98.0–99.5% active iodine and was used as purchased. Irradiation of reaction mixtures was effected with a G.E. Projector Spot 150-W, 130-V tungsten lamp.

Oxidation of 1,2-Diphenyl-1,2-ethanediol. A tetrahydrofuran solution (5 mL) containing 4.00 mmol of pinacol (1,2-dimethyl-1,2-ethanediol) was added to a 10-mL round-bottomed flask. To this solution was added 0.482 g (2.14 mmol) of *N*-iodosuccinimide. The mixture was stirred and samples of the solution were removed periodically. Aluminum foil covered the reaction flask except for the time samples were taken. Reaction times and percent yields were 15 min (22%), 30 min (32%), 1 h (47%), 2 h (62%), and 4 h (96%).

Iodine Determinations. To find the concentration of the iodine produced in the oxidation of 1,2-diols with NIS the completed reactions were added to 25 mL of 1:1 mixture of acetic acid and water. A few drops of concentrated hydrochloric acid was added and the iodine was titrated with a standardized solution of thiosulfate. The iodine was found in 85–90% yield, assuming that 1 mol of iodine is produced from 2 mol of *N*-iodosuccinimide during the reaction.

Succinimide Determination. Succinimide was recovered from the completed reactions by pouring the reactions into diethyl ether and extracting the ether solution with water. The combined water extracts were washed with fresh ether and the water solution was evaporated. Succinimide was recovered in yields of 85–96%.

Acknowledgment. We are grateful to the Research Corporation for financial support of this research.

Registry No. 1, 76-09-5; 2, 516-12-1; benzopinacol, 464-72-2; 1,2-diphenyl-1,2-ethanediol, 492-70-6; 2,3-butanediol, 513-85-9; 1-phenyl-1,2-ethanediol, 93-56-1.

Thermolysis of Dimethyl 3,3-(2,2′-Biphenylyl)-3*H*-pyrazole-4,5-dicarboxylate

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The photolysis of 3*H*-pyrazoles is a well-known preparative method for cyclopropenes.[1] Although some examples of thermal elimination of nitrogen affording cyclopropenes have been reported,[2] the Van Alphen–Hüttel rearrangement[3,4] is usually the predominant reaction pathway, giving 4*H*- and/or 1*H*-pyrazoles according to Scheme I.

Dimethyl 3,3-(2,2′-biphenylyl)-3*H*-pyrazole-4,5-dicarboxylate (1) was reported[4] to rearrange into 1*H*-pyrazole **2** in hot acetic acid and into 1*H*-pyrazole **3** in hot concentrated sulfuric acid (Scheme II). It was also reported[5] that 1 extrudes nitrogen in refluxing CH_2Cl_2, giving the corresponding cyclopropene **4** in 16% yield together with recovery of 1 in 65% yield. Recently, we reported[6] that the thermally labile 3*H*-pyrazoles **5**, the thieno analogues of 1, rearrange into the corresponding 3*H*-pyrazoles **6**

Scheme I

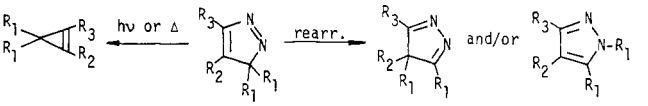
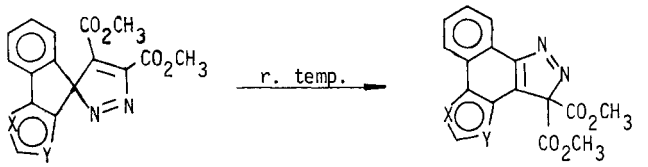


Table I. Pyrolysis of Dimethyl 3,3-(2,2′-Biphenylyl)-3*H*-pyrazole-4,5-dicarboxylate (1)

run	solvent	time, h	product yields, % 3	4	7	8	9
1	toluene	1		35	21	3	
2	benzene	1		70		7	1
3	acetonitrile	1	2	47		17	11
4	methanol	2	4	18		16	14
5	ethanol	1	3	35		16	15

which are formed via Van Alphen–Hüttel rearrangement followed by the migration of an ester group.



5 6

(X=S, Y=CH; X=CH, Y=S)

In this context, we investigated the pyrolysis of 1 in various solvents and the results are given in the present paper.

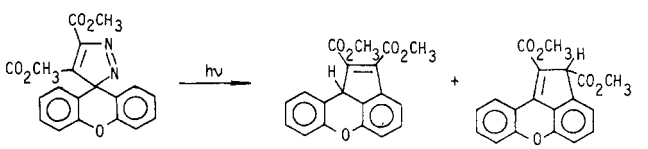
The pyrolysis of 1 was carried out at reflux in the solvent shown in Table I. The initial color of the reaction mixture faded away smoothly. Besides the expected cyclopropene **4**,[5] the compounds, **7–9** and **3**[4] were obtained in the yields summarized in Table I.

Although the structures of **7–9** are present, the cyclopropene formation is predominant in benzene, while the rearrangement into phenanthropyrazoles **3**, **8**, and **9** becomes a significant reaction pathway in polar solvents such as acetonitrile, methanol, and ethanol.

Compound **7** was obtained only in the pyrolysis in toluene. When **4a** was heated at reflux in toluene for 4 h, **7** was obtained in 48% yield. The structure of **7** was deduced as dimethyl 9b*H*-cyclopenteno[1,2,3-*l*,*m*]-fluorene-1,2-dicarboxylate (**7-1**) or its tautomer dimethyl

7-1 7-2

2*H*-cyclopenteno[1,2,3-*l*,*m*]fluorene-1,2-dicarboxylate (**7-2**) on the basis of analytical and spectral data as well as the chemical conversion mentioned above. It was reported[7] that photolysis of the cycloadduct of α-diazoxanthene with dimethyl acetylenedicarboxylate in ether yields **10** and **11**



10 11

(1) See the references cited in: Durr, H.; Gleiter, R. *Angew. Chem.* **1978**, *90*, 591.
(2) (a) Gale, D. M.; Middleton, W. J.; Krespan, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 3617. (b) Komendantov, M. I.; Bekmukhametov, R. R. *Khim. Geterstsikl. Soedin.* **1975**, *79*; *Chem. Abstr.* **1975**, *82*, 111337.
(3) Baumes, R.; Elguero, J.; Jacquier, R.; Tarrago, G. *Tetrahedron Lett.* **1973**, 3781.
(4) Van Alphen, J. *Recl. Trav. Chim. Pays-Bas* **1943**, *62*, 491; *Chem. Abstr.* **1944**, *38*, 1743*q*.
(5) Reimlinger, H. *Chem. Ber.* **1967**, 3097.
(6) Mataka, S.; Takahashi, K.; Ohshima, T.; Tashiro, M. *Chem. Lett.* **1980**, 915.
(7) Rosazza, J. P. *J. Chem. Soc., Chem. Commun.* **1977**, 842.

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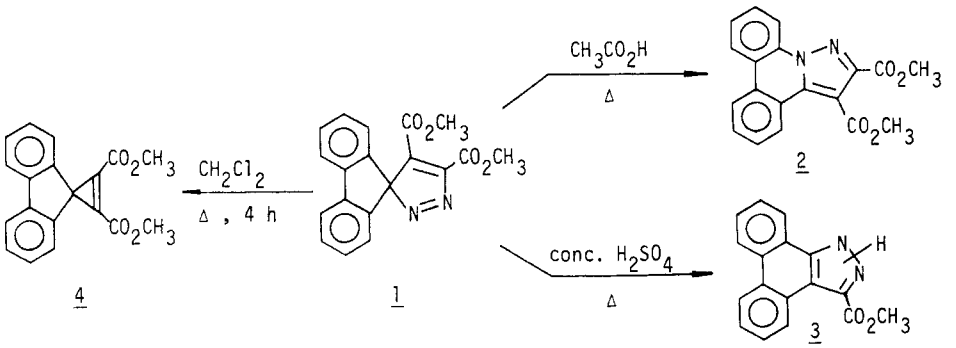
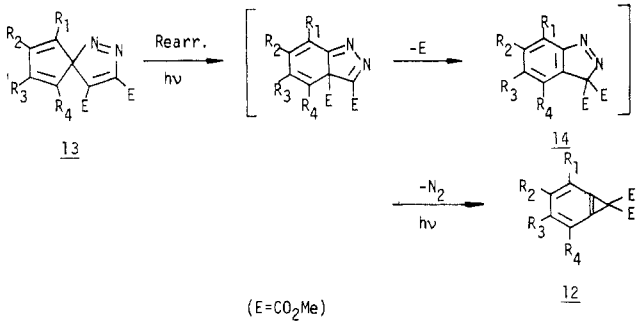
Scheme II



Scheme III



in 15% and 7% yields, repectively, as separable products, and the NMR data of **11** were given. From comparison of NMR data, we tentatively favor the structure of **7**-1 for **7**.

The ^1H and ^{13}C NMR and mass spectral data of **8** and **9** are given in Tables II and III (supplementary material).

In the ^1H NMR spectrum of **8**, a sharp singlet ascribable to methyl groups was observed at 4.07 ppm in $CDCl_3$, which appeared as two slightly separated peaks in CD_3CN and two definitely separated peaks in C_6D_6. In the ^{13}C NMR spectrum of **8**, two signals due to carbonyl carbon were observed. On the other hand, the ester methyl group of **9** was observed as one sharp singlet peak both in $CDCl_3$ and C_6D_6. The signal of the carbonyl carbon of **9** appeared at 163.0 ppm, and the signal ascribable to the tertiary carbon atom was observed at 104.4 ppm in the ^{13}C NMR. A mass spectrum of **8** gave a characteristic cleavage pattern of an ester compound; however, that of **9** is completely different from **8**, and the peak due to a loss of nitrogen was observed.

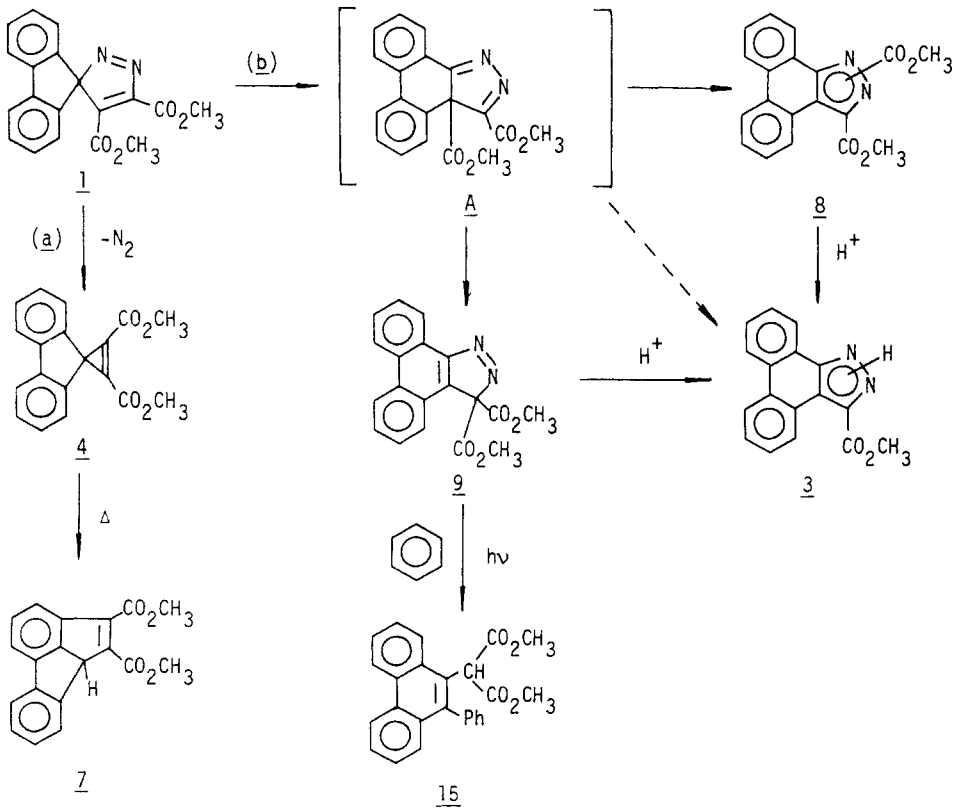
Hydrolysis of **8** in refluxing hydrochloric acid–ethanol gave **3** in 15% yield, and 19% of unchanged **8** was recovered, while **9** was easily hydrolyzed under the same reaction conditions to afford **3** in 54% yield (eq 1 and 2).

$$8 \xrightarrow[\text{reflux 1 h}]{\text{HCl-EtOH}} 3\ (15\%) + 8\ (19\%) \qquad (1)$$

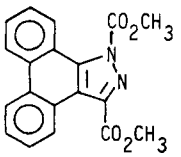
$$9 \xrightarrow[\text{reflux 1 h}]{\text{HCl-EtOH}} 3\ (54\%) \qquad (2)$$

From the above results, we assigned the structures as dimethyl 2*H*-phenanthro[9,10-*c*]pyrazole-1,3-dicarboxylate

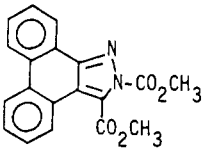
Scheme IV



(8-1) or its tautomer, dimethyl 3*H*-phenanthro[9,10-*c*]-



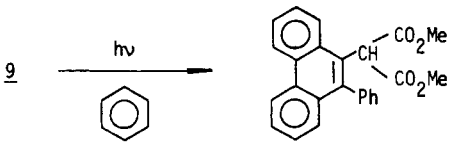
8-1



8-2

pyrazole-2,3-dicarboxylate (8-2), for **8** and as dimethyl 3*H*-phenanthro[9,10-*c*]pyrazole-3,3-dicarboxylate for **9**. The final structural assignment of **8** cannot yet be made.

It was reported[8] that benzocyclopropenes (**12**) are formed when the corresponding polyphenyl-substituted spiro-3*H*-pyrazoles (**13**) are photolyzed in benzene by using a high-pressure mercury lamp. The reaction pathway shown in Scheme III was proposed, though **14** was not isolated. Therefore, we carried out the photolysis of **9** in benzene using a high-pressure mercury lamp and obtained the phenanthrene derivative **15** in 18% yield with no



15

formation of the expected phenanthrocyclopropene. The pathway of the formation of the products is shown in Scheme IV. Cyclopropene is formed in the pyrolysis in benzene (path a) while the Van Alphen–Hüttel rearrangment followed by the migration of an ester phenyl group is the favorable reaction pathway in the pyrolysis in polar solvents (path b), affording phenanthropyrazoles **8** and **9**. Though the pathway of the formation of **3** is not known, **3** might be formed via **8** and **9** or directly from the intermediate A.

Experimental Section

Melting points were determined on a Yanagimoto micro-melting-point apparatus and were uncorrected. IR, NMR, and mass spectra were obtained on a Nippon Bunko IR-A spectrometer, Hitachi R-40 and Nippon Denshi JEOL FT-100 spectrometers, and a Nippon Denshi JMS-01SG-2 spectrometer, respectively. IR spectra were taken of KBr disks, and mass spectra were obtained at 75 eV.

Pyrolysis of 1. A solution of **1a** (500 mg) in a solvent (5 mL) was refluxed, and the solvent was evaporated in vacuo. The residue was triturated with benzene (2 mL) to afford the 2:1 complex of **8** and benzene, which on recrystallization from benzene gave colorless prisms: mp 155–156 °C dec; IR 1735 (C=O) cm^{-1}; ^1H NMR (CD_3CN) δ 3.96 (s, 3 H), 3.98 (s, 3 H), 7.35 (s, 3 H), 7.5–7.8 (m, 4 H), 8.4–8.6 (m, 4 H). Anal. Calcd for ($C_{19}H_{14}N_2O_4 \cdot 1/2C_6H_6$): C, 70.77; H, 4.59; N, 7.50. Found: C, 70.74; H, 4.58; N, 7.45. Recrystallization of the complex from methanol gave **8**: mp 156–157 °C; colorless needles; IR 1725 (C=O) cm^{-1}. Anal. Calcd for $C_{19}H_{14}N_2O_4$: C, 68.25; H, 4.22; N, 8.38. Found: C, 68.40; H, 4.37; N, 8.24. The benzene filtrate was chromatographed on silica gel (Wako gel, C-300). From the fractions with benzene and chloroform as eluents were isolated compounds **4**[5] and **7** and compounds **9** and **3**[4] were isolated, respectively. Compound **7** was recrystallized from hexane to give yellow prisms: mp 134–135 °C; IR 1740, 1700 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.76, 3.99 (each s, 3 H), 5.33 (s, 1 H), 7.2–7.9 (m, 6 H). Anal. Calcd for $C_{19}H_{14}O_4$: C, 74.45; H, 4.60. Found: C, 74.25; H, 4.59. Recrystallization of **9** from methanol afforded pale yellow needles: mp 168–169 °C; IR (C=O) 1760, 1740 cm^{-1}. Anal. Calcd for $C_{19}H_{14}N_2O_4$: C, 68.25; H, 4.22; N, 8.38. Found: C, 68.07; H, 4.30; N, 8.44.

(8) Dürr, H.; Schrader, L. *Chem. Ber.* **1970**, *103*, 1334.

Thermolysis of 4. A solution of **4** (100 mg) in toluene (3 mL) was refluxed for 4 h. The solvent was evaporated in vacuo, and the residue was chromatographed on silica gel (Wako gel, C-300) with benzene as an eluent to give 48 mg (48%) of **7**.

Hydrolysis of 8. A solution of **8** (100 mg) in a mixture of concentrated hydrochloric acid (1 mL) and ethanol (4 mL) was heated at reflux for 1 h. The reaction mixture was poured into water (100 mL) and extracted with chloroform (2 × 20 mL). The extract was dried over sodium sulfate, and the solvent was evaporated in vacuo to leave the residue which was triturated with ether to give 12 mg (15%) of **3**. The ether filtrate was evaporated, and the residue was recrystallized from methanol to give 19 mg (19%) of unchanged **8**.

Hydrolysis of 9. A solution of **9** (50 mg) in a mixture of concentrated hydrochloric acid (1 mL) and ethanol (4 mL) was heated at reflux for 1 h. The solvent was evaporated in vacuo, and the residue was washed with methanol to give 22 mg (54%) of **3**.

Photolysis of 9. A solution of **9** (100 mg) in benzene (50 mL) was irradiated at room temperature with Pyrex-filtered light from a 100-W, high-pressure mercury lamp for 1 h. The solvent was evaporated in vacuo, and the residue was column chromatographed on silica gel with benzene as an eluent to give white solids, which on recrystallization from ethanol gave 18 mg (16%) of dimethyl (10-phenylphenanthren-9-yl)malonate (**15**): mp 142–144 °C; colorless prisms; IR (C=O) 1740, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.63 (s, 6 H), 5.12 (s, 1 H), 7.2–7.7 (m, 10 H), 8.0–8.2 (m, 1 H), 8.65–8.85 (m, 2 H); mass spectrum, *m/e* (relative intensity) 384 (M^+, 57), 266 (26), 265 ($M^+ - CH_3CO_2H - CH_3CO_2$, 100). Anal. Calcd for $C_{25}H_{20}O_4$: C, 78.11; H, 5.24. Found: C, 78.01; H, 5.33.

Registry No. **1**, 53313-99-8; **3**, 76600-21-0; **4**, 39500-48-6; **7**, 76600-24-3; **8**, 76600-23-2; **9**, 76600-25-4; **15**, 76600-26-5.

Supplementary Material Available: Spectral data on phenanthropyrazoles **8** and **9** (Table II, ^1H and ^{13}C NMR; Table III, mass spectra) (2 pages). Ordering information is given on any current masterhead page.

Selected Reactions of 1,8-Divinylnaphthalene

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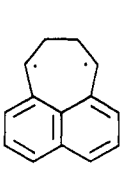
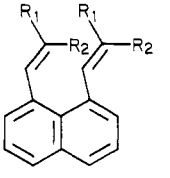
In connection with our work on the chemistry of the 1,8-naphthoquinodimethane biradical (**1**),[1] it was desirable



1



2a, $R_1 = R_2 = H$
b, $R_1 = D$; $R_2 = H$
c, $R_1 = H$; $R_2 = D$

to find a reaction of 1,8-divinylnaphthalene (**2a**) that brought the two vinyl groups together stereospecifically. For accomplishment of this end, it became necessary to look at a series of reactions of **2a** which a priori could bring the vinyl groups together. Once such a reaction was found, it was hoped that its stereospecificity could be ascertained by repeating the reaction on deuterium-labeled **2b** or **2c**,

(1) (a) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216. (b) Watson, C. R., Jr.; Pagni, R. M.; Dodd, J. R.; Bloor, J. E. *Ibid.* **1978**, *98*, 2551 and references cited therein.

0022-3263/81/1946-1931$01.25/0