137 (18), 69 (26), 43 (17), 28 (21). Anal. Calcd for $C_{14}H_{12}O_6$: C, 60.87; H, 4.38. Found: C, 60.76; H, 4.40.

Registry No. 1, 82-02-0; 2, 92611-82-0; 6, 102830-25-1; 7, 102830-36-4; 8, 102830-23-9; 9, 102830-24-0; 13, 102830-26-2; 14, 102830-27-3; 15, 102830-28-4; 16, 102830-30-8; 17, 102830-29-5; 18, 102830-31-9; 19, 92611-83-1; 20, 484-51-5; 21, 102830-32-0; 22, 102830-34-2; 24, 102830-33-1; 27, 92611-85-3; 28, 102830-35-3; ethyl bromoacetate, 105-36-2; bromoacetophenone, 70-11-1; chloroacetone, 78-95-5.

Bridgehead Hydrazines. 3. Unusual Photorearrangement of 1,4-Diphenylpyridazino[1,2-*b*]phthalazine-6,11-dione

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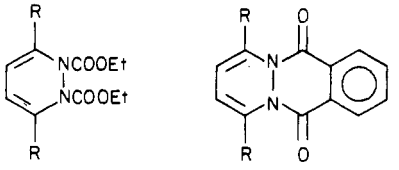
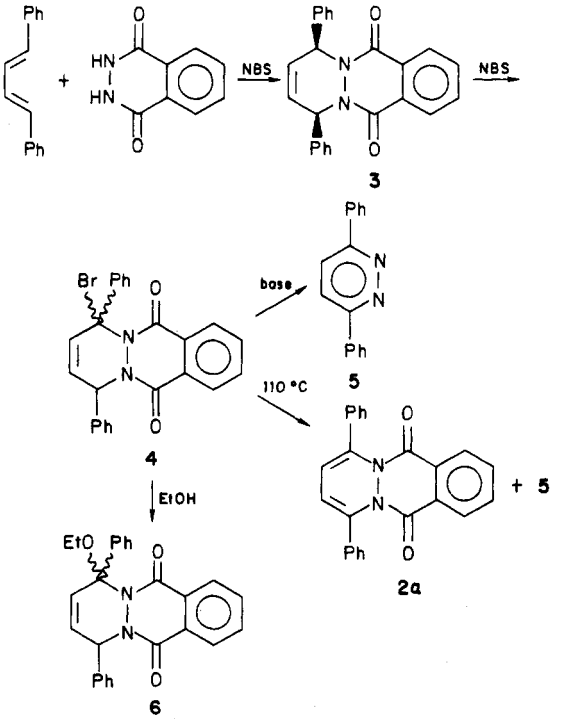
1,4-Diphenylpyridazino[1,2-*b*]phthalazine-6,11-dione (**2a**) was prepared through Diels–Alder reaction of phthalazine and 1,4-diphenylbutadiene, followed by allylic bromination and thermal 1,4-dehydrobromination. Upon photolysis, **2a** isomerized to an isoindolo[2,3-*a*]diazepine derivative, with an oxygen bridge across the seven-membered ring (**7**). A mechanism which involves an electrocyclic opening and a free radical cycloaddition is suggested.

The photoreactivity of 1,2-dihydro-1,2-diarylpyridazines is highly substituent dependent. Compound **1a**, for example, undergoes electrocyclic ring opening,[1] while **1b** gives, under the same conditions, mainly internal (2 + 2) cycloaddition.[2,3] We have recently reported[4] the synthesis and photolysis of the diazaanthraquinone **2b**. The photolysis resulted in (2 + 4) dimerization only and did not involve cleavage of the N–N bond. It was hoped that in analogy with **1a,b**, the introduction of two phenyl groups (**2a**) would direct the photolysis toward electrocyclic opening and formation of the diazecine ring system.



Synthesis of 2a. The Diels–Alder reaction of phthalazine (prepared in situ by NBS oxidation of phthalhydrazide) and *trans,trans*-1,4-diphenylbutadiene gave the tetrahydropyridazine **3** in 80% yield. Attempted direct selenium dioxide oxidation of **3** to **2a** (employed successfully in the synthesis of **1a**[5]) did not work. Allylic bromination of **3** with NBS proceeded smoothly and gave the bromide **4**, but all attempts to cause basic 1,4-dehydrobromination to **2a** resulted in complete removal of the phthaloyl portion and gave, even under very mild conditions, only 1,4-diphenylpyridazine **5**. It was noted that heating the bromide **4** to 110 °C (during melting point determination) caused orange-red coloring. We thus carried out pyrolysis of **4** on a preparative scale and obtained **2a** in 40% yield as a yellow-orange solid (λ_{max} 402 nm). Analytical and spectral properties of **2a** were in accord with the proposed structure. The two vinylic hydrogens appeared in the NMR spectrum as one singlet (δ 6.12). It should be noted that the bromide **4** is very sensitive toward nucleophiles and reacted with ethanol to give the ethoxy derivative **6**. Although **4** was prepared by a free radical process and **6** by an S_N1 reaction, both were obtained as single stereoisomers.



Photolysis of 2a. The reaction proceeded rapidly, was solvent independent, and gave as the main product (70%) an isomer of **2a**. The NMR spectrum indicated loss of symmetry, as the two nonaromatic hydrogens appeared as two doublets [δ 5.93 and 5.40 (J = 4.1 Hz)]. The IR car-

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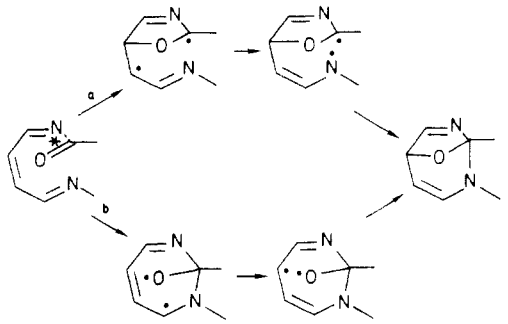
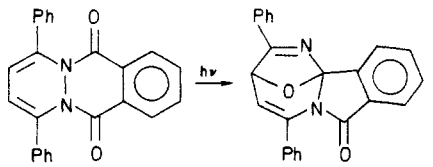
Scheme I

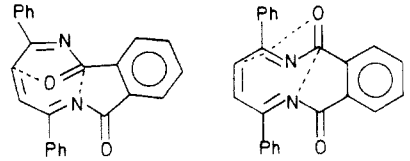


bonyl absorption appeared at 1730 cm^{-1} (in **2a** it absorbed at 1650 cm^{-1}). The structure was determined as **7** by X-ray crystallography.



2a **7**

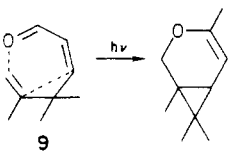
The transformation **2a** → **7** involves cleavage of the N–N bond and formation of new C–O and C–N bonds. It is reasonable to assume that it consists of two distinct photochemical stages, the first of which is the expected electrocyclic ring opening, while the second one is a Diels–Alder-like intramolecular cycloaddition of a carbonyl group to an aza diene moiety. The photochemical opening should be conrotatory and thus lead to the cis,trans diazecine **8a** rather than the trans,trans isomer **8b**. Indeed cyclo-



8a **8b**

addition appears to be sterically impossible in **8b**, while in **8a** the carbonyl is in a position suitable for intramolecular reaction. A concerted mechanism is unlikely, however. We suggest a free radical process initiated by photoexcitation of a carbonyl group (probably triplet, in acyl imines the carbonyl is not conjugated to the sp^2 nitrogen lone pair, resembling a ketonic rather than amidic carbonyl[6]). Reaction may then proceed either through formation of a C–O bond (path a, Scheme I) or a C–N bond (path b). Examination of a molecular model of **8a** favors path b.

Most known photochemical cycloadditions that involve carbonyl groups are of the (2 + 2) type (Paterno–Buchi reaction).[7] Cases of (2 + 4) addition are very rare because of their strict steric requirements. An example is the transformation **9** → **10**.[8] However, in this reaction the carbonyl is a part of the "dienic" component, while in the present case it is the "dienophilic" one.



9 **10**

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 were taken on a Bruker WH-300 instrument and mass spectra (70 eV) on a Varian MAT-311 instrument. 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.

1,4-Diphenyl-1,4,6,11-tetrahydropyridazino[1,2-*b*]phthalazine-6,11-dione (3). *N*-Bromosuccinimide (11.2 g, 63 mmol) was added in one portion to a stirred suspension of phthalhydrazide (4.86 g, 30 mmol) in dichloromethane (350 mL). A solution with green coloration occurred immediately. After 2 min a solution of 1,4-diphenylbutadiene (6.18 g, 30 mmol) in dichloromethane (50 mL) was added, and stirring was continued for 5 h, during which time the color turned brown, orange, and finally white. It was then washed with sodium thiosulfate solution and twice with water, dried (Na_2SO_4), and evaporated. The solid residue was dissolved in chloroform, and some insoluble material was filtered off. The filtrate was evaporated, and the residue was triturated with petroleum ether and then crystallized from ethanol to give 7.13 g (65%) of **3**; mp 223 °C; IR 1635 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.32, 7.80 (AA'BB' m, J = 9.3 Hz, 2 H each), 7.15–7.21 (m, 10 H), 6.51, 6.34 (dd, J = 3.1, 1.0 Hz, 2 H each); mass spectrum, m/e (relative intensity) 366 (M^+, 55), 289 (11), 262 (32), 236, (100), 219 (69), 206 (99), 191 (32), 130 (66), 129 (33), 115 (78), 104 (55), 91 (56). Anal. Calcd for $C_{24}H_{18}N_2O_2$: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.37; H, 5.13; N, 7.96.

1-Bromo-1,4-diphenyl-1,4,6,11-tetrahydropyridazino[1,2-*b*]phthalazine-6,11-dione (4). A solution of compound **4** (732 mg, 2 mmol), *N*-bromosuccinimide (360 mg, 2 mmol), and benzoyl peroxide (10 mg) in carbon tetrachloride (450 mL) was refluxed for 2 h under strong illumination. The solution was filtered and evaporated in vacuo (below 35 °C). The oily residue was stirred under ether to give a yellow solid (610 mg, 68%): mp 132–133 °C dec; IR 1670, 1640 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.35–7.37 (m, 14 H), 6.64 (d, J = 1.9 Hz, 1 H), 5.87 (d, J = 7.3 Hz, 1 H), 5.1, (dd, 1 H). Anal. Calcd for $C_{24}H_{17}BrN_2O_2$: C, 64.72; H, 3.84; N, 6.29. Found: C, 64.85; H, 4.14; N, 6.51.

1,4-Diphenyl-6,11-dihydropyridazino[1,2-*b*]phthalazine-6,11-dione (2a). A well-pulverized sample of **4** (650 mg) was placed in a Buchi rotating oven (KGR-50) and heated to 110 °C in vacuo (1 mmHg). After 20 min it was removed, repulverized, and reheated for 20 min further under the same conditions. The color changed gradually from light yellow to brown. It was chromatographed on silica gel (20 g). Elution with chloroform gave **2a** first as an orange solid, which was triturated with petroleum ether and crystallized from ethanol (200 mg, 65%): mp 192–194 °C; UV λ_{max} 402 nm (ϵ 14 700), 262 (58 000); IR 1650 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.32 (dd, 2 H), 7.89 (dd, J = 5.8, 3.3 Hz, 2 H), 7.15–7.34 (m, 10 H), 6.12 (s, 2 H); mass spectrum; m/e (relative intensity) 364 (M^+, 16), 335 (100), 205 (33), 167 (14), 102 (30), 77 (21). Anal. Calcd for $C_{24}H_{16}N_2O_2$: C, 79.11; H, 4.43; N, 7.69. Found: C, 78.81; H, 4.57; N, 7.41.

Further elution with chloroform gave 1,4-diphenylpyridazine (**5**), mp 222 °C (lit.[5] mp 222 °C).

Photolysis of 2a. Compound **2a** (300 mg) was partly dissolved in methanol (300 mL), and the stirred mixture was irradiated under nitrogen, they using a Hanovia 450-W high-pressure immersion lamp in a water-cooled Pyrex vessel. After 50 min, a light yellow homogeneous solution was formed (85% conversion) and was evaporated. The residue was treated with ether, which dissolved the remaining starting material. Crystallization from ethanol afforded 180 mg (70%) of **7**: mp 203–205 °C; IR 1730 cm^{-1} (C=O); NMr 7.30–7.95 (m, 14 H), 5.93 (d, 1 H), 5.40 (d, J = 4.1 Hz); mass spectrum, m/e (relative intensity) 364 (M^+, 1), 335 (100), 233 (50), 205 (35), 141 (80), 130 (11), 102 (49), 77 (30);

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Table I. Crystallography Data for 7

formula	$C_{24}H_{16}O_2N_2$
M	364.4
space group	$P2_1/c$
a, Å	9.688 (3)
b, Å	15.628 (3)
c, Å	12.399 (3)
β, deg	106.37 (2)
V, Å^3	1801.2 (9)
Z	4
ρ, g cm^{-3}	1.34
μ(Mo Kα), cm^{-1}	0.49
no. of unique reflections	2705
reflections used, $>2\sigma(I)$	2160
R	0.054
R_w	0.071
w	$(\sigma_F^2 + 0.000568F^2)^{-1}$

Anal. Calcd for $C_{24}H_{16}N_2O_2$: C, 79.11; H, 4.43; N, 7.69. Found: C, 78.89; H, 4.48; N, 7.36.

1-Ethoxy-1,4-diphenyl-1,4,6,11-tetrahydropyridazino[1,2-*b*]phthalazine-6,11-dione (6). Compound 4 (100 mg) was dissolved in ethanol (20 mL) by heating to reflux. On cooling, compound 6 crystallized out (60 mg, 67%): mp 240–241 °C; IR 1645 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.32–7.26 (m, 14 H), 6.47 (d, J = 1.9 Hz), 5.80 (d, J = 6.5 Hz), 4.46 (dd, 1 H), 3.73 (q, J = 6.9 Hz, 2 H), 1.23 (t, 3 H); mass spectrum, m/e (relative intensity) 410 (M^+, 14), 306 (10), 236 (100), 218 (10), 133 (11), 130 (35), 115 (22), 104 (50), 91 (21), 77 (63). Anal. Calcd for $C_{26}H_{22}N_2O_3$: C, 76.08; H, 5.40; N. 6.82. Found: C, 75.71; H, 5.78; N, 6.91.

X-ray Crystal Structure Analysis of 7.[9] Data were measured on an Enraf-Nonius Cad-4 automatic diffractometer. Mo K_α (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The standard CAD-4 centering, indexing, and data collection programs were used. The unit cell dimensions were obtained by a least-squares fit of 25 centered reflections in the range of $10 \leq \theta \leq 14°$.

Intensity data were collected by using the ω–2θ technique to a maximum 2θ of 50°. The scan width, $\Delta\omega$, for each reflection was $(0.80 + 0.35 \tan \theta)°$. An aperture with a height of 4 mm and a variable width, calculated as $(2 + {}^1/_2 \tan \theta)$ mm, was located 173 mm from the crystal. Reflections were first measured with a scan of 8.24°/min. The rate for the final scan was calculated from the preliminary scan results so that the ratio $I/\sigma(I)$ would be at least 40 and the maximum scan time would not exceed 90 s. If in a preliminary scan $I/\sigma(I) < 2$, this measurement was used as the datum. Scan rates varied from 1.03 to 8.24°/min. Of the 96 steps in the scan, the first and the last 16 steps were considered to be background. During data collection the intensities of three standard reflections were monitored after every hour of X-ray exposure. No decay was observed. In addition, three orientation standards were checked after 100 reflections to check the effects of crystal movement. If the standard deviation of the h, k, and l values of any orientation reflection exceeded 0.06, a new orientation matrix was calculated on the basis of the recentering of the 25 reference reflections.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the Multan direct method analysis.[10] After several cycles of refinements[11] the positions of the hydrogen atoms were found and added with a constant isotropic temperature factor of 0.05 Å^2 to the refinement process. Refinement proceeded to convergence by minimizing the function $\Delta w(|F_o| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 0.2 e/Å^3 scattered about the unit cell without a significant feature.

The discrepancy indices, $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ are presented with other pertinent crystallographic data in Table I.

Registry No. 2a, 102725-66-6; **3**, 82141-12-6; **4**, 102725-63-3; **5**, 891-22-5; **6**, 102725-64-4; **7**, 102725-65-5; (*E*,*E*)-PhCH=CHCH=CHPh, 886-65-7; $HOCH_2CH_3$, 64-17-5; phthalhydrazide, 253-52-1.

Supplementary Material Available: Complete X-ray data of 7, including positional and thermal parameters, bond distances and angles, and molecular structure (8 pages). Ordering information is given on any current masthead page.

(9) We wish to thank Dr. S. Cohen for this analysis.

(10) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. H. "Multan 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", Universities of York, England, and Louvain, Belgium.

(11) All crystallographic computing was done on a Cyber 74 computer at the Hebrew University of Jerusalem, using the Shelx 1977 structure-determination package.

1,3-Dipolar Cycloadditions of Nitrones Derived from the Reaction of Acetylenes with Hydroxylamines

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A study of the reaction of hydroxylamines with a variety of acetylenes has been carried out. Methylhydroxylamine readily reacts with methyl propiolate to give methyl 4-carbomethoxy-2-methyl-4-isoxazolidine-3-acetate. Further heating of this material results in the formation of *N*-methyl-2,4-dicarbomethoxypyrrole by a mechanism which involves homolysis of the O–N linkage. The transient aziridine which is suggested to be formed reacts further to give the pyrrole. Formation of the isoxazolidine ring is suggested to proceed by addition of the hydroxylamine onto the triple bond followed by a proton shift to give a nitrone intermediate. This species undergoes 1,3-dipolar cycloaddition across the triple bond. Support for this mechanism was obtained from the reaction of *N*-phenylhydroxylamine with a variety of acyl- and aryl-substituted alkynes bearing a neighboring π-bond. With these systems, the initially formed nitrone was found to undergo smooth intramolecular dipolar cycloaddition to give a variety of substituted isoxazolidines in synthetically useful yields.

The 1,3-dipolar cycloaddition of a nitrone with an olefin is an extremely powerful, yet mild, means of producing carbon–carbon bonds as well as carbon–oxygen and carbon–nitrogen bonds.[1-6] The ring constructive power of this reaction is now well appreciated and has been employed by numerous groups in the total synthesis of al-

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