Benzyl 4-[((Benzyloxy)carbonyl)methyl]-3,5-dimethylpyrrole-2-carboxylate. Ethyl 4-[(methoxycarbonyl)methyl]-3,5-dimethylpyrrole-2-carboxylate (119.6 g, 0.50 mol) and anhydrous benzyl alcohol (300 mL, distilled at 1 atm from K_2CO_3) were heated to boiling under N_2 (2-L 29/42 heavy-wall Erlenmeyer flask, magnetic stirrer/hot plate) until the solvent condensed at the top of the flask and any H_2O, noted as droplets therein, had been expelled. A fresh solution of Na in anhydrous benzyl alcohol was added in 1-mL portions to the boiling mixture, until a vigorous evolution of vapor ensued. When the reaction had subsided, further portions of catalyst were added periodically, until no further effect was noted and the vapor temperature was again in excess of 200 °C.

The hot mixture was then immediately quenched by being added cautiously to a magnetically stirred mixture of methanol (800 mL), H_2O (550 mL), and acetic acid (10 mL) in a 3-L Erlenmeyer flask. The mixture was chilled on ice and then filtered. The solids were washed with 50% aqueous methanol and then H_2O and dried in air, yield, 173.9 g (92.2%). After recrystallization from absolute ethanol (900 mL) (steam bath to ice bath), the first crop weighed 162.55 g (86.2% overall, or 93.5% recovery): mp 110.0–111.0 °C; ^1H NMR ($CDCl_3$) δ 2.15 (3 H, s), 2.29 (3 H, s), 3.42 (2 H, s), 5.11 (2 H, s), 5.31 (2 H, s), 7.31–7.39 (10 H, m), 9.36 (1 H, br); ^{13}C NMR ($CDCl_3$ at 77.12) δ 171.52 (CH_2CO), 161.65 (2-CO), 136.59 (2-Ar, 1), 136.02 (4-Ar, 1), 131.77 (5), 128.48 and 128.01 (11 C, 10 Ar + 3), 116.85 (2), 114.50 (4), 66.41 (4-Ar CH_2), 65.49 (2-Ar CH_2), 30.18 (CH_2CO), 11.41 (5-CH_3), 10.85 (3-CH_3). Anal. Calcd for $C_{23}H_{23}NO_4$: C, 73.19; H, 6.14; N, 3.71. Found: C, 73.00, H, 6.16, N, 3.65.

Benzyl 4-[(Methoxycarbonyl)methyl]-3,5-dimethylpyrrole-2-carboxylate. Benzyl 4-[(benzyloxycarbonyl)-methyl]-3,5-dimethylpyrrole-2-carboxylate (75.5 g, 0.20 mol) was dissolved in tetrahydrofuran (300 mL, distilled from CaH_2) and added, at room temperature, to a solution of sodium (2 g) in anhydrous methanol (500 mL). The mixture was monitored by TLC (CH_2Cl_2–silica) until the starting material was consumed (ca. 20 min). Acetic acid (50 mL) was added, and the solution was filtered, before removal of solvent in vacuo.

The residue was taken into ethanol (250 mL, 100%) and diluted to opalescence with H_2O (143 mL). After 4 h at room temperature, the solids were filtered off, rinsed with aqueous ethanol (70% and then 50%, v/v) and then H_2O, and dried in air. The first crop yield was 47.73 g (79.2%). A second crop crystallized readily, upon further aqueous dilution of the filtrates, 10.33 g (17.1%): total recovery, 58.1 g (96.3%); overall yield from methyl 3-acetyl-4-oxopentanoate,[51] 66.8%, in successive steps of 75.3%, 92.2%, and 96.3%; mp 95.5–96.5 °C (lit.[26] mp 93–94 °C); ^1H NMR ($CDCl_3$) δ 2.18 (3 H, s), 2.31 (3 H, s), 3.38 (2 H, s), 3.64 (3 H, s), 5.32 (2 H, s), 7.37 (5 H m), 9.63 (H, br); ^{13}C NMR ($CDCl_3$ at 77.19) [of the above second crop, found to be pure] δ 172.23 (CH_2CO), 161.78 (2-CO), 136.63 (Ar, 1), 131.91 (5), 128.51 and 127.91 (6, 5 Ar + 3), 116.82 (2), 114.50 (4), 65.50 (Ar CH_2O), 51.81 (CH_3O), 29.95 (CH_2CO), 11.34 (5-CH_3), 10.84 (3-CH_3).

(52) Methyl 4-acetyl-5-oxohexanoate was prepared from 2,4-pentanedione, methyl acrylate, and catalytic K_2CO_3 in boiling 2-butanone.[53]

(53) Battersby, A. R.; Hunt, E.; McDonald, E.; Paine, J. B. III; Saunders, J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1008.

Acknowledgment. This work was supported by the United States National Institutes of Health (GM 29198) and the Canadian Natural Sciences and Engineering Research Council.

Registry No. **1**, 2199-44-2; **2**, 2199-46-4; **3**, 2199-47-5; **4**, 4758-64-9; **5**, 99017-93-3; **6**, 2386-37-0; **7**, 34549-93-4; **8**, 16200-50-3; **9**, 99017-94-4; **10**, 99017-95-5; **10** (R_2 = Ac), 99018-01-6; **11**, 4989-26-8; **12**, 35011-45-1; **13**, 35030-47-8; **14**, 99017-96-6; **15**, 94827-35-7; **16**, 17266-77-2; **17**, 99017-97-7; A, 67-64-1; B, 78-93-3; D, 96-22-0; E, 108-24-7; G, 106-31-0; PrCOMe, 107-87-9; $EtCO_2COEt$, 123-62-6; MeCOCH(Me)COMe, 815-57-6; MeCOCH(Et)COMe, 1540-34-7; EtCOCH(Me)COEt, 1187-04-8; $Me(CH_2)_3COMe$, 591-78-6; $Me(CH_2)_2COEt$, 589-38-8; EtCOCH(Et)COEt, 55552-65-3; EtCOCH(Me)COMe, 4220-52-4; PrCOCH(Me)COMe, 13152-54-0; PrCOCH(Et)COMe, 34581-50-5; PrCH(Ac)COPr, 94827-34-6; PrCH(Ac)COEt, 99017-98-8; PrCH(Ac)COMe, 1540-35-8; $EtCOCH_2COMe$, 3002-24-2; MeCOCH(Et)COEt, 71703-50-9; $EtOCOCH_2CO_2Et$, 105-53-3; $EtOCOCH(NH_2)CO_2Et$, 6829-40-9; $EtCOCH_2COEt$, 7424-54-6; $EtCO_2Et$, 105-37-3; $MeCOCH(Me)CO(CH_2)_2CO_2Et$, 17266-65-8; $MeCOCH_2CO(CH_2)_2CO_2Et$, 20754-03-4; $Me(CH_2)_3COCH_2COPr$, 13882-02-5; $H_2C{=}CHCO_2Me$, 96-33-3; $MeOCO(CH_2)_2CH(Ac)CO(CH_2)_2CO_2Et$, 99017-99-9; $MeCOCH(Ac)CH_2CO_2Me$, 39265-95-7; $MeCOCH_2COMe$, 123-54-6; $MeCOCH(Ac)(CH_2)_2CO_2Me$, 13984-53-7; $MeCOC(Me){=}C(Me)OBF_2$, 367-16-8; $MeCOC(Et){=}C(Me)OBF_2$, 71896-31-6; $EtCOC(Me){=}C(Et)OBF_2$, 1549-46-8; $EtCOC(Et){=}C(Et)OBF_2$, 99018-03-8; $MeCOC(Pr){=}C(Me)OBF_2$, 99018-02-7; (3-ethyl-2,4-hexanedionato)difluoroborane, 71736-28-2; (3-methyl-2,4-pentanedionato)difluoroborane, 14947-58-1; (3-ethyl-2,4-pentanedionato)difluoroborane, 71736-26-0; (4-methyl-3,5-heptanedionato)difluoroborane, 14643-73-3; (4-ethyl-3,5-heptanedionato)difluoroborane, 15130-21-9; (3-methyl-2,4-hexanedionato)difluoroborane, 15130-19-5; (3-methyl-2,4-heptanedionato)difluoroborane, 15130-18-4; (3-ethyl-2,4-heptanedionato)difluoroborane, 99018-04-9; (3-propyl-2,4-heptanedionato)difluoroborane, 99018-05-0; (3-propyl-2,4-hexanedionato)difluoroborane, 99018-06-1; (3-propyl-2,4-pentanedionato)difluoroborane, 99018-07-2; (2,4-hexanedionato)difluoroborane, 15130-15-1; benzyl 4-[((benzyloxy)carbonyl)methyl]-3,5-dimethylpyrrole-2-carboxylate, 99018-00-5; benzyl 4-[(methoxycarbonyl)methyl]-3,5-dimethylpyrrole-2-carboxylate, 31837-62-4; diethyl oximinomalonate, 6829-41-0; bis(3,5-heptanedionato)copper, 15716-70-8.

Bridgehead Hydrazines. 2.[1] Preparation and Photolysis of 2-Phenyl-*s*-triazolo[1,2-*a*]pyridazine-1,3-dione and of Pyridazino[1,2-*b*]phthalazine-6,11-dione

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Received June 26, 1985

The two title compounds **6** and **10** were prepared by Diels–Alder reactions of the appropriate cyclic azo compounds with butadiene followed by bromination and bisdehydrobromination. Photolysis of **6** in methanol resulted in 1,2- and 1,4-additions of the solvent to the dienic system and in (2 + 2) dimerization. Photolysis in dichloromethane resulted in rearrangement to a pyrrolo[1,2-*a*]triazine and in (2 + 2) dimerization. Photolysis of **10** was solvent independent and gave only (4 + 2) dimer. Mechanistic aspects of the photoreactions are discussed.

Previous work on the photolysis of 1,2-dihydropyridazines revealed two main pathways, internal (2 + 2) cycloaddition[2] (path a) and electrocyclic opening[2,3] (path b).

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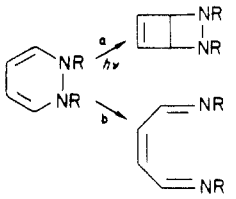
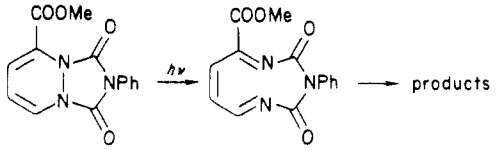
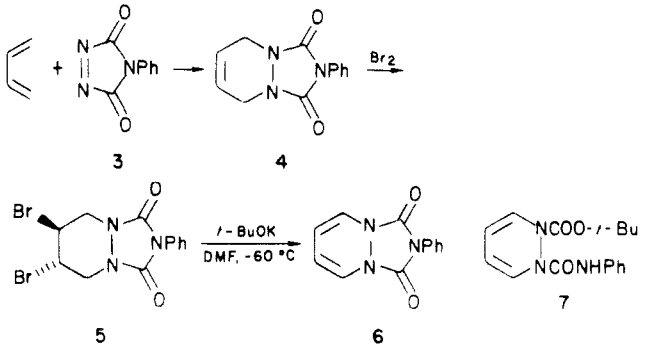


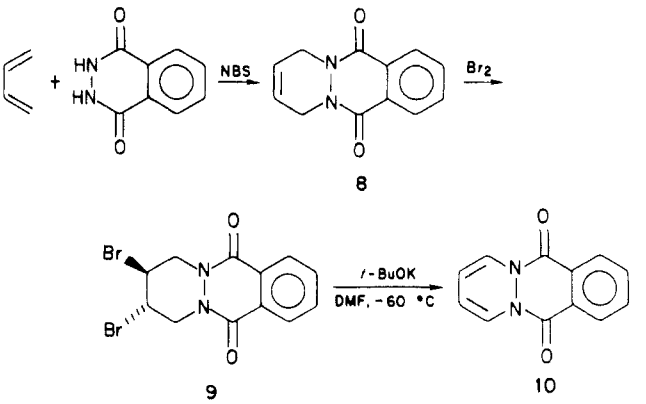
We have recently reported[1] the first photolysis of a bicyclic 1,2-derivative (**1**), which proceeded exclusively through path b. It produced initially the triazonine **2**, which was not isolable due to its photolytic and electrophilic reactivities and reacted further. Now we describe the photolyses of two bicyclic pyridazines unsubstituted on carbon, which took completely different courses.



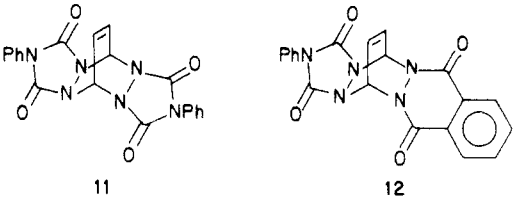
Synthesis of the Substrates 6 and 10. Compound **6** was prepared by bromination–dehydrobromination of **4**, which is the Diels–Alder adduct of 4-phenyl-1,2,4-triazoline-3,5-dione (**3**) with butadiene.[4] The double dehydrobromination of **5** was a difficult step due to the high sensitivity of the triazole ring toward bases. After many attempts it was accomplished in 60% yield by using potassium *tert*-butoxide in dimethylformamide at −60 °C (just above the freezing point of the solvent). Even a slight increase in the temperature caused the *tert*-butoxide to act also as a nucleophile, to give only the monocyclic diene **7**. Compound **10** was prepared in a similar manner. The



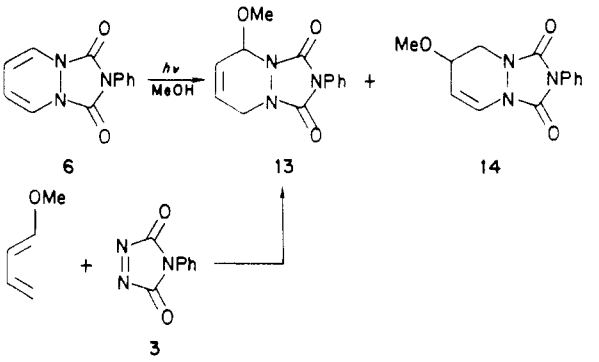
requisite phthalazine is unstable and was prepared in situ by oxidation of phthalhydrazide in the presence of butadiene. We found the use of *N*-bromosuccinimide as oxidant far more convenient and efficient than the published procedures for **8** which utilized lead tetraacetate[5] or *tert*-butyl hypochlorite.[6] The dihydropyridazines **6** (λ_{max} 369 nm) and **10** (λ_{max} 400 nm) were obtained as yellow-orange stable solids. The NMR spectra indicated high symmetry; thus, the vinylic protons of **6** appeared as a pair of 2 H AA′BB′ multiplets at δ 6.89 and 5.35 ($J_{AB+AB'}$ = 8.9 Hz) with a 5 H aromatic multiplet at δ 7.49–7.53. The spectrum of **10** consisted of two pairs of 2 H AA′BB′ multiplets, the vinylic one at δ 7.83 and 5.77 (J = 9.4 Hz)



and the aromatic one at δ 8.48 and 7.92 (J = 9.4 Hz). Both **6** and **10** were unreactive as Diels-Alder dienes with carbon dienophiles but reacted with **3** to give the bridged tetrazines **11** and **12**, respectively.



Photolysis of 6. The conversion of **6** to photoproducts progressed rapidly and was complete after 40–60 min of irradiation (compared with 7–8 h required for the photolysis of **1** under the same conditions). The combined yields of identifiable products were 60–80% (NMR analysis). Our initial experiments were carried out in methanol in order to trap highly reactive products, and indeed, the photolysis yielded two methanol monoadducts in a ratio of 2:1 and small amounts of two dimers. Both adducts were formed by direct addition of methanol to **6** without any skeletal rearrangement. The major product was identified through its ^{1}H and ^{13}C NMR spectra as the 1,4-adduct **13** and the minor one as the 1,2-adduct **14**. The structure of **13** was verified by an independent synthesis through the Diels–Alder reaction of 1-methoxybutadiene with **3**. The addition of methanol through its O–H bond



indicates a ionic mechanism. A highly likely intermediate that would furnish both **13** and **14** on reacting with methanol is the allyl cation **15**, formed by proton abstraction from the solvent. Photoprotonations of cyclic double bonds by methanol are well-known[7] and are either polar singlet excited-state direct reactions or ground-state reactions of the initially formed highly strained *trans*-cycloolefins. The excited singlet state of 1,3-dienes is highly polarized and can even be presented as a zwitterion[8] (**16**);

(1) Part 1: Sheradsky T.; Moshenberg, R. *J. Org. Chem.* **1984**, *49*, 587.
(2) Altman, L. J.; Semmelhack, M. F.; Hornby, R. B.; Vederas, J. C. *Chem. Commun.* **1968**, 686.
(3) Rigaudy, J.; Breliere, J. C. *Bull. Soc. Chim. Fr.* **1968**, 455.
(4) Cookson, R. C.; Gilani, S. S. H.; Stevens, I. D. R. *J. Chem. Soc. C* **1967**, 1905.
(5) Clement, R. A. *J. Org. Chem.* **1960**, *25*, 1724.
(6) Kealy, T. J *J. Am. Chem. Soc.* **1962**, *84*, 966.
(7) Kropp, P. J. *Org. Photochem.* **1979**, *4*, *1*.
(8) Bruckmann, P.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 5037.

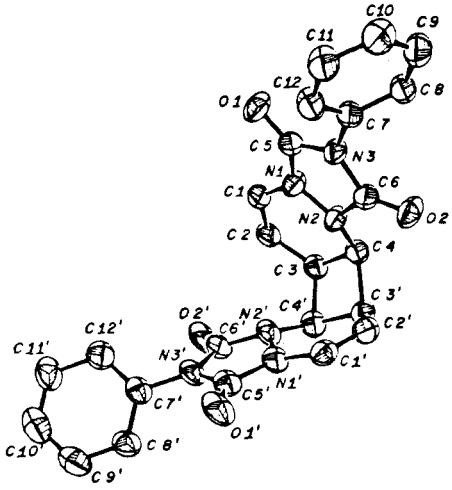
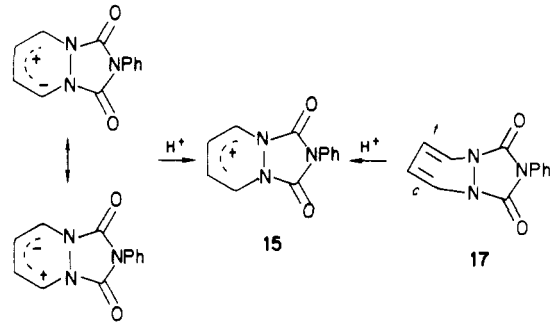


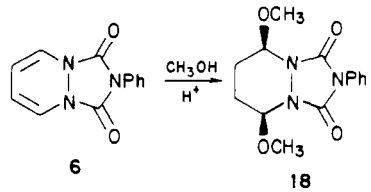
Figure 1. Molecular structure of **22** (hydrogens and the inclusion of CH_2Cl_2 omitted in order to maintain legibility).

however, examples of methanol photoadditions to it are scarce.[9,10] Formation of a trans double bond in cyclohexadienes is generally precluded and is also very unlikely in **6**; however, this possibility should not be completely ruled out (**17**) as it is supported by the results of the photolysis of **10** described below. For comparison we have



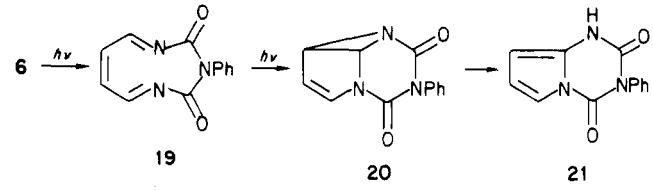
16 **15** **17**

also tried the acid-catalyzed nonphotochemical addition of methanol to **6**. Reaction occurred only under very acidic conditions (15% H_2SO_4) and gave a bis adduct. Its NMR spectra exhibited complete symmetry and established structure **18** (probably the cis isomer). Clearly, **18** could not have been formed via either **13** or **14**. It was probably formed by two consecutive methanol additions, each being regiocontrolled by the adjacent acylamino group. The



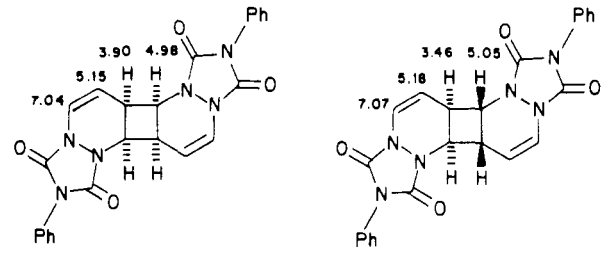
6 **18**

photolysis of **6** in dichloromethane or in ether afforded three products: an isomer of **6** and the same two dimers formed in methanol (ratio 2:2:1). The monomer was identified as the pyrrolotriazine **21** through its ^1H NMR spectrum which showed the three pyrrole protons at δ 7.16 (dd), 6.37 (t), and 5.60 (dd), J = 3.5 and 1.6 Hz. Its formation follows the pathway suggested previously[1] for the



19 **20** **21**

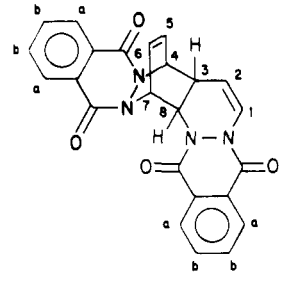
photolysis of **1** and involves electrocyclic opening to the triazonine **19**, followed by photorearrangement to **20** and aromatization through an aziridine ring opening. The two dimeric products exhibited four types of nonaromatic protons, which may indicate two equal components combined unsymmetrically. X-ray analysis of the major one, **22** (after slow crystallization from dichloromethane),



22 **23**

showed it to be an intermolecular (2 + 2) adduct, with head-to-tail structure and cis-syn-cis geometry (see Figure 1) with inclusion of a molecule of CH_2Cl_2 in the cavity formed by the two "wings". The minor dimer **23** was assigned as the head-to-tail dimer with cis-anti-cis geometry. Comparison of the NMR spectra of **22** and **23** (marked on the drawings) reveals that all the corresponding protons have very close chemical shifts, except that of the allylic ones which in **23** are shifted by ca. 0.5 ppm upfield. It can be seen that the syn to anti change would cause shielding of the allylic protons as it would bring them above the plane of carbonyl groups.

Photolysis of 10. This reaction proceeded more slowly than the photolysis of **6** (2.5–3 h) and in either methanol or dichloromethane afforded a single dimeric product in 80% yield. the ^1H NMR spectrum indicated complete asymmetry as it exhibited eight different types of nonaromatic protons and also four different aromatic protons adjacent to carbonyls. The spectrum is very well in accord only with structure **24**, which is an intermolecular (2 + 4)



24

adduct of **10**. The NMR data and assignments for **24** are presented in Table I. A very significant feature of the spectrum is the high coupling constant of 11 Hz between H-3 and H-8, which indicates axial–axial conformation and thus trans fusion of the two six-membered rings. Such trans juncture was noted in all reported photochemical Diels–Alder reactions.[11-14] Both the dienophilic activity

(9) Baldry, P. J. *J. Chem. Soc., Perkin Trans. 2*, **1980**, 809.

(10) A striking example is the photoaddition of methanol to (11*H*)-indolo[1,2-*a*]azepines described by: Hayes, P. C.; Jones, G. *J. Chem. Soc., Perkins Trans. 1* **1982**, 1871. However, the interpretation of this addition as an excited singlet reaction seems inconclusive, as the seven-membered ring can probably accommodate a trans double bond.[11]

(11) Dunkelblum, E.; Hart, H.; Suzuki, M. *J. Am. Chem. Soc.* **1977**, *99*, 5074.

(12) Dauben, W. G.; Van Riel, H. C. H. A.; Haniv, C.; Leroy, F.; Joussot-Dubien, J.; Bonneu, R. *J. Am. Chem. Soc.* **1979**, *101*, 1901.

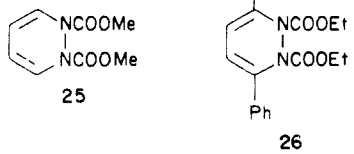
Table I. ^{1}H NMR Spectrum of 24 (300 MHz in $CDCl_3$)

	chem shifts, ppm	coupling const,[a] Hz
	nonaromatic	vicinal couplings
H-1	7.39 (dd)	$J_{1,2}$ = 8.6
H-2	5.35 (dd)	$J_{2,3}$ = 3.9
H-3	3.18 (dh)	$J_{3,4}$ = 2.7
H-4	5.95 (ddd)	$J_{4,5}$ = 6.3
H-5	6.88 (ddd)[b]	$J_{5,6}$ = 7.8
H-6	6.81 (ddd)[b]	$J_{6,7}$ = 6.3
H-7	6.22 (dt)	$J_{7,8}$ = 1.6
H-8	5.42 (dd)	$J_{8,3}$ = 11.0
	aromatic	J_{ab} = 7.0
H-a	8.38 (d)	allylic couplings
	8.31 (d)	$J_{1,3}$ = 1.2
	8.21 (d)	$J_{4,6}$ = 1.6
	8.09 (d)	$J_{5,7}$ = 1.6
H-b	7.70–7.90 (m, 4 H)	

[a] All were verified by spin decouplings. [b] The two central doublets merged to a triplet. [c] Comparison of $J_{3,4}$ and $J_{7,8}$ suggests that H-3 is exo and H-8 is endo.

of a double bond in **10** and the stereochemistry of the product **24** can be rationalized either by assuming an initial formation of a trans bond and then the usual ($^\pi4_s + {}^\pi2_s$) Diels–Alder reaction[12,13] or alternatively a direct photochemical Diels–Alder reaction that is antarafacial in one of its components.[14] Both possibilities are difficult to accept, as the dienophile structure in one mechanism and the transition state in the other seem to be impossibly strained. However, the formation of *24* can be accounted for only by one of them.

Conclusions. Results are now available on the photolysis of five 1,2-dihydropyridazines, namely **6** and **10** in this work, **1** in our previous work[1], and **25** and **26** in the literature.[2,3] Each of the five behaved differently, and it



25

26

appears that any alteration in the structure causes a complete change in the course of the photolysis. The high diversity of the small amount of data does not allow, at this stage, us to make any structure–reactivity correlation or even to explain the differences, and we had to be content with the discussion of individual reactions. Most of the results obtained in this work were quite surprising. Notable is the minor role of electrocyclic opening, which is quite common in cyclohexadienes[15] and should be thermodynamically favorable in dihydropyridazines as it involves cleavage of the weak nitrogen–nitrogen bond. Evaluation of the contribution of the special features of 1,2-dihydropyridazines such as the nitrogen stereochemistry, the lone pair–lone pair interactions, and the 8π cyclic conjugation (antiaromaticity) to the unusual photoreactivity will probably be possible when more data have been obtained.

Experimental Section

General Methods. Melting points (uncorrected) were taken on a Thomas-Hoover capillary apparatus. Spectra were obtained on the following instruments: IR (Nujol mulls) on a Perkin-Elmer 157 spectrometer; UV (ethanol solutions) on a Varian Techtron 635 spectrometer; NMR on Bruker WH-200 or WH-300 spectrometers; mass spectra (70 eV) on a Varian MAT-311 instrument. Photolyses were carried out (under nitrogen with stirring) by using a Hanovia 450-W high-pressure immersion lamp in a water-cooled Pyrex vessel. E. Merck silica gel 60 (70–230 mesh) was used for chromatography. Petroleum ether refers to the fraction with a boiling range of 40–60 °C.

6,7-Dibromo-2-phenyltetrahydro-*s*-triazolo[1,2-*a*]-pyridazine-1,3-dione (5). Bromine (15.8 g, 0.1 mol) was added in one portion to a solution of the dihydro derivative 4[4] (11.54 g, 50 mmol) in chloroform (200 mL), and the solution was stirred at room temperature. After 1 h a precipitate began to form, and after 7 h it was collected by filtration and washed with chloroform to give 10.5 g of pure **5**. The red filtrate was washed with sodium thiosulfate solution until colorless and then with water, dried (Na_2SO_4), and evaporated to give additional 6.1 g of **5**: combined yield 85%; mp 252 °C; IR 1775, 1715 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.49–7.52 (m, 5 H), 4.57 (t, J = 1.4 Hz, 2 H), 4.18 (d, 4 H); NMR [$(CD_3)_2SO$] δ 7.49 (s, 5 H), 5.94 (s, 2 H), 4.12, 3.99 (d, J = 13.6 Hz, 2 H each). Anal. Calcd for $C_{12}H_{11}Br_2N_3O_2$: C, 37.04; H, 2.85; N, 10.80; Br, 41.08. Found: C, 37.30; H, 2.79; N, 10.92; Br, 40.73.

2-Phenyl-*s*-triazolo[1,2-*a*]pyridazine-1,3-dione (6). A solution of **5** (1.95 g, 5 mmol) in 75 mL of dry dimethylformamide (distilled over P_2O_5) was cooled to −65 °C (dry ice–acetone bath) and vigorously stirred. Potassium *tert*-butoxide (1.68 g, 15 mmol) was added, and the solution turned yellow. Stirring was continued for 2.5 h while the temperature was carefully maintained at −55 to −60 °C. The solution was then poured into water (150 mL), and after the precipitate settled, it was collected by filtration. Crystallization from ethanol gave **6** (0.67 g, 59%) as yellow needles: mp 209 °C; UV λ_{max} 369 nm (ε 1200); IR 1780, 1760, 1665 cm^{-1} (C=O); NMR, see text; mass spectrum m/e (relative intensity) 227 (M^+, 38), 119 (40), 91 (17), 80 (100). Anal. Calcd for $C_{12}H_9N_3O_2$: C, 63.43; H, 3.99; N, 18.49. Found: C, 63.23; H, 4.01; N, 18.83.

1-(Phenylcarbamoyl)-2-[(*tert*-butyloxy)carbonyl]-1,2-dihydropyridazine (7). When during the preparation of **6** described above the temperature was raised above −55 °C, the same workup gave only **7** in 65% yield: mp 141–142 °C; UV λ_{max} 241 nm (ε 14400), 299 (4350); IR 3200 (NH), 1735, 1655 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.30–7.44 (m, 5 H), 7.08 (d, J = 6.4 Hz, 1 H), 6.50 (d, J = 6.4 Hz, 1 H), 5.89 (t, 1 H), 5.70 (t, 1 H), 1.51 (s, 9 H); mass spectrum, m/e (relative intensity) 301 (M^+, 1), 246 (6), 201 (8), 182 (62), 126 (79), 119 (65), 109 (24), 91 (62), 81 (100). Anal. Calcd for $C_{16}H_{19}N_3O_3$: C, 63.77; H, 6.36; N, 13.95. Found: C, 63.86; H, 6.06; N, 13.69.

1,4-Dihydropyridazino[1,2-*b*]phthalazine-6,11-dione (8). *N*-Bromosuccinimide (37.4 g, 0.21 mol) was added to a stirred suspension of phthalhydrazide (16.2 g, 0.1 mol) in dichloromethane (600 mL). A green color developed immediately, and after 2 min a solution of butadiene (13.5 g, 0.25 mol) in dichloromethane (100 mL) was added. Stirring was continued for 6 h, during which the solution became clear and colorless. It was washed twice with water, dried (Na_2SO_4), and evaporated. The solid residue was triturated with chloroform to give **8**: 15 g (70%); mp 268–269 °C (lit.[6] mp 263–268 °C; lit.[5] mp 272–275 °C).

2,3-Dibromotetrahydropyridazino[1,2-*b*]phthalazine-6,11-dione (9). A solution of **8** (10.7 g, 50 mmol) and bromine (12 g, 75 mmol) in chloroform (300 mL) was stirred at room temperature for 6 h. It was then washed twice with sodium thiosulfate solution and once with water, dried (Na_2SO_4), and evaporated. The solid residue was triturated with ether and crystallized from ethanol to give **9**: (14.4 g (78%); mp 209 °C; IR 1655, 1645 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.30, 7.83 (AA'BB' m, J = 9.4 Hz, 2 H each), 4.80, 4.47 (d, J = 14.5 Hz, 2 H each), 4.60 (s, 2 H); NMR [$(CD_3)_2SO$] δ 8.36, 8.14 (AA'BB' m, J = 9.3 Hz, 2 H each), 5.18 (s, 2 H), 4.82, 4.60 (d, J = 14.6 Hz, 2 H each). Anal. Calcd for $C_{12}H_{10}Br_2N_2O_2$: C, 38.52; H, 2.69; N, 7.49; Br, 42.72. Found: C, 38.63; H, 2.80; N, 7.44; Br, 42.72.

Pyridazino[1,2-*b*]phthalazine-6,11-dione (10). To a cooled (−65 °C) solution of **9** (1.86 g, 5 mmol) in dry dimethylformamide (150 mL) was added potassium *tert*-butoxide (1.85 g, 17.5 mmol). The solution was vigorously stirred with cooling (internal temperature −55 to −60 °C) for 2.5 h and then poured into water (500

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mL). After 2 h the precipitate was collected by filtration, washed with water, and crystallized from ethyl acetate–petroleum ether to give 0.45 g (42%) of **10**: mp 203 °C; UV λ_{max} 400 nm (ϵ 3100); IR 1650 cm^{-1} (C=O); NMR, see text; mass spectrum, *m/e* (relative intensity) 212 (M^+, 80), 156 (22), 132 (18), 129 (12), 104 (100), 76 (44). Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.79; H, 3.77; N, 12.82.

***N,N'*-Diphenyl-1,2,4,5-tetraazabicyclo[2.2.2]oct-7-ene-1,2,4,5-bis(dicarboximide) (11).** To a solution of **6** (114 mg, 0.5 mmol) in dichloromethane (10 mL) was added a solution of **3** (90 mg in 2 mL of acetone) dropwise. The precipitate formed was collected by filtration and triturated with ether to give 150 mg (74%) of **12**, mp 216 °C. In all respects it was identical with material prepared from α-pyrone and **3** according to the literature.[16]

***N*-Phenyl-1,2-phthaloyl-1,2,4,5-tetraazabicyclo[2.2.2]oct-7-ene-4,5-dicarboximide (12)**: prepared by the procedure described above for **11** using **10** and **3** (38%); mp 213–215 °C; NMR [$(CD_3)_2SO$] δ 8.21, 7.96 (AA'BB' m, J = 9.5 Hz, 2 H each), 7.42–7.50 (m, 7 H), 7.16 (dd, J = 4.0, 3.1 Hz, 2 H). Anal. Calcd for $C_{20}H_{13}N_5O_4$: C, 62.02; H, 3.38; N, 18.08. Found: C, 61.81; H, 3.61; N, 18.31.

Photolysis of 6 in Methanol. A solution of **6** (454 mg) in methanol (300 mL) was irradiated for 1 h. The light yellow solution was evaporated in vacuo to give a brown semisolid residue, which was chromatographed on silica gel (25 g). Elution with chloroform–ethyl acetate (9:1) gave first pure **13** (22 mg), followed by mixtures of **13** and **14** (215 mg) and dimers (12 mg). A 100-mg sample of the mixture of **13** and **14** (ratio 1.5:1) was chromatographed twice on a preparative TLC silica gel plate (20 × 20 cm, 2-mm thickness) using chloroform–ethyl acetate (3:1) to produce one broad band on the plate. The bottom part of the band produced a pure sample (7 mg) of **14**.

5,8-Dihydro-5-methoxy-2-phenyl-*s*-triazolo[1,2-*a*]-pyridazine-1,3-dione (13): 40% yield by NMR of the crude photoproduct; mp 138–139 °C; IR 1765, 1700 cm^{-1} (C=O); NMR ($CDCl_3$) 7.55–7.38 (m, 5 H), 6.16 (dm, 1 H), 6.05 (dm, 1 H), 5.66 (dd, 1 H), 4.46, 4.02 (ddd, 1 H each), 3.61 (s, 3 H); mass spectrum, *m/e* (relative intensity) 259 (M^+, 86), 228 (66), 119 (28), 109 (48), 91 (13), 85 (100). Anal. Calcd for $C_{13}H_{13}N_3O_3$: C, 60.23; H, 5.05; N, 16.21. Found: C, 60.15; H, 4.99; N, 16.39.

5,6-Dihydro-6-methoxy-2-phenyl-*s*-triazolo[1,2-*a*]-pyridazine-1,3-dione (14): 20% yield; mp 253–256 °C dec; IR 1755, 1700 cm^{-1} (C=O); NMR ($CDCl_3$) 7.49–7.39 (m, 5 H), 7.04 (dd, 1 H), 5.39 (dd, 1 H), 4.16 (m, 1 H), 4.13, 3.82 (dd, 1 H each), 3.48 (s, 3 H). Anal. Calcd for $C_{13}H_{13}N_3O_3$: C, 60.23; H, 5.05; N, 16.21. Found: C, 60.31; H, 5.32; N, 16.02.

Independent Preparation of 13. A solution of 1-methoxy-1,3-butadiene (100 mg) in dichloromethane (2 mL) was added dropwise to a solution of **3** (175 mg) in acetone (3 mL). The red color disappeared immediately and the solution was evaporated. The solid residue was crystallized from ethanol to give 260 mg (95%) of **13**, in all respects identical with the photoproduct.

***cis*-5,8-Dimethoxy-2-phenyltetrahydro-*s*-triazolo[1,2-*a*]-pyridazine-1,3-dione (18).** A solution of **6** (0.45 g) and sulfuric acid (12 mL) in methanol (80 mL) was refluxed until the yellow color disappeared (ca. 2.5 h). It was cooled, poured into water (300 mL), and extracted four times with chloroform. The combined extract was washed four times with water, dried, and evaporated. The solid residue was crystallized from ethanol to give **18**: 0.39 g (66%); mp 141–142 °C; IR 1765, 1710, 1695 cm^{-1} (C=O); NMR ($CDCl_3$) 7.51–7.48 (m, 5 H), 5.46 (s, 2 H), 3.46 (s, 6 H), 2.19–1.94 (d, J = 10.3 Hz, 2 H each); mass spectrum (relative intensity), 291 (M^+, 89), 260 (88), 228 (50), 220 (88), 141 (46), 119 (88), 115 (100), 109 (20), 101 (47), 91 (61), 85 (37). Anal. Calcd for $C_{14}H_{17}N_3O_4$: C, 57.52; H, 5.88; N, 14.42. Found: C, 57.88; H, 6.02; N, 14.08.

Photolysis of 6 in Dichloromethane. A solution of **6** (454 mg) in dichloromethane (300 mL) was irradiated for 40 min and evaporated in vacuo. The brown residue was chromatographed on silica gel (25 g). Elution with chloroform–ethyl acetate (9:1) afforded the following fractions (pure materials, intermediate fractions that contained their mixtures were discarded): (1) unreacted **6** (60 mg); (2) compound **21** (45 mg); (3) dimer **22** (40 mg); (4) dimer **23** (30 mg); (5) dark brown tar, which exhibited only aromatic peaks in the NMR.

3-Phenylpyrrolo[1,2-*a*]-*s*-triazine-2,4-dione (21): 25%; mp 219–220 °C (EtOH); IR 1740, 1665 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.30–7.54 (m, 5 H), 7.16 (dd, J = 3.5, 1.6 Hz, 1 H), 6.37 (t, J = 3.5 Hz, 1 H), 5.60 (dd, 1 H); mass spectrum (relative intensity), 227 (M^+, 100), 120 (83), 119 (80), 108 (99), 91 (59), 80 (66), 77 (55). Anal. Calcd for $C_{12}H_9N_3O_2$: C, 63.43; H, 3.99; N, 18.49. Found: C, 63.37; H, 4.11; N, 18.15.

Dimer 22: 21%; mp 251–252 °C (EtOH); IR 1760, 1705 cm^{-1} (C=O); ^1H NMR δ 7.41–7.58 (m, 10 H), 7.04 (d, J = 8.5 Hz, 2 H), 5.15 (dd, J = 8.5, 4.1 Hz, 2 H), 4.98 (t, J = 8.1 Hz, 2 H), 3.90 (m, 2 H). Anal. Calcd for $C_{24}H_{18}N_6O_4$: C, 63.43; H, 3.99; N, 18.49. Found: C, 63.56; H, 4.25; N, 18.08.

Dimer 23: 13%; mp 196–198 °C (EtOH); IR 1780, 1765, 1705 cm^{-1} (C=O); ^1H NMR 7.37–7.44 (m, 10 H), 7.07 (d, J = 8.5 Hz, 2 H), 5.18 (dm, 2 H), 5.05 (m, 2 H), 3.46 (m, 2 H). The multiplets have unusual shapes due to second-order splittings of the AA'BB'XX' system. Anal. Calcd for $C_{24}H_{18}N_6O_4$: C, 63.43; H, 3.99; N, 18.49. Found: C, 63.24; H, 3.76; N, 18.82.

Photolysis of 10 in Methanol. A 425-mg sample of **10** was partly dissolved in methanol (300 mL) and irradiated for 2.5 h. The colorless precipitate was collected by filtration to give 235 mg of pure **24**. Concentration of the filtrate to 20 mL and cooling afforded a second crop (150 mg) slightly contaminated with the starting material **10**. For purification procedure, see below.

Photolysis of 10 in Dichloromethane. A solution of **10** (454 mg) in CH_2Cl_2 (300 mL) was irradiated for 2.5 h and then concentrated to a volume of 20 mL. The brown precipitate (380 mg) was collected and chromatographed on silica gel (25 g, eluant chloroform–ethyl acetate 9:1). The early fractions were yellow and afforded unreacted **10** (60 mg). Subsequent colorless fractions afforded 290 mg (79%) of **24**: mp 330–332 °C (microcrystlas from ethyl acetate); IR 1675, 1645, 1625 cm^{-1} (C=O); NMR, see Table I. Anal. Calcd for $C_{24}H_{16}N_4O_4$: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.65; H, 3.61; N, 12.91.

X-ray Crystal Structure of 22.[17] The procedure of measurement, determination, and refinement was described in our previous work.[1]

Supplementary Material Available: Complete X-ray data of compound **22**, including crystal data, atomic positional and thermal parameters, and bond distances and angles, and complete ^1H and ^{13}C NMR data of compounds **13**, **14**, and **18** (9 pages). Ordering information is given on any current masthead page.

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(17) We thank Dr. S. Cohen for his help with this analysis.