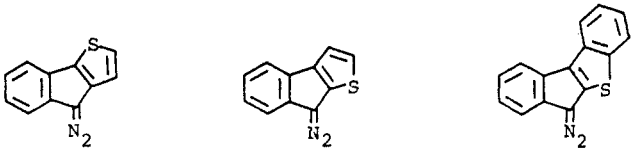
Recently, we have reported[3] that the reaction of 4-diazoindeno[2,3-*c*]1,2,5-thiadiazoles (**1**) with acetylenic esters (**2**) generally gave the diazoalkenes (**3**), while the corresponding pyrazolenine (**4**) was isolated when a steric interaction between the ester group and a 5-methyl group of the indenothiadiazole ring was present, as is the case in the reaction of **1** ($R_1$ = 5-$CH_3$, $R_2$ = 8-$CH_3$) with **2a**.



**4** **1** **2** a: $R_3$=$CO_2CH_3$ b: $R_3$=H **3**

It was reported[4] that 9-diazofluorene, a benzo analogue of **1**, reacted with **2a** and **2b** to afford the corresponding pyrazoles, in both cases.

From these results, it is assumed that in the reaction of diazo compounds of polycyclic aromatics with acetylenic esters, diazoalkene formation is favored because of resonance stabilization (Scheme I), and when such resonance is inhibited by a steric factor, the pyrazole may be isolated. To examine this question, we have now examined the reaction of diazoindenothiophenes **5a–c**, the thieno analogues of **1**, with acetylenic esters **2**; the results are described in the present paper.

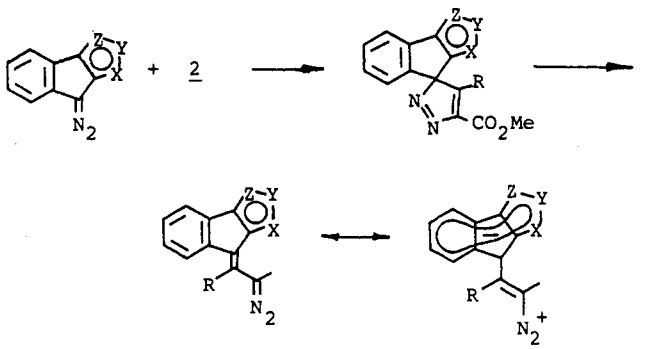


**5a** **5b** **5c**

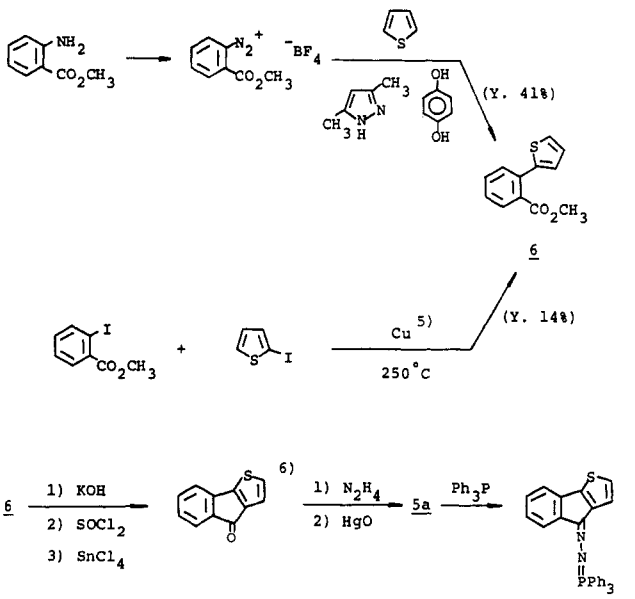
## Results and Discussion

**Preparation of Diazoindenothiophenes (5).** Three diazo compounds (**5a–c**) were prepared by HgO oxidation of the corresponding hydrazones. The parent ketones were prepared by the reported methods[5–9] and the sequence for the preparation of **5a** is shown in Scheme II. The reported method[5] for the preparation of the ester **6** is unsatisfactory because of the poor yield and inaccessible starting materials. Thus, we applied the improved Gomberg–Bachmann reaction according to Taguchi and Fukata's procedure[10]

Scheme I



Scheme II



(1) A part of this paper was published in a preliminary communication: Mataka, S.; Takahashi, K.; Ohshima, T.; Tashiro, M. *Chem. Lett.* **1980**, 915.
(2) (a) Research Institute of Industrial Science. (b) Department of Molecular Science and Technology.
(3) Mataka S.: Takahashi K.; Tashiro M. *Chem. Lett.* **1979**, 1033.
(4) Reimlinger H. *Chem. Ber.* **1967**, *100*, 3097.
(5) Chow W. A.; Hall M. N.; Hoover J. R. E.; Dolan M. M.; Ferlauto R. J. *J. Med. Chem.* **1966**, *9*, 551.
(6) MacDowell D. W. H.; Joffries A. T. *J. Org. Chem.* **1970**, *35*, 871.
(7) Arcus, C. L.; Barrett, G. C. *J. Chem. Soc.* **1960**, 2098.
(8) Steinkopf W.; Guenther E. *Justus liebigs Ann. Chem.* **1936**, *522*, 33.
(9) Higa T.; Krubsack A. J. *J. Org. Chem.* **1976**, *41*, 3399.

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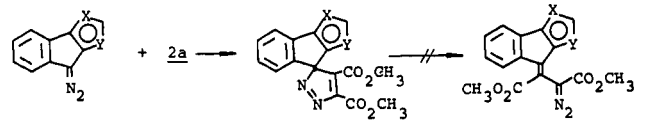
and successfully prepared the desired **6** in a practical yield.

Of the three diazo compounds, **5a** and **5b** are thermally labile red solids; analytically pure samples could not be obtained. Compound **5c** could be recrystallized from hexane to give brown prisms, mp 50–53 °C dec. Diazo compounds **5a–c** showed the characteristic diazo band at 2060–2070 $cm^{-1}$ in their infrared spectra and afforded the corresponding triphenylphosphazines in 65%, 56%, and 92% yields, respectively, on reaction with triphenylphosphine.

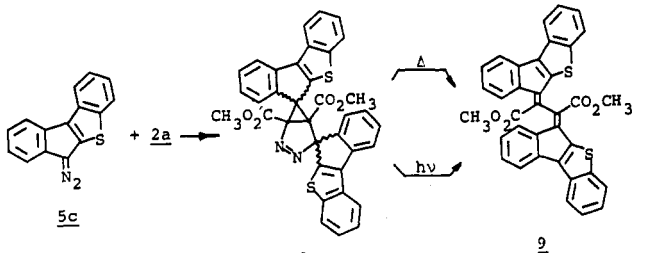
**Reaction of 5a–c with Acetylenic Esters (2).** The reaction of **5a** and **5b** with dimethyl acetylenedicarboxylate (**2a**) in ether at 0 °C afforded the pyrazoles **7a** and **7b**;



5a; X=S, Y=CH
5b; X=CH, X=S
7a; X=S, Y=CH
7b; Y=CH, X=S

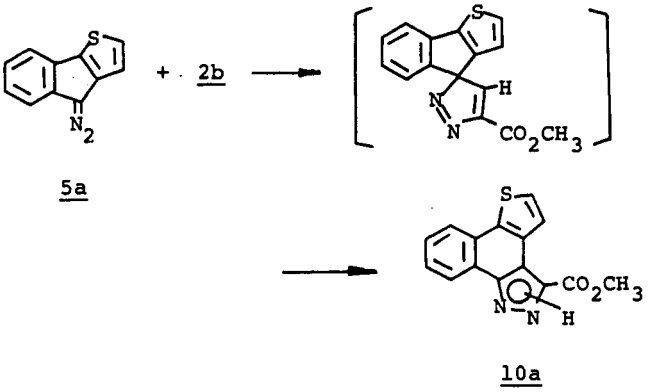
however, the formation of the corresponding diazoalkenes was not detected. Pyrazoles **7a** and **7b** are unstable and could not be purified through recrystallization or chromatography; however, they gave satisfactory spectral data (see Experimental Section). The thermal behavior of **7a** and **7b** will be mentioned later.

The product (**8**) obtained in the reaction of **5c** and **2a** is not a 1:1 adduct but a 2:1 adduct with loss of nitrogen. The compound **8** liberated 1 mol of nitrogen on being



heated in toluene at reflux or being irradiated in benzene at room temperature to give **9** in 63% or 52% yield, respectively. The structures of **8** and **9** were elucidated from analysis and spectral data. The stereochemistry of **8** is not known, but that of **9** was deduced as trans-s-cis on the basis of its $^1H$ NMR spectrum, in which the presence of two kinds of ester groups was observed.

The reaction of diazo compounds **5a–c** with **2b** was investigated in benzene at room temperature. The reaction of **5a** gave a 14% yield of NH pyrazole **10a**, the Van Al-



**Scheme III**

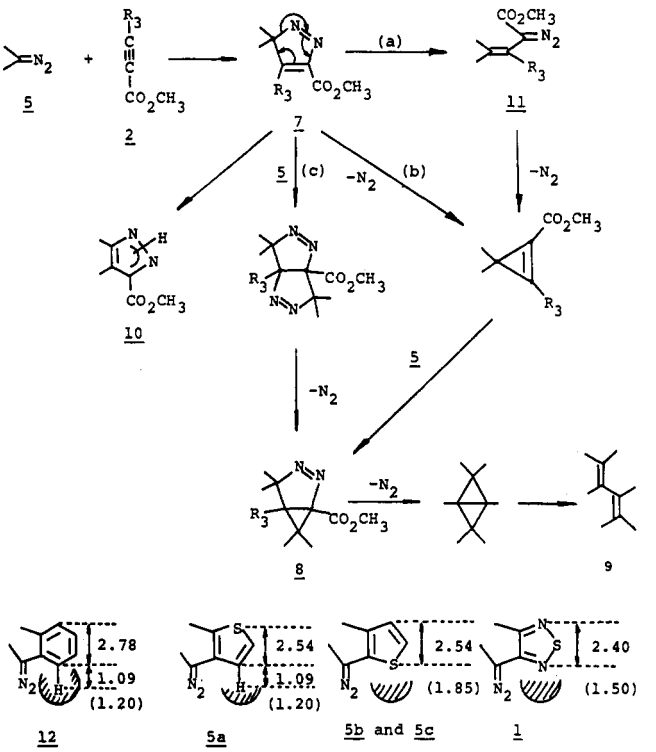
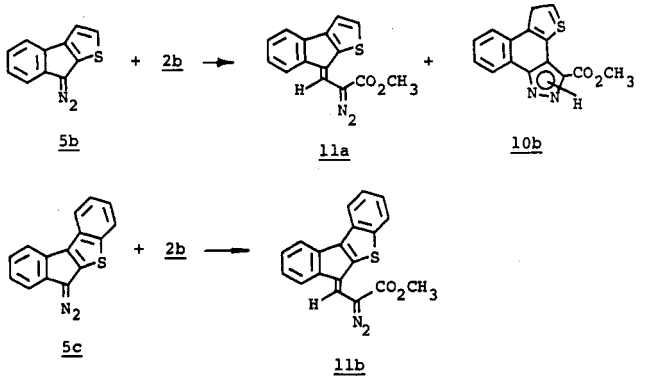




**Figure 1.** Steric circumstances of **1**, **5**, and **12**. The numbers are in angstroms, and the numbers in parentheses are van der Waals radii of H, S, and N atoms, respectively.

phen-Hüttel rearrangement[11] product of the initially formed pyrazolenine. In contrast, the reaction of **5b** gave a brown solid, together with a small amount of NH pyrazole, **10b**. The IR spectrum of this solid exhibited a characteristic diazo band at 2100 $cm^{-1}$ with a carbonyl band at 1700 $cm^{-1}$. In its $^1H$ NMR spectrum, a sharp singlet was observed at $\delta$ 6.64, which is ascribable to a diazoolefinic proton. These data suggest the formation of the expected diazoolefin, **11a**. The reaction of **5c** also



afforded brown solid product, and its spectral data support the formation of diazoolefin **11b**. Unfortunately, all attempts to purify **11** were unsuccessful, and the reaction with triphenylphosphine gave only tarry material.

A plausible pathway for the reaction of **5** with **2** is depicted in Scheme III. We prefer the pathway b or c for the formation of **8** in light of the reaction of **5b** and **5c** with **2a**.

The steric circumstances of **5** are depicted in Figure 1, together with those of **1** and 9-diazofluorene (**12**), along with ring sizes,[12,13] bond lengths, and van der Walls radii.

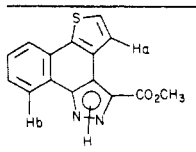
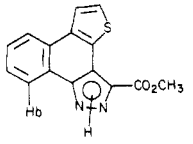
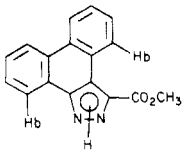
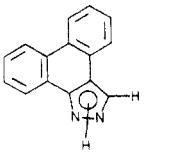
(10) Fukata G.; Kawazoe K.; Taguchi T. *Yakugaku Zasshi* **1974**, *94*, 852.

(11) Van Alphen J. *Recl. Trav. Chim. Pays-Bas* **1943**, *62*, 485, *Chem. Abstr.* **1944**, *38*, 1743q.

Table I. Rearrangement of 7 into 13 at Room Temperature

| product | solvent | yield, % |
|---|---|---|
| 13a | $CHCl_3$ | 76 |
| 13a | $C_6H_6$ | 31 |
| 13b | $CHCl_3$ | 38 |
| 13b | $C_6H_6$ | 41 |

Table II. $^1H$ NMR Spectral Data of 10, 16 and, 17 in $Me_2SO$-$d_6$

| compd | shift, δ: $CH_3$ (s) | thiophene ring proton [a] | benzene ring proton [b] |
|---|---|---|---|
|  10a | 3.99 (3 H) | 7.90 (1 H), 8.51 (1 H, $H_a$) | 7.60-7.77 (2 H), 8.10-8.24 (1 H), 8.54-8.62 (1 H) |
|  10b | 3.99 (3 H) | 7.81 (1 H), 8.21 (1 H) | 7.64-7.74 (2 H), 8.49-8.66 (2 H) |
|  16 | 4.01 (3 H) | | 7.60-7.79 (4 H), 8.49-8.82 (3 H), 9.29-9.40 (1 H, $H_b$) |
|  17 | | | 7.50-7.60 (4 H), 8.30-8.62 (5 H) |

[a] All doublets; $J$ = 5 Hz. [b] All multiplets.

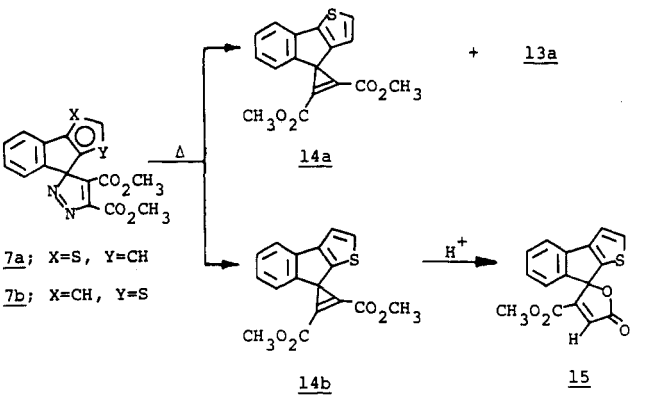
As is shown in Figure 1, the crowding due to the bulkiness of the fused ring is in the order of **12** ≃ **5a** > **5b**, **5c** > **1a**, **5a** presenting as large a steric interaction as **12**. Thus, the reaction of **5a** and **2** does not give rise to diazoalkene. On the other hand, the space occupied by **5b** or **5c**, where the mode of the annulation is reversed with **5a**, is much smaller than that occupied by **5a** but larger than that by **1a**. The result of the reaction of **5b** or **5c** with **2** seems to be consistent with the above.

Diazoalkenes **11a** and **11b** are formed in the reaction with monoester **2b**, while pyrazole **7b** is formed in the reaction of **5b** with diester **2a**.

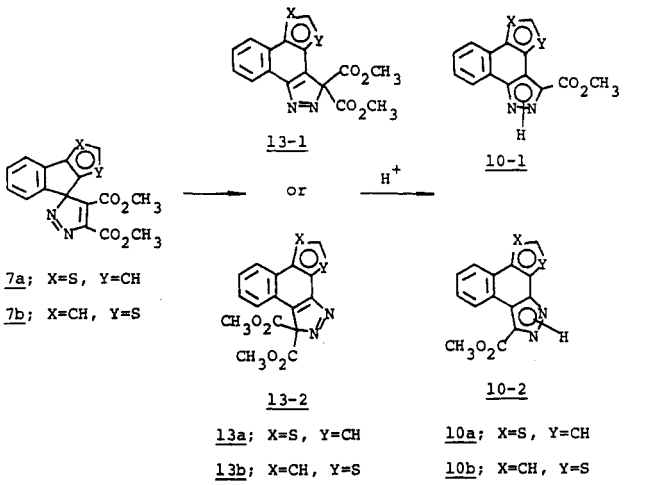
As a conclusion, our assumption mentioned earlier is supported by the reaction of **5** with **2**.

**Thermal Behavior of the Pyrazole 7.** As mentioned above, the pyrazoles **7a** and **7b** are unstable and, on being allowed to stand at room temperature in benzene or chloroform, gradually rearranged into **13**. After 3 days, **13a** and **13b** were obtained in the yields summarized in Table I.

When **7a** was thermolyzed in benzene at reflux, the cyclopropene derivative, **14a**, and the rearranged product, **13a**, were isolated by column chromatography in 28% and 4% yields, respectively, accompanied with a large amount of resinous materials. Although the formation of cyclopropene **14b** was detected in the infrared spectrum of the pyrolyzed product of **7b** ($\nu$ (C=C) 1860 $cm^{-1}$), **14b** could not be isolated but was converted into the lactone derivative **15** ($\nu$ (C=O) 1760 $cm^{-1}$) on chromatography. This reaction was also brought about by treatment of the pyrolyzed mixture with dilute hydrochloric acid. The structures of **14a** and **15** were deduced from spectral data and elemental analysis.




The structure of **13** was elucidated on the basis of elemental analysis, spectral data, and hydrolysis to give **10**. Of the two possible structures of **10** and **13**, we preferred the structure **10-1** and **13-1** on the basis of the $^1H$ NMR study. The NMR data of **10** are summarized in Table II together with those of its analogue **16**[14] and parent compound **17**.[4] Because of the ester group on the pyrazole ring, the $H_b$ proton of **16** appeared at δ 9.29–9.40, which is ca. 0.6–0.8 ppm lower than that of **17**, while such a downfield shift of the $H_b$ proton of **10** was not observed. Furthermore, the thiophene ring proton ($H_a$) appeared at δ 8.51, which is also explained in the terms of the effect of the ester group. Therefore, the ester group is situated on the same side as the thiophene ring.

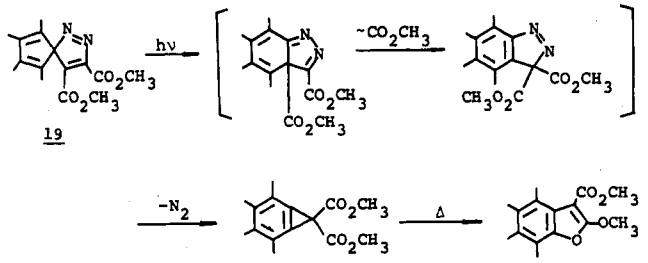



The formation of **13** is now considered to proceed via the Van Alphen–Hüttel rearrangement followed by the migration of an ester group. An analogous rearrangement was reported[14] in the pyrolysis of the pyrazole **18** prepared by the reaction of **12** with **2a**.

It has been reported[15] that the photolysis of the phenyl-substituted pyrazoles **18** affords the corresponding

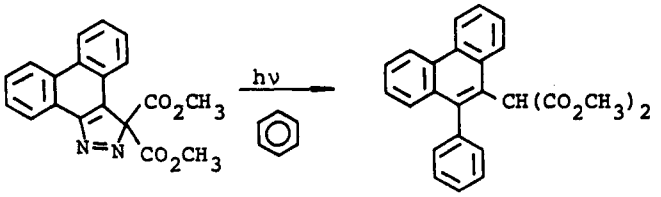
(12) Acheson R. M. "An Introduction to the Chemistry of Heterocyclic Compounds", 3rd ed.; Wiley: New York, 1976; p 153.
(13) Weinstock L. M.; Pollak P. I. "Advances in Heterocyclic Chemistry"; Academic Press: New York, 1968; Vol. 9, p 148.
(14) Mataka, S.; Tashiro M. *J. Org. Chem.* **1981**, *46*, 1929.
(15) Dürr H.; Schrader L. *Chem. Ber.* **1970**, *103*, 1334.

Scheme IV

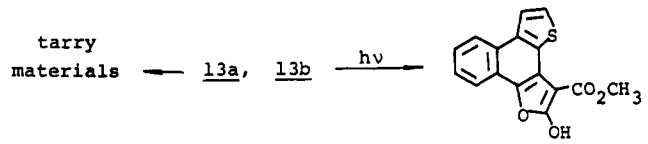


benzocyclopropenes and the pathway shown in Scheme IV was proposed.

On the other hand, the photolysis of 18 in benzene gave the phenanthrene derivative, with no formation of ben-



zocyclopropene and furan derivatives.[14] The photolysis of **13a** in benzene gave a large amount of resinous materials, while photolysis of **13b** afforded the furan derivative



**20** in 63% yield. As **13a** and **13b** showed very similar UV spectra, the cause for their behavior upon photolysis is obscure.

## Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on a Nippon Bunko A-102 spectrophotometer as KBr pellets. $^1H$ NMR (internal $Me_4Si$) spectra were taken on a Nippon Denshi JEOL FT-100 NMR spectrometer. Mass spectra were recorded on a Nippon Denshi JMS-01SG-2 mass spectrometer at 75 eV using a direct-inlet system.

**Preparation of 2-(2-Thienyl)benzoate (6).** To a stirred mixture of 11.24 g of 2-(methoxycarbonyl)benzene diazonium tetrafluoroborate (prepared from methyl 2-aminobenzoate) in 30 mL of thiophene was added dropwise a solution of 4.5 g of 3,5-dimethylpyrazole and 0.56 g of hydroquinone in 30 mL of thiophene. After the addition was completed, the mixture was stirred at 0 °C for 3 h and then at room temperature for an additional 1 h. The reaction mixture was evaporated in vacuo to remove the excess of thiophene, and the condensate was column chromatographed on silica gel (Wako gel, C-300) with benzene as an eluant. The benzene fraction was evaporated in vacuo, and the resultant liquid was subjected to distillation to afford 0.53 g (9%) of methyl benzoate: bp 40–45 °C (4 mmHg). Second fraction from the distillation afforded 3.97 g (41%) of **6**, bp 160–162 °C (4 mmHg) [lit.[5] 147–152 °C (2.5 mmHg)].

**Preparation of Hydrazones.** The following hydrazones were prepared by refluxing the starting ketones for 0.5 h in ethanol containing 2 equiv of hydrazine.

The hydrazone of 4*H*-indeno[1,2-*b*]thiophen-4-one[6] was, obtained in 91% yield as yellow needles, mp 180–182 °C (recrystallized from hexane). Anal. Calcd for $C_{11}H_8N_2S$: C, 65.99; H, 4.03; N, 13.99. Found: C, 65.77, H, 4.22; N, 13.80.

The hydrazone of 8*H*-indeno[2,1-*b*]thiophen-8-one[8] was obtained in 86% yield as yellow needles: mp 161–163 °C (recrystallized from hexane). Anal. Calcd for $C_{11}H_8N_2S$: C, 65.99; H, 4.03; N, 13.99. Found: C, 66.11; H, 4.05; N, 13.94.

The hydrazone of 6*H*-benzo[*b*]indeno[1,2-*d*]thiophen-6-one[9] was obtained in 71% yield as orange needles: mp 206–207 °C (recrystallized from a mixture of benzene and hexane). Anal. Calcd for $C_{15}H_{10}N_2S$: C, 71.97; H, 4.03; N, 11.19. Found: C, 71.65; H, 4.16; N, 10.94.

**Preparation of 4-Diazoindeno[1,2-*b*]thiophene (5a).** To a mixture of the hydrazone (1.00 g), yellow mercuric oxide (1.65 g), and anhydrous sodium sulfate (1.00 g) in 100 mL of ether was added 1 drop of saturated potassium hydroxide solution, and the mixture was stirred at room temperature for 24 h. Inorganics were filtered off, and the filtrate was evaporated in vacuo without external heating. The crystalline residue was washed with *n*-pentane to give 0.91 g (90%) of **5a** as red solid: mp 59 °C dec; IR 2060 $cm^{-1}$.

**Preparation of 8-Diazoindeno[2,1-*b*]thiophene (5b).** A mixture of the hydrazone (1.00 g), yellow mercuric oxide (1.65 g), and anhydrous sodium sulfate (1.00 g) in 100 mL of ether was treated as described above to give 0.93 g (92%) of **5b** as red solid; mp 57 °C dec; IR 2060 $cm^{-1}$. Anal. Calcd for $C_{11}H_6N_2S$: C, 66.66; H, 3.05; N, 14.14. Found: C, 66.76; H, 3.26; N, 12.63.

**Preparation of 6-Diazobenzo[b]indeno[1,2-*d*]thiophene (5c).** To a mixture of the hydrazone (0.80 g), yellow mercuric oxide (1.06 g), and anhydrous sodium sulfate (0.80 g) was added a drop of saturated potassium hydroxide solution, and the mixture was stirred at room temperature for 4 h. Inorganics were filtered off, and the filtrate was evaporated in vacuo to give the crystalline residue, which, on recrystallization from hexane, afforded 0.57 g of **5c** as brown prisms: mp 50–53 °C dec; IR 2070 $cm^{-1}$. Anal. Calcd for $C_{15}H_8N_2S$: C, 72.56; H, 3.25; N, 11.28. Found: C, 72.48; H, 3.41; N, 11.18.

**Reaction of 5 with Triphenylphosphine.** An equimolecular amount of triphenylphosphine in ether was added dropwise to the ether solution of **5** and the mixture was stirred at room temperature for 1 h. The precipitated phosphazine was collected by filtration and recrystallized from hexane to give yellow prisms.

The triphenylphosphazine of 4*H*-indeno[1,2-*b*]thiophen-4-one was obtained in 65% yield; mp 243–245 °C. Anal. Calcd for $C_{29}H_{21}N_2PS$: C, 75.63; H, 4.60; N, 6.08. Found: C, 75.22; H, 4.66; N, 6.30.

The triphenylphosphazine of 8*H*-indeno[2,1-*b*]thiophen-8-one was obtained in 56% yield; mp 277–230 °C. Anal. Calcd for $C_{29}H_{21}N_2PS$: C, 75.63; H, 4.60; N, 6.08. Found: C, 75.20; H, 4.62; N, 6.18.

The triphenylphosphazine of 6*H*-benzo[*b*]indeno[1,2-*d*]thiophen-6-one was obtained in 92% yield; mp 176–177 °C. Anal. Calcd for $C_{33}H_{23}N_2PS$: C, 77.63; H, 4.54; N, 5.49. Found: C, 77.52; H, 4.69; N, 5.51.

**Reaction of 5a with 2a.** To a solution of **5a** (500 mg) in 35 mL of ether was added at 0 °C dropwise a solution of **2a** (355 mg) in 35 mL of ether, and the mixture was stirred at 0 °C for 3 h. Evaporation of ether in vacuo afforded the residue which, on trituration with hexane, gave spiro[dimethyl pyrazole-4,5-dicarboxylate-3,4′-4*H*-indeno[1,2-*b*]thiophene] (**7a**) as orange crystalline solid in 54% yield: mp 88 °C dec; IR 1750, 1730 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.54 (Me, s), 4.00 (Me, s), 6.50 (1 H, d, $J$ = 5 Hz), 6.5–6.7 (1 H, m), 7.0–7.5 (4 H, m). Anal. Calcd for $C_{17}H_{12}N_2O_4S$: C, 60.00; H, 3.55; N, 8.23. Found: C, 60.15; H, 3.64; N, 7.73.

**Reaction of 5b with 2a.** The reaction was carried out and the mixture was treated as described above, affording spiro[dimethyl pyrazole-4,5-dicarboxylate-3,8′-8*H*-indeno[2,1-*b*]thiophene] (**7b**) as orange crystalline solid in 32% yield: mp 82 °C dec; IR 1740, 1720 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.72 (Me, s), 4.06 (Me, s), 7.1–7.7 (6 H, m). Anal. Calcd for $C_{17}H_{12}N_2O_4S$: C, 60.00; H, 3.55; N, 8.23. Found: C, 60.17; H, 3.85; N, 7.82.

**Reaction of 5c with 2a.** At room temperature, a solution of **2a** (57 mg) in 10 mL of ether was added dropwise to a solution of **5c** (100 mg) in 10 mL of ether and the mixture was stirred at room temperature for 12 h. Ether was evaporated in vacuo to leave the residue which, on trituration with hexane, gave 40 mg (40% yield) of dispiro[6*H*-benzo[*b*]indeno[1,2-*d*]thiophene-6,4′-dimethyl 2′,3′-diazabicyclo[3.1.0]hex-2-ene-1′,5′-dicarboxylate-6′,6″-6″*H*-benzo[*b*]indeno[1,2-*d*]thiophene] (**8**) as dark brown prisms: mp 111–114 °C dec (recrystallized from a mixture of hexane and benzene); IR 1770, 1740 $cm^{-1}$; $^1H$ NMR ($CDCl_3$)

δ 3.04 (Me, s), 4.04 (Me, s), 7.1–7.6 (12 H, m), 7.8–8.3 (4 H, m); mass spectrum, *m/e* 582 ($M^+ - N_2$), 523 ($M^+ - N_2 - CO_2CH_3$), 464 ($M^+ - N_2 - 2CO_2CH_3$). Anal. Calcd for $C_{36}H_{22}N_2O_4S_2$: C, 70.81; H, 3.63; N, 4.59. Found: C, 70.32; H, 3.77; N, 4.39.

**Reaction of 5a with 2b.** A solution of **2b** (42 mg) in 10 mL of benzene was slowly added to a solution of **5a** (100 mg) in 10 mL of benzene. The mixture was stirred at room temperature for 24 h and filtered to give analytically pure **10a** in 14% yield. Methyl benzo[*g*]thieno[3,2-*e*]indazole-4-carboxylate (**10a**) was obtained as colorless crystals: mp 252–255 °C; IR 3150, 1710 $cm^{-1}$; mass spectrum, *m/e* 282 ($M^+$). Anal. Calcd for $C_{15}H_{10}N_2O_2S$: C, 63.83; H, 3.57; N, 9.93. Found: C, 63.81; H, 3.86; N, 9.72.

**Reaction of 5b with 2b.** A solution of **2b** (42 mg) in 10 mL of benzene was slowly added to a solution of **5b** (100 mg) in 10 mL of benzene, and the mixture was stirred at room temperature for 18 h. The precipitated **10b** (yield 7%) was filtered, and the filtrate was evaporated in vacuo to leave the residue which, on trituration with hexane, gave 45 mg of brown solid: mp 66 °C dec; IR 2100, 1700 $cm^{-1}$; $^1H$ NMR ($CCl_4$) δ 3.82 (s), 6.64 (s), 6.9–7.5 (m).

**Reaction of 5c with 2b.** A solution of **2b** (34 mg) in 10 mL of benzene was slowly added to a solution of **5c** (100 mg), and the mixture was stirred at room temperature for 24 h. Evaporation of the solvent and trituration of the resultant residue with hexane afforded 55 mg brown solid: mp 74–79 °C dec; IR 2100, 1710 $cm^{-1}$; $^1H$ NMR ($CCl_4$) δ 3.84 (s), 6.79 (s), 6.9–8.2 (m).

**Rearrangement of 7 at Room Temperature.** A solution of **7** in chloroform or benzene was stirred at room temperature for 3 days. Solvent was evaporated in vacuo, and the resultant residue was column chromatographed with benzene as an eluant, affording the corresponding **13** in the yield shown in Table I.

Dimethyl 4*H*-benzo[*g*]thieno[3,2-*e*]indazole-4,4-dicarboxylate (**13a**) was obtained as colorless needles: mp 159–160 °C (recrystallized from methanol); IR 1750, 1730 $cm^{-1}$; $^1H$ NMR ($Me_2MSO$-$d_6$) δ 3.87 (2Me, s), 7.8–7.9 (2 H, m), 7.72 (1 H, d, *J* = 5 Hz), 8.11 (1 H, d, *J* = 5 Hz), 8.2–8.4 (1 H, m), 8.85–8.95 (1 H, m); mass spectrum, *m/e* 340 ($M^+$), 312 ($M^+ - N_2$), 297; UV (ethanol) 340, 250 nm (ε 1190, 11 050). Anal. Calcd for $C_{17}H_{12}N_2O_4S$: C, 60.00; H, 3.55; N, 8.23. Found: C, 59.94; H, 3.65; N, 8.08.

Dimethyl 4*H*-benzo[*g*]thieno[2,3-*e*]indazole-4,4-dicarboxylate (**13b**) was obtained as colorless needles: mp 144–146 °C (recrystallized from methanol); IR 1750, 1730 $cm^{-1}$; $^1H$ NMR ($Me_2SO$-$d_6$) δ 3.78 (2Me, s), 7.8–7.9 (2 H, m). 8.30 (1 H, d, *J* = 5 Hz), 8.45 (1 H, d, *J* = 5 Hz), 8.6–8.8 (1 H, m), 8.9–9.0 (1 H, m); mass spectrum, *m/e* 340 ($M^+$), 312 ($M^+ - N_2$), 297; UV (ethanol) 342, 252 nm (ε 1275, 10 370). Anal. Calcd for $C_{17}H_{12}N_2O_4S$: C, 60.00; H, 3.55; N, 8.23. Found: C, 60.17; H, 3.85; N, 7.82.

**Thermolysis of 7a.** A solution of **7a** (460 mg) in benzene (50 mL) was refluxed for 0.5 h. The solvent was evaporated in vacuo to leave the residue which, on column chromatography with benzene as an eluant afforded **13a** (yield; 20 mg, 4%) and **14a** (yield; 120 mg, 28%).

Spiro[dimethyl cyclopropene-2,3-dicarboxylate-1,4′-4′*H*-indeno[1,2-*b*]thiophene) (**14a**) was obtained as orange plates: mp 139–140 °C (recrystallized from hexane); IR 1850, 1720 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 3.82 (2Me, s), 6.93 (1 H, d, *J* = 5 Hz), 7.1–7.6 (5 H, m); mass spectrum, *m/e* 312 ($M^+$), 281, 280 ($M^+ - CO_2CH_3$), 253 ($M^+ - CO_2CH_3$), 195, 194 ($M^+ - 2CO_2CH_3$). Anal. Calcd for $C_{17}H_{12}O_4S$: C, 65.38; H, 3.87. Found: C, 65.24; H, 3.88.

**Thermolysis of 7b.** A solution of **7b** (273 mg) in 10 mL of benzene was refluxed for 0.5 h, and the mixture was treated as described above to give spiro[8*H*-indeno[2,1-*b*]thiophene-8,4′-(methoxycarbonyl)-2′-buten-4′-olide] (**15**; yield 140 mg, 59%) as yellow needles: mp 192–193 °C (recrystallized from hexane); IR 1760, 1720 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 3.62 (Me, s), 7.00 (1 H, s), 7.1–7.6 (4 H, m); mass spectrum, *m/e* 298 ($M^+$), 239 ($M^+ - CO_2CH_3$), 195 ($M^+ - CO_2 - CO_2CH_3$). Anal. Calcd for $C_{16}H_{14}O_4S$: C, 64.43; H, 3.38. Found: C, 64.36; H, 3.24.

**Pyrolysis of 8.** A solution of **8** (50 mg) in 10 mL of toluene was refluxed for 1 h, and the solvent was evaporated in vacuo. The resultant crystalline residue was recrystallized from a mixture of benzene and hexane to give dimethyl bis(benzo[2,3-*d*]-indenylidene)-(*Z*,*E*)-succinate **9** in 63% yield as brown prisms: mp 141–145 °C; IR 1720 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 3.82 (Me, s), 6.77–6.94 (1 H, m), 7.0–8.2 (14 H, m), 8.4–8.5 (1 H, m); mass spectrum, *m/e* 582 ($M^+$), 523 ($M^+ - CO_2CH_3$), 464 ($M^+ - 2CO_2CH_3$). Anal. Calcd for $C_{36}H_{22}O_4S_2$: C, 74.21; H, 3.81. Found: C, 73.75; H, 4.02.

**Photolysis of 8.** A solution of **8** (50 mg) in 50 mL of benzene was irradiated at room temperature with Pyrex-filtered light from a 100-W high pressure mercury lamp for 1 h. The mixture was treated as described above, affording **9** in 52% yield.

**Hydrolysis of 13.** A solution of **13** (50 mg) in 4 mL of ethanol containing 1 mL of concentrated hydrochloric acid was refluxed for 1 h. The mixture was poured into 50 mL of water, extracted with 30 mL of chloroform, dried over anhydrous $Na_2SO_4$, and evaporated in vacuo to afford analytically pure **10a** and **10b** in 58% and 42% yields, respectively.

Methyl benzo[*g*]thieno[2,3-*e*]indazole-4-carboxylate (**10b**) was obtained as colorless crystals: mp 259–263 °C; IR 3150, 1710 $cm^{-1}$; mass spectrum, *m/e* 282 ($M^+$). Anal. Calcd for $C_{15}H_{10}N_2O_2S$: C, 63.83; H, 3.57; N, 9.93. Found: C, 63.34; H, 3.70; N, 9.76.

**Photolysis of 13b.** A solution of **13b** (180 mg) in 50 mL of benzene was irradiated at room temperature with Pyrex-filtered light from a 100-W high-pressure mercury lamp for 1 h. The mixture was evaporated in vacuo, and the residue was column chromatographed with benzene as an eluant to give methyl benzo[*g*]thieno[2,3-*e*]-5-hydroxybenzofuran-4-carboxylate (**20**) in 63% yield as colorless needles: mp 133–134 °C (recrystallized from methanol); IR 3450, 1765, 1735 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 3.57 (Me, s), 7.0–7.6 (7 H, m); mass spectrum, *m/e* 298 ($M^+$), 239 ($M^+ - CO_2CH_3$). Anal. Calcd for $C_{16}H_{14}O_4S$: C, 64.43; H, 3.38. Found: C, 64.27; H, 3.52.

**Registry No. 2a**, 762-42-5; **2b**, 922-67-8; **5a**, 76177-64-5; **5b**, 76177-65-6; **5c**, 78515-54-5; **6**, 17595-84-5; **7a**, 76177-66-7; **7b**, 76177-67-8; **8**, 78515-55-6; **9**, 78515-56-7; **10a**, 78529-77-8; **10b**, 78529-75-6; **13a**, 76360-34-4; **13b**, 76360-35-5; **14a**, 76177-68-9; **15**, 78515-57-8; **16**, 78529-81-4; **17**, 78529-79-0; **20**, 78515-58-9; 2-(methoxycarbonyl)-benzenediazonium tetrafluoroborate, 342-54-1; thiophene, 110-02-1; 4*H*-indene[1,2-*b*]thiophen-4-one hydrazone, 78515-59-0; 4*H*-indeno-[1,2-*b*]thiophen-4-one, 5706-08-1; 8*H*-indeno[2,1-*b*]thiophen-8-one hydrazone, 78515-60-3; 8*H*-indeno[2,1-*b*]thiophen-8-one, 13132-12-2; 6*H*-benzo[*b*]indeno[1,2-*d*]thiophen-6-one hydrazone, 78515-61-4; 6*H*-benzo[*b*]indeno[1,2-*d*]thiophen-6-one, 23339-77-7; triphenylphosphine, 603-35-0; 4*H*-indeno[1,2-*b*]thiophen-4-one triphenylphosphazine, 78515-62-5; 8*H*-indeno[2,1-*b*]thiophen-8-one triphenylphosphazine, 78515-63-6; 6*H*-benzo[*b*]indeno[1,2-*d*]thiophen-6-one triphenylphosphazine, 78515-64-7; **11a**, 78515-65-8; **11b**, 78515-66-9; methyl benzoate, 93-58-3.