Synthesis and Electrophilic Substitution of 1-Methyl-, 1,2-Dimethyl-, and 1-Methyl-2-phenyl-2*H*-cyclopenta[*d*]pyridazines[1]

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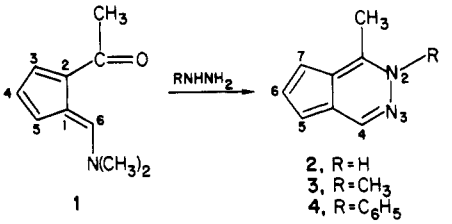
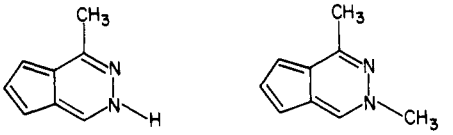
1-Methyl- (2), 1,2-dimethyl- (3), and 1-methyl-2-phenyl-2*H*-cyclopenta[*d*]pyridazines (4) were prepared from 2-acetyl-6-(dimethylamino)fulvene (1) and their structures established with the aid of T_1 NMR and X-ray analysis. The relative chemical shifts of hydrogens adjacent to π-equivalent vs. π-excessive ring nitrogens in such structures were determined. Electrophilic trifluoroacetylation of these was shown to occur at the 5- and 7-positions. The effect of solvent polarity on the long wavelength absorption maxima was examined for 2–4 and their trifluoroacetyl derivatives. The 5-bromo and 5,7-dibromo substitution products of 2–4 were formed by reactions with *N*-bromosuccinimide.

An earlier paper described the synthesis of 2-acetyl-6-(dimethylamino)fulvene (1) and its reactions with primary and secondary amines.[2] These studies were preliminary to the formation of 1-methyl-2*H*-cyclopenta[*d*]-pyridazines **2**–**4** from the reaction of **1** with hydrazine, methylhydrazine, and phenylhydrazine, respectively. The preparation of **2**–**4** and the electrophilic acylation and bromination of these are now reported.



1 **2**, R=H; **3**, R=CH_3; **4**, R=C_6H_5

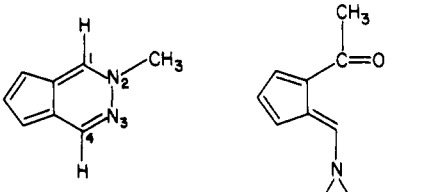
The ^1H NMR spectrum for **2** (sharp singlet for H-4, single peak at δ 12.01 for N–H, triplet for H-6, overlapping doublets centered at δ 6.71 for H-5 and H-7) was interpreted to indicate rapid equilibration between tautomers **2** and **5**, as for the unsubstituted parent compounds.[3]



5 **6**

The reaction of an unsymmetrical hydrazine with **1** could yield either, or both, of two products, e.g., **3** and **6**. The fact that the reactions of **1** with several primary and secondary amines gave very predominantly products from the displacement of the dimethylamino group[2] showed C-6 to be the more reactive site but did not address the question of the relative nucleophilicities of the two nitrogens in methyl- or phenylhydrazine. It was thought that knowledge of the identity of the NMR signals for H-1 and H-4 in the 2-methyl compound **7** might be helpful in distinguishing **3** from **6**. The assignments for **7** were originally based[4] on the somewhat tenuous hypothesis that the π-equivalent nitrogen at position-3 would be more electronegative than the π-excessive nitrogen at position-2, and therefore H-4 would be the less shielded of the two. This reasoning received support from the spectra of 1,3- and 1,5-dimethylpyrazoles,[5] and the assignments for **7** correlated well with the spectra of a variety of 5, 7, 5,7, and 5,6,7 substitution derivatives.[6-8] Subsequently, the spin–lattice relaxation (T_1) NMR spectra for **7**[9] clearly showed different relative relaxation rates (0.24 and 0.19 s^{-1}) for the H-1 and H-4 peaks with the more shielded one (δ 8.50 vs. δ 8.80) having the faster rate (adjacent to N–CH_3) in agreement with the preliminary assignment.

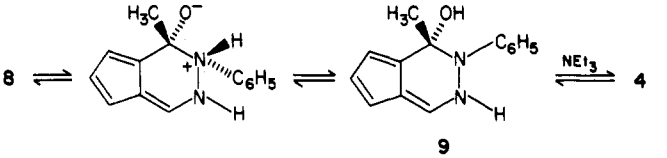
A single dimethyl product (91%) was obtained from the reaction of **1** with methylhydrazine. The NMR signal for the six-ring hydrogen was at δ 8.54, midway between the values for H-1 and H-4 for **7**. Evidence for **3** rather than



7 **8**

6 as the structure of the product was provided by the T_1 spectrum.[9] This exhibited a slow relaxation rate for the six-ring hydrogen (0.16 s^{-1} compared to 0.18–0.22 s^{-1} for the five-ring hydrogens). Final proof of structure **3** was obtained from an X-ray structure determination of a derivative (vide infra).[10]

Scheme I



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Treatment of **1** with excess phenylhydrazine gave 71% of the same compound obtained (72%) from the cyclization of **8**.[2] Accordingly, this product was assigned structure **4** with the ^1H NMR peak at δ 8.79 for H-4. The requirement

(1) Taken in part from the Ph.D. Thesis of R. P. Ko, University of Washington, 1981.
(2) Anderson, A. G., Jr.; Ko, R. P. *J. Org. Chem.* **1982**, *47*, 1971–1974.
(3) Anderson, A. G., Jr.; Forkey, D. M. *J. Am. Chem. Soc.* **1969**, *91*, 924–927.
(4) D. M. Forkey, Ph.D. Thesis, University of Washington, 1970.
(5) Habraken, C. L.; Moore, J. A. *J. Org. Chem.* **1965**, *30*, 1892.
(6) Anderson, A. G., Jr.; Forkey, D. M.; Grina, L. D. *J. Org. Chem.* **1978**, *43*, 1602–1603. Anderson, A. G., Jr.; Grina, L. D.; Forkey, D. M. *Ibid.* **1978**, *43*, 664–667.
(7) Anderson, A. G., Jr.; Forkey, D. M.; Grina, L. D. *J. Org. Chem.* **1972**, *37*, 3499–3503.
(8) Anderson, A. G., Jr.; Forkey, D. M.; Grina, L. D.; Hickernell, L. W.; Tober, T.; Wills, M. T. *J. Org. Chem.* **1975**, *40*, 2196–2200.
(9) This experiment was performed by Professors L. D. Colebrook and L. D. Hall at the University of British Columbia. They will report the details elsewhere. For a description and other applications of the method, cf. Colebrook, L. D.; Hall, L. D. *Can. J. Chem.* **1980**, *58*, 2016.
(10) Stenkamp, R. E.; Ko, R. P. *Acta Crystallogr., Sect. B.* **1982**, *B38*, 994–996.

0022-3263/84/1949-4769$01.50/0

Table I. ^{1}H NMR Spectral Data of Compounds 10–14

compd	1-CH_3	2-R	H-4	H-5	H-6	H-7
10[a]	s, 2.75[b]		s, 9.47		m, 7.75	d, 6.82
11[c]	s, 3.03	s, 4.42[d]	s, 9.47		m, 7.68	d, 6.92
12[c]	s, 3.31	s, 4.39[d]	s, 8.93	d, 6.75	m, 7.90	
13[a]	s, 2.70	m, 7.67[e]	s, 9.63		m, 7.80	d, 7.02
14[c]	s, 3.00	m, 7.70[e]	s, 9.02	d, 6.87	m, 8.00	

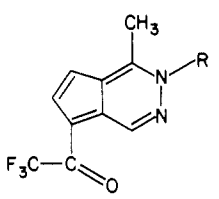
[a] CD_3CN solvent. [b] δ. [c] Acetone-d_6 solvent. [d] CH_3. [e] C_6H_5.

of base to effect the cyclization of 8 to 4 suggested the intermediacy of 9 (Scheme I).

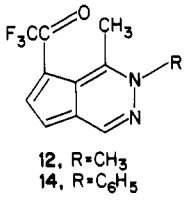
The electronic spectra of 2–4 closely resembled that of 7[3] in shape, wavelength region, E_{max}, and the occurrence of a hypsochromic shift of the long wavelength transitions with an increase in solvent polarity (vide infra). Compounds 2–4 were unstable in air and were kept and handled under an inert atmosphere.

The ^{1}H NMR spectrum of the conjugate acid of 7 had shown the presence of the 5- and 7-protonated isomers in a ratio of 1:2.7[3] and, subsequently, electrophilic trifluoroacetylation was found to give the 5- and 7-derivatives in a ratio of 1:2.57.[7] The preparations of 2–4 provided the opportunity to examine the effect of a 1-methyl group along with the comparison of different substituents on the 2-nitrogen in representative electrophilic substitution reactions.

Treatment of 2 with 1 equiv of trifluoroacetic anhydride formed the 5-trifluoroacetyl derivative 10 in 71.2% yield.[11]



10, R=H
11, R=CH_3
13, R=C_6H_5



12, R=CH_3
14, R=C_6H_5

The 7-isomer was not found. The ^{1}H NMR assignments are given in Table I. As was found with the products from 7,[7] the multiplet for H-6 indicated coupling with the CF_3 group.

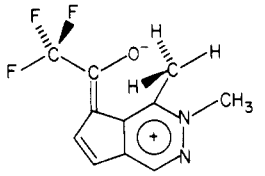
Trifluoroacetylation of 3 gave the 5 and 7 derivatives 11 and 12 in 51% and 24.8% yields, respectively, in approximately the reverse ratio at that found for 7. The structure of 11 and, therefore, indirectly, of 12, was establihsed by X-ray analysis.[10] The analogous products 13 and 14 were obtained from 4 in similar proportions (45.5% and 32.9%). The ^{1}H NMR assignments are listed in Table I.

For azulene, cyclopenta[c]thiapyran, 2-methyl-2-pyrindene, and a number of their derivatives formed by electrophilic substitution, it was found that the shifts in the long wavelength transitions of the electronic spectra with changes in solvent polarity were in agreement with the proposed existence and stabilization or destabilization by the solvent of excited states with dipoles reduced or reversed relative to those of the ground states of these compounds.[12] This effect was examined with 3 and its trifluoroacetyl derivatives 11 and 12. An increase in solvent polarity caused a hypsochromic shift with 3, a bathochromic shift with 11, and no shift with 12. These observations are indicative of a reduction or reversal of the dipole on excitation for 3, an enhancement of the dipole on excitation for 11, and a cancellation of the effects with 3 and 11 for 12. Molecular models showed rather severe hindrance to solvation of the negative charge in the less crowded dipolar conformer of 12 (15). Analogous results were obtained with 4 and its corresponding derivatives 13 and 14 and for 2 and its derivative 10. The data are summarized in Table II.

Table II. Effect of Solvent Polarity on Long Wavelength Transitions of 2–4 and 10–14

solvent	2	10	3	11	12	4	13	14
hexanes[a]	387[b]	395	388	360	394	393.5	365	398
methanol	375	381	378	374	394	385	376	398

[a] Mixture of n-hexane and methylcyclopentane. [b] λ_{max} nm.



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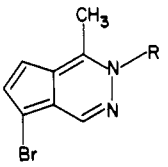
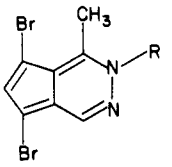
Reaction of 2 with 1 equiv of N-bromosuccinimide (NBS) gave monobromo (27.4%) and dibromo (13.4%) products which were formulated as 16 and 17 (along with their N–H tautomers), respectively. The identity of the former, which was less stable and not obtained analytically pure, was based on mass spectral and NMR analyses with the pattern of the latter spectrum (doublets for H-7 and H-6, singlet H-4; cf. Table I) corresponding to those of the 5-substituted derivatives of 3 and 4. This also fits with the hypothesis that the introduction of a substituent on the 7-position of a 5-substituted 1-methyl compound will occur more slowly than the introduction of a substituent on the 5-position of a 7-substituted 1-methyl compound.



16, R=H
18, R=CH_3
20, R=C_6H_5



17, R=H
19, R=CH_3
21, R=C_6H_5

Similarly, from 3 and 1 equiv of NBS were obtained the 5-bromo (18) (35%) and 5,7-dibromo (19) (17.5%) derivatives, and a comparable result (59.3% of 20 and 7.7% of 21) was found with 4.

A qualitative reaction of 3 with tetracyanoethene afforded a product (56.5%) which appeared (NMR, mass spectrum) to contain the δ-tricyanoethenyl substituent in the 5-position.

Experimental Section

All chemicals were reagent grade. Petroleum ether was 35–65 °C unless otherwise specified. THF was distilled from sodium benzophenone ketyl immediately prior to use. DMF was distilled from 4-Å molecular sieves and stored over these. Liquid amines and trifluoroacetic anhydride were distilled from CaH_2 or CaO immediately prior to use. All reactions were conducted under an inert atmosphere of O_2-free Ar or N_2. Melting points below 180 °C were obtained in sealed capillary tubes with a Thomas-Hoover apparatus, and those above 180 °C were taken on a Mel-Temp apparatus; all are uncorrected.

(11) The existence of 10 as a mixture of this structure and the 3-H tautomer, expecially in solution, is recognized. Structure 10 provides some additional resonance stabilization of the dipolar form.

(12) Anderson, A. G., Jr.; Steckler, B. M. *J. Am. Chem. Soc.* **1959**, *81*, 4941–4946. Anderson, A. G., Jr.; Harrison, W. F.; Anderson, R. G. *Ibid.* **1963**, *85*, 3448–3553. Anderson, A. G., Jr.; Forkey, D. M. *Ibid.* **1969**, *91*, 924–927. Anderson, A. G., Jr.; Forkey, D. M.; Grina, L. D. *J. Org. Chem.* **1972**, *37*, 3499–3503.

Spectrophotometric grade hexanes (hexane and methylcyclopentane mixture) or methanol (Mallinokrodt, Inc.) were used in the recording of ultraviolet–visible spectra on a Cary Model 14 recording spectrophotometer with 1-cm quartz cells. IR spectra were obtained with a Beckman Model Acculab 4 spectrometer using NaCl prisms. ^{1}H NMR spectra were measured on a Varian Model EM 360L or a Varian CFT-20 spectrometer. T_1 spin–lattice relaxation spectra were recorded by Prof. L. D. Colebrook on a HA-270 spectrometer.[9] Analytical TLC plates were coated with ca. 0.2 mm of Merck 200-mesh silica gel. Preparative TLC plates had a coating of 2 mm of Merck 60 F_{254} silica gel. UV light or I_2 vapor was used to locate spots on dried plates. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

1-Methyl-2*H*-cyclopenta[*d*]pyridazine (2). A mixture of 0.83 g (5 mmol) of 1 and 2.5 g (50 mmol) of 99–100% hydrazine hydrate in 50 mL of absolute ethanol was refluxed for 10 h under N_2. Removal (reduced pressure at 40 °C) of the solvent and excess reagent from the dried (Na_2SO_4) solution and recrystallization of the yellow orange residue from 40–60 °C petroleum ether gave 0.4 g (61%) of **2** as yellow crystals: mp 113–114 °C;[13] UV ($HCCl_3$) (log ϵ) 247.5 (3.97), 271.5 (sh, 3.64), 317 nm (sh, 3.19); ^{1}H NMR (CCl_4) δ 8.50 (s, 1, H-4), 7.24 (apparent t, 1, H-6, $J_{6,5}$ = 4.0 Hz, $J_{6,7}$ = 4.2 Hz), 6.72 (overlapping d, 2, H-5 and H-7), 2.60 (s, 3, CH_3). Anal. Calcd for $C_8H_8N_2$: C, 72.70; H, 6.10. Found: C, 72.92; H, 6.26.

1,2-Dimethyl-2*H*-cyclopenta[*d*]pyridazine (3). A solution of 0.163 g (1 mmol) of 1 and 0.27 mL (0.23 g, 5 mmol) of methylhydrazine in 10 mL of dry THF was stirred at room temperature for 2 h at which time TLC analysis (1:3 EtOAc–petroleum ether) showed a single product. Removal of the solvent (rotary evaporator) and recrystallization of the dark yellow residue from petroleum ether gave 0.1335 g (91%) of **3** as yellow crystals: mp 102–103 °C; UV (hexanes) (log ϵ) 247 (4.59), 267 (sh, 4.35), 310 (3.83), 317 (3.81), 323.5 (3.77), 388 nm (3.24); UV (CH_3OH) (log ϵ) 203 (4.31), 247 (4.65), 267 (sh 4.31), 313 (3.86), 378 (317); ^{1}H NMR (acetone-d_6) δ 2.84 (s, 3, 1-CH_3), 4.15 (s, 3, NCH_3), 6.61 (dd, 1, H-5, $J_{5,6}$ = 4.0 Hz, $J_{5,7}$ = 2.0 Hz), 6.83 (dd, 1, H-7, $J_{7,6}$ = 4.2 Hz, $J_{7,5}$ = 2.0 Hz), 7.16 (apparent t, 1, H-6, $J_{6,5}$ = 4.0 Hz, $J_{6,7}$ = 4.2 Hz), 8.54 (s, 1, H-4); IR ($CHCl_3$), 1590 cm^{-1} (C=C). Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 74.03; H, 6.81; N, 19.05.

1-Methyl-2-phenyl-2*H*-cyclopenta[*d*]pyridazine (4). After a mixture of 0.408 g (2.5 mmol) of 1, 0.5 mL (3.0 mmol) of phenylhydrazine, and 20 mL of absolute ethanol had been heated under reflux for 9 h, a TLC analysis showed no 1 present. The addition of 30 mL of H_2O followed by cooling to −10 °C for 1 h with stirring precipitated 0.398 g (76.5%) of crude **4**, mp 103–108 °C. Recrystallization from petroleum ether gave 0.338 g (65%) of golden-yellow needles, mp 108–109 °C. Sublimation at 70 °C and 15 torr afforded an analytical sample: mp 112–113 °C; UV (hexanes) (log ϵ) 247.5 (4.33), 276.5 (4.19), 311 (sh, 3.66), 319 (sh, 3.64), 324.5 (3.60), 393.5 nm (3.16); UV (CH_3OH) (log ϵ) 203.5 (4.35), 248 (4.49), 272 (sh, 4.26), 314 (3.78), 385 nm (3.16); ^{1}H NMR (acetone-d_6) δ 2.63 (s, 1, 1-CH_3), 6.80 (dd, 1, H-5, $J_{5,6}$ = 4.0 Hz, $J_{5,7}$ = 2.0 Hz), 7.20 (dd, 1, H-7, $J_{7,5}$ = 2.0 Hz, $J_{7,6}$ = 4.2 Hz), 7.36 (apparent t, 1, H-6, $J_{6,5}$ = 4.0 Hz, $J_{6,7}$ = 4.2 Hz), 7.67 (m, 5, Ar), 8.79 (s 1, H-4); IR ($CHCl_3$) 1590 cm^{-1} (C=C). Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81. Found: C, 80.56; H, 5.84.

5-(Trifluoroacetyl)-1-methyl-2*H*-cyclopenta[*d*]pyridazine (10). To 0.119 g (0.9 mmol) of **2** and 0.25 mL (1.8 mmol) of triethylamine dissolved in 10 mL of cold (0 °C) CH_2Cl_2 was added 0.13 mL (0.9 mmol) of trifluoroacetic anhydride, and the mixture was stirred for 24 h. A TLC analysis (4:5 EtOAc–petroleum ether) showed one major product. Chromatography of the concentrate (3 mL) of the product mixture on 20 × 20 cm preparative plate with EtOAc–petroleum ether (4:5) afforded three UV-absorbing bands. From the second, major band (R_f 0.58) was obtained 0.173 g of brown crystals which yielded 0.146 g (71.2%) of **10** as dark yellow crystals: mp 188–190 °C after recrystallization from CH_2Cl_2; UV (hexanes) (log ϵ) 207.5 (4.02), 246.5 (4.16), 296 (3.80), 321 (3.75), and 395 nm (3.77); UV (CH_3OH) 209 (4.34), 244 (4.32), 256 (4.32), 294 (4.16), 320 (3.93), 381 (4.15); ^{1}H NMR (Table I); IR (CH_2Cl_2) 3380 (NH), 1657 (C=O), 1610 cm^{-1} (C=C). Anal. Calcd for $C_{10}H_7N_2OF_3$: C, 52.64; H, 3.09; N, 12.28. Found: C, 52.44; H, 3.02; N, 12.17.

5-(Trifluoroacetyl)- and 7-(Trifluoroacetyl)-1,2-dimethyl-2*H*-cyclopenta[*d*]pyridazine (11 and 12). To a stirred solution of 0.117 g (0.8 mmol) of **3** and 0.22 mL (1.7 mmol) of triethylamine in 10 mL of CH_2Cl_2 at 0 °C was added dropwise 0.113 mL (0.8 mmol) of trifluoroacetic anhydride. The mixture was allowed to come to room temperature and was stirred for an additional 24 h at which time the TLC analysis (5:1 EtOAc–petroleum ether) showed two major products. After 24 h at −25 °C, the separated (filtration) pale reddish-yellow plates were washed with 2 mL of H_2O and set aside (47 mg). Chromatography of the concentrate (3 mL) from the organic filtrate with 5:1 EtOAc–petroleum ether on a 20 × 20 cm preparative plate gave two UV-absorbing bands. A CH_2Cl_2 extract of the first yielded a yellow solid which, after recrystallization from petroleum ether, amounted to 48 mg (24%) of **12** as thin yellow crystals: mp 127–128.5 °C; UV (hexanes) (log ϵ) 209 (4.25), 245.5 (4.42), 268 (sh, 4.16), 284 (3.95), 295 (3.90), 331 (3.99), 394 nm (4.07); UV (CH_3OH) (log ϵ) 221.5 (4.16), 248 (4.17), 267 (sh, 3.99), 294 (3.71), 326 (3.78), 394 nm (4.04); ^{1}H NMR (Table I); IR (CH_2Cl_2) 1665 (C=O), 1580 cm^{-1} (C=C). Anal. Calcd for $C_{11}H_9N_2OF_3$: C, 54.55; H, 3.75; N, 11.57. Found: C, 54.71; H, 3.75; N, 11.59.

From the second band was obtained in the same manner 52 mg of yellow crystals which were combined with the reddish yellow plates isolated earlier. Recrystallization from CH_2Cl_2 gave 99 mg (51.1%) of **11** as pale yellow plates: mp 199–200.5 °C; UV (hexanes) (log ϵ) 207 (4.18), 245 (4.02), 257 (sh, 3.97), 265 (3.99), 298.5 (4.21), 360 nm (3.86); UV (CH_3OH) (log ϵ) 210 (4.29), 245.5 (4.07), 264 (4.14), 297 (4.20), 374 nm (4.10); ^{1}H NMR (Table I); IR (CH_2Cl_2) 1650 (C=O), 1560 cm^{-1} (C=O). Anal. Calcd for $C_{11}H_9N_2OF_3$: C, 54.55; H, 3.75; N, 11.57. Found: C, 54.30; H, 3.82; N, 11.31.

5-(Trifluoroacetyl)- and 7-(Trifluoroacetyl)-1-methyl-2-phenyl-2*H*-cyclopenta[*d*]pyridazine (13 and 14). To a solution of 125 mg (0.6 mmol) of **4** and 0.17 mL (1.2 mmol) of triethylamine in 10 mL of dry CH_2Cl_2 t 0 °C was added 0.85 mL (0.6 mmol) of trifluoroacetic anhydride dropwise with stirring. The mixture was allowed to come to room temperature, and stirring was continued for 24 h at which time at TLC analysis (1:8 EtOAc–petroleum ether) showed two major products. Chromatography of the concentrate (ca. 3 mL) on a 20 × 20 cm preparative plate with the same solvent separated three UV absorbing bands, the first of which contained only a trace of material. The second band (R_f 0.43) yielded 60 mg (32.9%) of **14** as yellow crystals: mp 120–121.5 °C after recrystallization from petroleum ether; UV (hexanes) (log ϵ) 204 (4.43), 251.5 (4.46), 286 (sh, 4.02), 297 (4.03), 331 (4.00), 398 nm (4.09); UV (CH_3OH) (Log ϵ) 209 (4.46), 251 (4.48), 297 (sh, 4.00), 398 nm (4.23); ^{1}H NMR (Table I); IR (CH_2Cl_2) 1657 (C=O), 1605 cm^{-1} (C=C). Anal. Calcd for $C_{16}H_{11}N_2OF_3$: C, 63.16; H, 3.64; N, 9.21. Found: C, 63.36; H, 3.83; N, 9.13.

The third band (R_f 0.21) yielded 83 mg (45.5%) of **13** as pale yellow crystals: mp 170–171.5 °C after precipitation from CH_2Cl_2 by the addition of petroleum ether; UV (hexanes) (log ϵ) 203 (4.09), 245 (3.85), 257 (3.85), 265 (sh, 3.84), 300 (4.11), 365 nm (3.73); UV (CH_3OH) (log ϵ) 208 (4.58), 234 (sh, 4.24), 247 (sh, 4.15), 263 (4.20), 301 (4.23), 376 nm (4.05); ^{1}H NMR (Table I); IR (CH_2Cl_2) 1657 (C=O), 1600 (C=C) cm^{-1}. Anal. Calcd for $C_{16}H_{11}N_2OF_3$: C, 63.16; H, 3.64; N, 9.21. Found: C, 63.05; H, 3.79; N, 9.18.

5-Bromo- and 5,7-Dibromo-1-methyl-2*H*-cyclopenta[*d*]-pyridazine (16 and 17). To a stirred solution of 119 mg (0.9 mmol) of **2** in 10 mL of dry CH_2Cl_2 was added dropwise 160.2 mg (0.9 mmol) of *N*-bromosuccinimide dissolved in 15 mL of dry CH_2Cl_2. The mixture was stirred overnight at which time a TLC analysis (2:5 EtOAc–petroleum ether) showed two major products. Chromotography of the concentrate (ca. 3 mL) on a preparative TLC plate (20 × 20 cm) with 2:5 and then 1:6 EtOAc–petroleum ether separated four UV-absorbing bands. The small amount of material from the first band was not identified, and a trace of **2** was obtained from the fourth band. Extraction of the second band with CH_2Cl_2 and precipitation of the product by the careful addition of petroleum ether to the concentrated CH_2Cl_2 solution gave 35 mg (13.4%) of **16** as yellow crystals: mp 136–137 °C; UV

(13) In agreement with that reported by T. Fujisawa, Sagami Chemical Research Center, personal communication, 1976, for a compound thought to be **2**.

(ether) (log ϵ) 207 (4.05), 252 (4.08), 267 (4.06), 318 (3.48), 328 (sh, 3.42), 400 nm (3.76); ^{1}H NMR (acetone-d_6) δ 2.93 (s, 3, 1-CH_3), 7.05 (s, 1, H-6), 8.53 (s, 1, H-4); IR ($CHCl_3$) 3410 (NH), 1612 cm^{-1} (C=C); mass spectrum, calcd for $C_8H_6N_2Br_2$ m/e 288.2 (M^+), 290.2 ($M^+ + 2$), 292.2 ($M^+ + 4$); found, m/e 288.0 (M^+), 289.9 ($M^+ + 2$), 292.2 ($M^+ + 4$). Anal. Calcd for $C_8H_6N_2Br_2$: C, 33.14; H, 2.09; N, 9.66. Found: C, 33.25; H, 2.21; N, 9.69.

The same procedure yielded 52 mg (27.4%) of somewhat unstable yellow crystals, mp 97.98 °C dec, which were not obtained analytically pure, from the third band. The product was spectrally characterized as **15**: UV (ether) (log ϵ) 206.2 (4.07), 248 (4.29), 264 (4.15), 312.5 (3.60), 325 (sh, 3.54), 3.90 nm (2.93); ^{1}H NMR (CD_3CN) δ 2.67 (s, 3, 1-CH_3), 6.77 (d, 1, H-7, J = 4.0 Hz), 7.09 (d, 1, H-6, J = 4.0 Hz), 8.50 (s, 1, H-4); IR ($CHCl_3$) 3400 (NH), 1612 cm^{-1} (C=C); mass spectrum, calcd lcd for $C_8H_7N_2Br$ m/e 210.2 (M^+), 212.2 ($M^+ + 2$); found, m/e 210.0 (M^+), 212.1 ($M^+ + 2$).

5-Bromo- and 5,7-Dibromo-1,2-dimethyl-2*H*-cyclopenta[*d*]pyridazine (18 and 19). To a magnetically stirred solution of 117 mg (0.8 mmol) of **3** in 10 mL of dry CH_2Cl_2 was added dropwise 142.4 mg (0.8 mmol) of *N*-bromosuccinimide in 15 mL of CH_2Cl_2. A TLC test (petroleum ether–CH_2Cl_2 (2:1) after 24 h showed the presence of two major products. Chromatography of the concentrated (ca. 3 mL) reaction mixture on a preparative TLC plate (20 × 20 cm) with petroleum ether–CH_2Cl_2 (2:1) separated four bands. The material from the first band was not identified and a small amount of **3** was obtained from the fourth band. The second band (R_f 0.35) afforded 51 mg of crude **18** as a yellow-orange solid. Recrystallization from petroleum ether gave 42.5 mg (17.5%) of **18** as yellow crystals: mp 132–133 °C; UV (ether) (log ϵ) 208 (4.00), 257 (4.13), 272 (4.11), 325 (3.54), 336 (sh, 3.51), 400 nm (2.88); ^{1}H NMR (CD_3CN) δ 3.01 (s, 3, 1-CH_3), 4.05 (s, 3, N-CH_3), 7.09 (s, 1, H-6), 8.46 (s, 1, H-4). Anal. Calcd for $C_9H_8N_2Br_2$: C, 35.56; H, 2.65; N, 9.22. Found: C, 35.58; H, 2.63; N, 9.17.

The third band (R_f 0.13) yielded 89 mg of a brownish yellow solid. Recrystallization from petroleum ether gave 63 mg (35%) of **17** as yellow crystals: mp 108–109.5 °C; UV (ether) (log ϵ) 208 (4.27), 249 (4.51), 272 (4.35), 320 (3.86), 330 (sh, 3.83), 390 nm (3.13); ^{1}H NMR (CD_3CN) δ 2.72 (s, 3, 1-CH_3), 4.06 (s, 3, N-CH_3), 6.82 (d, 1, H-7, J = 4 Hz), 7.05 (d, 1, H-6, J = 4 Hz), 8.46 (s, 1, H-4). Anal. Calcd for $C_9H_9N_2Br$: C, 48.03; H, 4.03; N, 12.45. Found: C, 47.84; H, 4.12; N, 12.42.

5-Bromo- and 5,7-Dibromo-1-methyl-2-phenyl-2*H*-cyclopenta[*d*]pyridazine (20 and 21). In the manner described for the preparation of **17** and **18**, 0.125 g (0.6 mmol) of **4** was treated with 0.1068 g (0.6 mmol) of *N*-bromosuccinimide, and the products were chromatographically separated (1:1 petroleum ether–CH_2Cl_2). Extraction of the second band (R_f 0.66) with CH_2Cl_2 and precipitation by the addition of petroleum ether gave 17 mg (7.7%) of **20** as yellow crystals: mp 125–126 °C dec; UV (ether) (log ϵ) 207 (4.41), 255 (4.42), 280 (4.46), 326 (3.91), 336 (sh, 3.89), 412 nm (3.32); ^{1}H NMR (CD_3CN) δ 2.80 (s, 3, 1-CH_3), 7.20 (s, 1, H-6), 7.55 (m, 5, 2-C_6H_5), 8.59 (s, 1, H-4); mass spectrum, m/e 364.1 (M^+), 365.9 ($M^+ + 2$), 368.0 ($M^+ + 4$). Anal. Calcd for $C_{14}H_{10}N_2Br_2$: C, 45.94; H, 2.75; N, 7.65. Found: C, 45.76; H, 3.04; N, 7.60.

In the same manner from the third band was obtained 102.2 mg (59.3% of **19** as yellow crystals: mp 108–109.5 °C; UV (ether) (log ϵ) 207 (4.38), 249 (4.48), 280 (4.41), 320 (3.92), 331 (sh, 3.89), 396 nm (3.30); ^{1}H NMR (CD_3CN) δ 2.53 (s, 3, 1-CH_3), 6.98 (d, 1, H-7, J = 4 Hz), 7.18 (d, 1, H-6, J = 4 Hz), 7.55 (m, 5, phenyl), 8.61 (s, 1, H-4). Anal. Calcd for $C_{14}H_{11}N_2Br$: C, 58.56; H, 3.86; N, 9.76. Found: C, 58.56; H, 4.03; N, 9.76.

Reaction of 1,2-Dimethyl-2*H*-cyclopenta[*d*]pyridazine (3) with Tetracyanoethene. The addition of a solution of 117 mg (0.8 mmol) of **3** in 5 mL of benzene to 104.6 mg (0.8 mmol) of tetracyanoethene in 10 mL of benzene at the boiling point caused an immediate color change from yellow to dark blue. Dry pyridine (0.13 mL, 1.6 mmol) was added and the mixture heated under reflux for 15 min. The red solid which formed was separated (filtration) and set aside. Chromatography of the concentrated (ca 2 mL) filtrate on a preparative TLC plate (20 × 20 cm) using ethyl acetate–petroleum ether (3:1) as the eluent separated a very small (R_f 0.8) and a larger (R_f 0.3) band. Extraction of the latter with THF and removal of the solvent gave a red solid which was combined with the material separated earlier. Precipitation from a concentrated ethyl acetate solution by the addition of petroleum ether gave 0.112 g (56.5% calculated as a tricyanoethenyl derivative) of product as red crystals not obtained analytically pure, but tentatively identified as the 5-tricyanoethenyl compound: mp 235–236.5 °C; UV (ether) (log ϵ) 256 (3.78), 285 (sh, 3.58), 312 (sh, 3.17), 348 (sh, 3.35), 390 (s, 3.44), 451 (sh, 4.29), 477 nm (4.38); ^{1}H NMR (acetone-d_6) δ 3.05 (s, 3, 1-CH_3), 4.43 (s, 3, N-CH_3), 7.23 (d, 1, H-7, J = 5 Hz), 8.13 (d, 1, H-6, J = 5 Hz), 9.52 (s, 1, H-4); IR ($CHCl_3$) 2220 (C≡N), 1718 (tetrasubstituted C=C), 1610 cm^{-1} (C=C); mass spectrum, m/e 247.0 (M^+).

Registry No. 1, 61857-23-6; **2**, 92671-43-7; **3**, 92671-44-8; **4**, 92671-45-9; 2*H*-**10**, 92671-46-0; 3*H*-**10**, 92671-57-3; **11**, 81323-77-5; **12**, 92671-47-1; **13**, 92671-48-2; **14**, 92671-49-3; **16**, 92671-50-6; **17**, 92671-51-7; **18**, 92671-52-8; **19**, 92671-53-9; **20**, 92671-54-0; **21**, 92671-55-1; H_2NNH_2, 302-01-2; $MeNHNH_2$, 60-34-4; $PhNHNH_2$, 100-63-0; $CF_3C(O)OC(O)CF_3$, 407-25-0; $(NC)_2C=C(CN)_2$, 670-54-2; 1,2-dimethyl-5-(tricyanoethenyl)-2*H*-cyclopenta[*d*]pyridazine, 92671-56-2.