also gave a solvate, mp 76–80 °C.

Anal. Calcd for $C_{18}H_{12}Cl_2N_2O_5S \cdot {}^1/_2C_6H_6$: C, 52.74; H, 3.16; N, 5.85. Found: C, 52.60; H, 3.30; N, 5.57.

***N*-(2,3,4-Trichloro-6-hydroxyphenyl)-*N*-(5-methoxy-2-thienyl)-4-nitrobenzamide (12).** Compound 11 (115 mg, 0.32 mmol) was added to a solution of 37 mg (0.32 mmol) of 2-methoxythiophene in 1.07 g of $CH_2Cl_2$. The reaction mixture was allowed to stand for 4 days at ambient temperature, and the solvent was evaporated. The residue was slurried with a small quantity of MeOH and the slurry was filtered to give 120 mg (80%) of 12. Two recrystallizations from $CH_3CN$ afforded 12, mp 207–209 °C.

Anal. Calcd for $C_{18}H_{11}Cl_3N_2O_5S$: C, 45.64; H, 2.34; N, 5.92. Found: C, 45.62; H, 2.30; N, 5.88.

**(*Z*)-Methyl 3-[4,6-Dichloro-2,3-dihydro-3-(4-nitrobenzoyl)-2-benzoxazolyl]-2-propenate (14).** Compound 1 (315 mg, 0.96 mmol) was added in portions to a solution of 94 mg (0.96 mmol) of 2-methoxyfuran in 2.5 g of $CHCl_3$. The reaction mixture was allowed to stand 1.5 h, and the solvent was evaporated. The residue was triturated with MeOH, and the MeOH was evaporated. The crude 14 weighed 390 mg (96%) and melted at 145–155 °C with decomposition. Recrystallization from acetonitrile gave 14, mp 177–180 °C.

Anal. Calcd for $C_{18}H_{12}Cl_2N_2O_6$: C, 51.08; H, 2.86; N, 6.62. Found: C, 51.08; H, 2.92; N, 6.58.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(1-methyl-1*H*-indol-3-yl)-4-nitrobenzamide (19a).** A mixture of 89 mg (0.68 mmol) of 1-methylindole, 1.6 mL of $CH_2Cl_2$, and 220 mg (0.68 mmol) of 1 was allowed to stand at ambient temperature for 1 day. The reaction mixture was filtered to give 256 mg (83%) of 19a. A similar reaction with benzene as a solvent gave a precipitate of 19a immediately on admixing. The yield was 82%. Recrystallization from $CH_3CN$ gave 19a, mp 248–250 °C.

Anal. Calcd for $C_{22}H_{15}Cl_2N_3O_4$: C, 57.90; H, 3.31; N, 9.21. Found: C, 57.47; H, 3.37; N, 9.13.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(2-methyl-1*H*-indol-3-yl)-4-nitrobenzamide (19b).** An instantaneous reaction took place when 325 mg (1 mmol) of 1 was added to a solution of 131 mg (1 mmol) of 2-methylindole. The reaction mixture turned black, and then an orange precipitate of 19b formed, which when filtered weighed 425 mg (93%), mp 269–273 °C. Dissolution of 19b in hot MeOH, cooling, and addition of water to turbidity gave 19b, which darkens slightly at 265 °C and decomposed at 274–276 °C.

Anal. Calcd for $C_{22}H_{15}Cl_2N_3O_4$: C, 57.90; H, 3.31; N, 9.21. Found: C, 57.80; H, 3.27; N, 9.15.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(1,2-dimethyl-1*H*-indol-3-yl)-4-nitrobenzamide (19c).** Compound 1 (163 mg, 0.50 mmol) was added in small portions to a solution of 73 mg (0.50 mmol) of 1,2-dimethylindole. The surface of 1 turned black as it was added to the solution. Stirring caused immediate dissolution, and the reaction mixture turned light yellow. After a short time (3–5 min) a precipitate formed. The reaction mixture was filtered after it stood for 8 h. The yield of crude 19c was 222 mg (94%). It was recrystallized twice from $CH_3CN$ to give 19c, mp 255–256 °C dec, with slight discoloration occurring at 248 °C.

Anal. Calcd for $C_{23}H_{17}Cl_2N_3O_4$: C, 58.74; H, 3.64. Found: C, 58.63; H, 3.97.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for Grant CHE-84058555. We thank Dr. Mary F. Garbauskas and Carolyn Hejna for the X-ray crystallographic studies on compounds 8, 10, and 14 and Ashraf Chatterjee and Kim Shepherd for the initial work on 1-methyl- and 1,2-dimethylindoles. We also thank Dr. Robert W. White, Senior Advisor, Chemical Abstracts for checking the nomenclature of compounds.

**Supplementary Material Available:** Crystal structure data and ORTEP drawings for 8, 10, and 14 (16 pages). Ordering information is given on any current masthead page.

# Bridgehead Hydrazines. 4. Oxidative and Basic Ring Cleavage of Pyrazolo- and *s*-Triazolo[1,2-*a*]pyridazines

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Selenium dioxide oxidation of 2,2-diethyl-5,8-dihydro-5,8-diphenylpyrazolo[1,2-*a*]pyridazine-1,3-dione (6) resulted in oxidative cleavage of the pyrazole ring. Treatment of 6 and of its *s*-triazolo analogue 5 with lithium diisopropylamide resulted in cleavage of the pyridazine ring and formation of 1-hydrazinobutadiene derivatives. Reasons for the instability of the bicyclic systems are discussed. 2,5,8-Triphenyl-*s*-triazolo[1,2-*a*]pyridazine-1,3-dione was prepared from 5 by allylic bromination and basic dehydrobromination.

Available results[1-3] on the photolysis of 1,2-diacyl-1,2-dihydropropyridazines are highly diversified, as any alteration in the structure caused a complete change in the course of the photolysis. However, one trend can be detected, exhibited by the two pairs **1a–1b**[1,2] and **2a–2b**.[3,4] The unsubstituted derivatives **1a** and **2a** behave mainly as dienic $4\pi$ systems, and their photoreactions do not involve the nitrogens. The diphenyl derivatives **1b** and **2b**, on the other hand, behave as cyclic $6\pi$ systems, and their exclusive initial photoreaction is a conrotatory electrocyclic opening with cleavage of the nitrogen–nitrogen bond. The photolysis of **3a**[3] also fits this pattern, and we were therefore interested in the complementary **3b**. This paper describes some observations made during the synthesis of compound **3b**.

The reported preparation of **1b**[5] involves selenium dioxide oxidation of the corresponding tetrahydro derivative **4**. Accordingly we tried the oxidation of **5** and **6** under the same conditions. The reaction of **5** resulted in decompo-

(1) Altman, L. J.; Semmelhack, M. F.; Hornby, R. B.; Vedenas, J. C. *Chem. Commun.* **1968**, 686.
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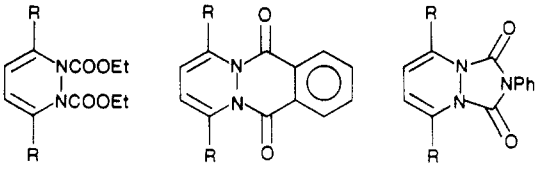
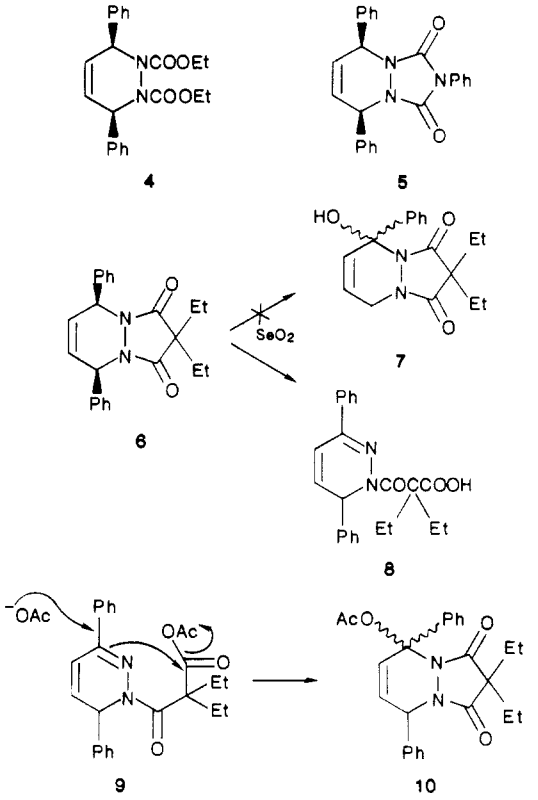


1 2 3

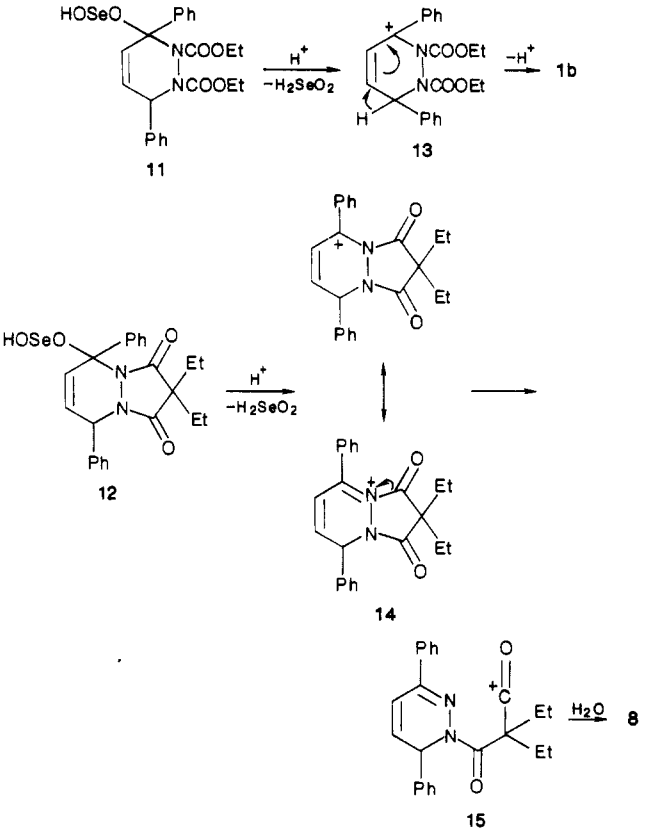
a, R = H; b, R = Ph

sition and that of **6** gave a single product in 72% yield. Analyses (elemental, MS) showed an addition of oxygen atom to **6**: however, the chemical and spectral properties of the product precluded its structural assignment as the allyl alcohol **7** but indicated the carboxylic acid **8**, and structure **8** was confirmed by X-ray analysis. With acetic anhydride **8** undergoes cyclization to **10**, probably via the mixed-anhydride **9**. Attempts to cause basic 1,4 elimination of acetic acid from **9** to **3b** also failed.



4 5 6 7 8 9 10

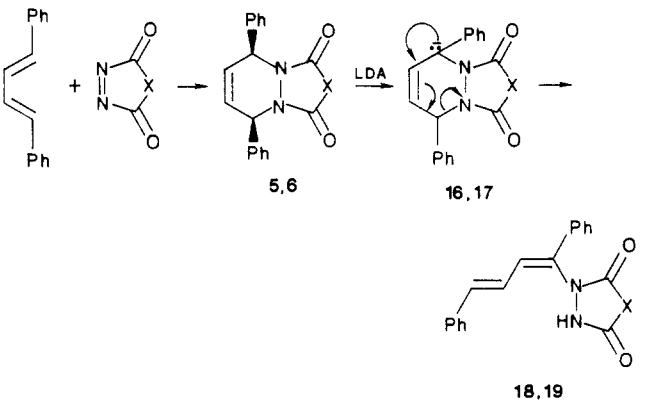
The transformation **6** → **8** presents an unusual mode of allylic selenium dioxide oxidation, particularly when compared to the normal oxidation of **4**. In the last steps[6] the selenium(II) esters **11** and **12** solvolize to the carbocations **13** and **14**. Cation **13** then eliminates a proton to give **1b**, while **14** reacts with water to give **8**, either through direct hydrolysis of the N–CO bond or, more likely, after ring cleavage to the acyl cation **15**. The difference in oxidation course between **4** and **6** originates in the difference in the conformations of the pyridazine rings. In compound **4** it exists[7-9] in a fixed half-chair conformation, with unusually large ($\Delta G$ = 19 kcal/mol) barrier of inversion due to strong nonbonded interaction of the NCO groups in the inversion transition state. Compound **6**, on the other hand, is planar or nearly planar, and that allows the nitrogen atoms in **6** to be trigonal or near-trigonal. Electronic overlap with the



11 13 1b 12 14 15 8

carbocation in **14** is therefore possible and leads to ring opening. In **13**, however, donation of electrons by the nitrogen lone pair would result in rehybridization to give trigonal hydrogen and hence disfavored due to the severe nonbonded interaction.

In order to introduce other leaving groups onto **5** and **6** we have prepared the corresponding carbanions **16** and **17** using lithium diisopropylamide. As these did not react with electrophiles (e.g., PhSeCl) in the expected manner, they were quenched with aqueous HCl and indeed did not revert to **5** and **6** but rearranged to isomers, which were identified as the hydrazino diene derivatives **18** and **19**, respectively. Anion formation thus causes opening of the



5,6 16,17 18,19

**5, 16, 18:** X = NPh
**6, 17, 19:** X = $CEt_2$

left-hand ring, while cation formation opens the right-hand one. The sequence of Diels–Alder reaction with azo dienophile followed by treatment of the adducts with base constitutes a useful method of transforming dienes to hydrazino dienes with retention of the diene stereochemistry.

The synthesis of **3b** was finally accomplished by allylic bromination of **5** using *N*-bromosuccinimide followed by

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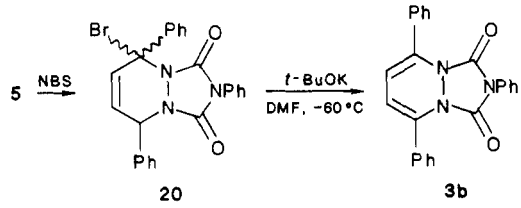


1,4-dihydrobromination with potassium *tert*-butoxide at −60 °C. As expected, it was orange ($\lambda_{max}$ = 400 nm), and its two vinylic hydrogens appears as a singlet (δ 5.51). Compound **3b** was very sensitive to light, and study of its photolysis, which is very complex, will be reported separately.

## Experimental Section

Melting points were taken on a Thomas-Hoover capillary apparatus. UV spectra (in EtOH) were recorded on a Kontron Uvikon 860 spectrophotometer and IR (Nujol mulls) on a Perkin-Elmer 157 spectrophotometer. NMR spectra (in $CDCl_3$) were taken on a Bruker WH-300 instrument and mass spectra on a Varian MAT-311 instrument.

**5,8-Dihydro-2,5,8-triphenyl-*s*-triazolo[1,2-*a*]pyridazine-1,3-dione (5).** A solution of 4-phenyltriazoline-3,5-dione (5.25 g, 30 mol) in acetone (40 mL) was added dropwise to a stirred cooled (0 °C) solution of (*E*,*E*)-1,4-diphenylbutadiene in 150 mL of acetone. After stirring at room temperature for 90 min, the solution was evaporated and the residue crystallized from ethyl acetate to give 10.85 g (95%) of **5**: mp 161–162 °C; IR 1770, 1730, 1705 $cm^{-1}$ (C=O); NMR δ 7.24–7.56 (m, 15 H), 6.00 (d, *J* = 1.3 Hz, 2 H), 5.55 (d, 2 H); mass spectrum, *m/e* (relative intensity) 381 ($M^+$, 18), 206 (78), 191 (15), 128 (35), 119 (24), 115 (36), 90 (100), 77 (31). Anal. Calcd for $C_{24}H_{19}N_3O_2$: C, 75.57; H, 5.02; N, 11.02. Found: C, 75.86; H, 4.96; N, 11.01.

**3-(3,6-Diphenyl-1,6-dihydro-1-pyridazyl)-3-oxo-2,2-diethylpropionic Acid (8).** A solution of **6**[10] (1.09 g, 3 mmol) and selenium dioxide (0.9 g, 8 mmol) in acetic acid (50 mL) was refluxed for 4 h. Precipitated selenium was filtered off, and the filtrate was poured into water (150 mL). The precipitate formed was collected and crystallized from ethyl acetate to give **8** as light yellow crystals: mp 192 °C; 0.81 g (72%); UV 346 nm (ε 9000), 243 (26 000); IR 1700, 1660 $cm^{-1}$ (C=O); NMR δ 7.70–7.24 (m, 10 H), 6.58 (d, *J* = 9.8 Hz, 1 H), 6.44 (dd, 1 H), 6.20 (d, *J* = 5.8 Hz, 1 H), 2.10–1.95 (m, 4 H), 0.60 (t, *J* = 7.5 Hz 3 H), 0.40 (t, *J* = 7.5 Hz, 3 H); mass spectrum, *m/e* (relative intensity) 376 ($M^+$, 9), 233 (100), 204 (9), 203 (8), 157 (86), 115 (9), 102 (58), 77 (11), 69 (14). Anal. Calcd for $C_{23}H_{24}N_2O_3$: C, 73.38; H, 6.43; N, 7.44. Found: C, 73.55; H, 6.46; N, 7.26.

**5-Acetoxy-2,2-diethyl-5,8-diphenyl-5,8-dihydropyrazolo[1,2-*a*]pyridazine (10).** A solution of **8** (1 g) in acetic anhydride (20 mL) was refluxed for 5 h, filtered hot, and poured into water (50 mL). The oil that separated solidified on cooling and was crystallized from ethanol to give **10**: 0.47 g (42%); mp 158–160 °C; IR 1725, 1680 $cm^{-1}$ (C=O); NMR δ 7.90–7.30 (m, 10 H), 6.02 (d, *J* = 2 Hz, 1 H), 5.63 (dd, 1 H), 5.45 (d, *J* = 7 Hz), 2.08 (s, 3 H), 1.91–1.82 (m, 4 H), 0.95 (t, *J* = 7.4 Hz, 3 H), 0.92 (t, *J* = 7.4 Hz, 3 H); mass spectrum, *m/e* (relative intensity) 418 ($m^+$, 36), 359 (56), 233 (100), 219 (23), 174 (27), 132 (48), 102 (24), 97 (68), 83 (46), 77 (23), 71 (30), 69 (54). Anal. Calcd for $C_{25}H_{26}N_2O_4$: C, 71.75; H, 6.26; N, 6.69. Found: C, 71.98; H, 6.12; N, 6.67.

**(*Z*,*E*)-1-(4-Phenyl-3,5-dioxo-1-*s*-triazolidinyl)-1,4-diphenylbutadiene (18).** A solution of diisopropylamine (0.62 g, 6.2 mmol) in dry tetrahydrofuran (70 mL) was cooled to −70 °C and butyllithium (3.6 mL of 1.55 M solution in hexane, 5.6 mmol) was added. The solution was stirred at −70 °C under argon atmosphere for 20 min, and **5** (1.53 g, 4 mmol) was added. After it was stirred for 30 min in the cold, the dark brown solution was allowed to reach room temperature (ca. 2.5 h) and poured into 2% aqueous HCl solution (200 mL). The mixture was extracted four times with ethyl acetate and the extract washed with water and dried. Evaporation and crystallization from benzene gave **18**: 1.24 g (81%); mp 160–161 °C; UV 327 nm (ε 30 700); IR 1765, 1690 $cm^{-1}$ (C=O); NMR δ 7.6–7.22 (m, 15 H), 7.05 (dd, 1 H), 6.80 (d, *J* = 15.3 Hz, 1 H), 6.75 (d, *J* = 10.9 Hz); mass spectrum, *m/e* (relative intensity) 381 ($M^+$, 100), 219 (76), 204 (20), 167 (18), 119 (15), 115 (42), 91 (17), 78 (39), 77 (23). Anal. Calcd for $C_{24}H_{19}N_3O_2$: C, 75.57; H, 5.02; N, 11.02. Found: C, 75.76; H, 5.24; N, 10.70.

**(*Z*,*E*)-1-(4,4-Diethyl-3,5-dioxo-1-pyrazolidinyl)-1,4-diphenylbutadiene (19).** A solution of diisopropylamine (1.5 mL) in dry tetrahydrofuran (150 mL) was cooled to −70 °C under argon atmosphere, and butyllithium (6.23 mL of 1.55 M solution in hexane) was added. After the mixture was stirred for 20 min at −70 °C compound **6** (2.53 g, 7 mmol) was added. The orange solution was stirred for 3 h in the cold and allowed to reach room temperature. It was poured in 2% HCl solution (350 mL) and extracted four times with ethyl acetate and the extract washed three times with water, dried ($Na_2SO_4$), and evaporated. The oily residue was crystallized from ethyl acetate–hexane to give **19**: 212 mg (84%); mp 168–169 °C; UV (EtOH) 322 nm (ε 19 000); IR 1725, 1670 $cm^{-1}$ (C=O); NMR δ 7.40–7.30 (m, 10 H), 6.90–6.65 (m, 3 H), 1.91 (h, *J* = 7.4 Hz, 4 H), 1.06 (t, 6 H); mass spectrum, *m/e* (relative intensity) 360 ($M^+$, 100), 262 (11), 234 (12), 219 (71), 204 (29), 115 (24), 83 (12), 77 (11), 69 (14). Anal. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.42; H, 7.00; N, 8.02.

**2,5,8-Triphenyl-*s*-triazolo[1,2-*a*]pyridazine-1,3-dione (3b).** A solution of **5** (1.9 g, 5 mmol), *N*-bromosuccinimide (0.89 g, 5 mmol), and benzoyl peroxide (10 mg) in carbon tetrachloride (200 mL) was refluxed under strong illumination for 30 min, cooled (ice bath), filtered, and evaporated under vacuum below 35 °C. The yellow oily residue solidified upon stirring under ether. Filtration afforded 1.42 g (62%) of the bromide **20**; which was used directly in the next step: mp 82–84 °C; NMR δ 7.56–7.24 (m, 15 H), 6.08 (d, *J* = 1.6 Hz, 1 H), 5.55 (d, *J* = 6.8 Hz, 1 H), 5.15 (dd, 1 H).

A solution of 1.38 g (3 mmol) of **20** in dry dimethylformamide (20 mL) was cooled to −60 °C and potassium *tert*-butoxide (0.56 g, 5 mmol) was added. The mixture was stirred at −60 to −55 °C for 2.5 h and then poured into 120 mL of water. After 2 h the precipitate was collected by filtration and crystallized from ethanol to give **3b** [0.48 g (43%)] as yellow-orange crystals: mp 195–196 °C; UV (EtOH) 400 nm (ε 1750); IR 1780, 1710 $cm^{-1}$ (C=O); NMR δ 7.40–7.30 (m, 15 H), 5.51 (s, 2 H); mass spectrum, *m/e* (relative intensity) 379 ($M^+$, 48), 260 (27), 232 (70), 204 (18), 129 (14), 119 (17), 102 (100), 91 (19), 77 (17). Anal. Calcd for $C_{24}H_{17}N_3)_2$: C, 75.98; H, 4.52; N, 11.07. Found: C, 75.85; H, 4.20; N, 10.68.

**X-ray Structure Determinations.** Methods and procedures were described previously.[11,12]

**Registry No. 3b**, 105140-33-8; **5**, 57964-87-1; **6**, 105140-34-9; **8**, 105140-35-0; **10**, 105140-36-1; **18**, 105140-37-2; **19**, 105140-38-3; **20**, 105140-39-4; (*E*),*E*)-PhCH=CHCH=CHPh, 538-81-8; 4-phenyltriazoline-3,5-dione, 4233-33-4.

**Supplementary Material Available:** Complete X-ray data for compound **8**, including molecular structure, crystal data, atomic positional and thermal parameters, and bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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(12) We thank Dr. S. Cohen for his help with these analyses.