17.

Sodium–Pentyl Alcohol Reduction of 21 and 24. The lactone 21 (200 mg) was subjected to reduction in the manner described for 20. Usual workup followed by column chromatography over silica gel afforded 18 (100 mg), mp and mmp 126 °C. Similarly 24 was transformed into 18.

Acknowledgment. We thank Professor Wasiur Rehman, Head, Chemistry, for the facilities and CSIR (New Delhi) for financial assistance (G.M. and I.A.K.).

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(9) As the initial product of oxidation reported by Fonken and Miles[2] seems to have been a mixture of 5 and 6, its acetate hydrolysis would only have given another mixture of isomeric hydroxy lactones 7 and 8. This was shown to be the case as revealed by a mixture melting point determination of a mixture of 7 and 8 in the ratio of 1:1, which corresponded with the reported[2] melting point for 7.
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(13) From the melting point range (158–164 °C) of an admixture of isomeric lactones 20 and 21, which is very close to the melting point of 20 reported[3] earlier, there appears no doubt that the reported lactone 20 was, in fact, a mixture of 20 and 21.
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(15) A mixture of 23 and 24 in the ratio of their respective yields melted at 177–179 °C corresponding to the melting point reported[3] for 23. It clearly indicates that the earlier reported lactone 23 was a mixture of 23 and 24.

Rotational Deactivation in the Triplet Photochemistry of 5,5-Diphenylcyclohepta-1,3-diene[1a]

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The importance of rotational deactivation on the excited-state processes of numerous systems has now been established.[2,3] An early example illustrating this phenomenon was the divergent triplet chemistry of the exocyclic diene 1[4] vs. the endocyclic diene 2.[5] Thus, while 1 was unreactive in the triplet state, 2 undergoes facile rearrangement to a ca. 90:10 mixture of 3 and 4 ($\Phi = 0.24$). To examine the effect of ring size on the
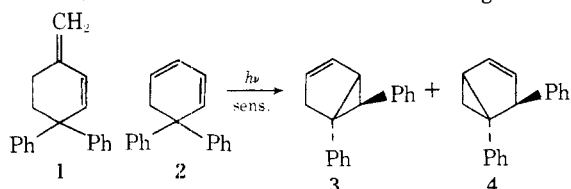
Table I. Quantum Yields for Irradiation of 5,5-Diphenylcyclohepta-1,3-diene (5)

| Run	Conc of diene $\times 10^{-3}$ M	Sensitizer	λ (nm)	mE absorbed	Φ_{dis}[b]	Φ_{app}
1[a]	19.6	2-Acetonaphthone	345	0.068	0.30	0.25
2	19.6	Benzophenone	345	0.069	0.30	0.20
3[a]	20.6	None	255	0.039	0.42	0.38

[a] These values are an average of two determinations. [b] Conversions of 5–8% were utilized for these measurements.

triplet chemistry of endocyclic dienes, we have prepared 5,5-diphenylcyclohepta-1,3-diene (5) and studied its singlet and triplet photochemistry. The change from the six-membered ring of 2 to the seven-membered ring of 5 has a dramatic effect on the triplet photochemistry of the endocyclic diene.[6]

The required diene 5 was synthesized from the epoxide 6 as outlined below. The singlet chemistry of 5 was studied first,
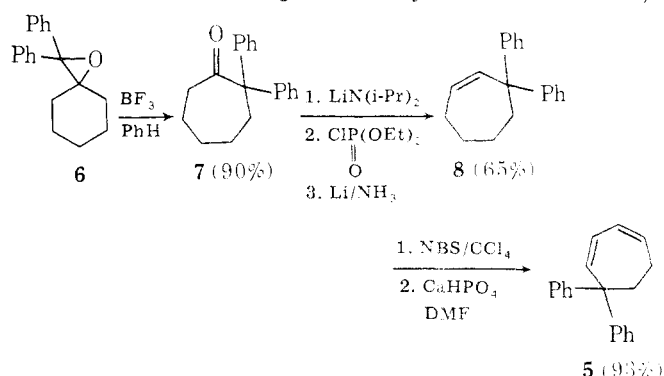
since phenyl migration would allow a comparison of the efficiency of the Woodward–Hoffmann allowed product 9 with that of the forbidden product 10.[5a] Direct preparative irradiation of 5 in cyclohexane with Vycor-filtered light afforded 59% of an isomeric hydrocarbon. The NMR spectrum of the material showed two vinyl protons at δ 5.92 (d, $J = 3$ Hz, 1 H) and 5.52 (m, 1 H), in addition to two broad one-hydrogen singlets at δ 3.95 and 3.30 and aromatic absorption. The coupling constant was suggestive of a cyclobutene fragment;[7] thus, structure 11 was favored. This structure assignment was
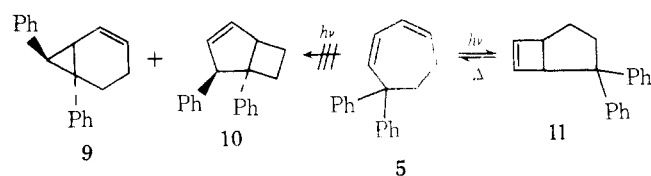
confirmed by pyrolysis of 11 at 500 °C to afford 5 (67%), a known process for cyclobutenes.[8] The preparative sensitized reaction of 5 using 2-acetonaphthone as sensitizer again afforded 11 as the major product (68% isolated) after chromatography on neutral alumina.

For comparison of the efficiencies of these reactions, the quantum yields for the 2-acetonaphthone- and benzophenone-sensitized reactions as well as that for the direct excitation were measured. For both the singlet and triplet excited state, the cyclobutene 11 is formed with reasonable efficiency.

While the photoproducts from both direct and sensitized irradiations are the same, their mechanism for formation is probably different. The low intersystem crossing efficiency in the excited diene together with the well-precedented excited singlet-state diene–cyclobutene conversion suggest the

5 → 11 conversion in the singlet state occurs via the electrocyclic ring-closure route. For the sensitized reaction, decay of the twisted diene triplet state to a highly strained cis–trans isomer followed by rapid ring closure to the cyclobutene appears most reasonable. This route has been rigorously established for the conversion of triplet 1,3-cyclooctadiene to bicyclo[4.2.0]oct-6-ene by isolation of the cis–trans isomer[9a,b] and has been suggested for the sensitized formation of the respective cyclobutene from 3,5-cycloheptadienone.[9c] The absence of di-π-methane products in the triplet chemistry of 5 indicates that the seven-membered ring allows sufficient flexibility for rotational deactivation to be the dominant pathway for the excited triplet state. A comparison of the direct irradiation products of 2 vs. 5 suggests that both the Woodward–Hoffmann allowed cyclohexadiene ring opening (i.e., 2) and cycloheptadiene ring closure (i.e., 5) are preferred over the di-π-methane rearrangement in the spin-paired reactant.

Experimental[10] Section

2,2-Diphenylcycloheptanone (7). To a benzene solution (25 mL) of 2.5 g (9.5 mmol) of cyclohexylidenediphenylmethane epoxide was added 1.3 mL of freshly distilled boron trifluoride etherate, the reaction mixture being protected from moisture. After stirring for 1 h at room temperature, the reaction mixture was decomposed with water (20 mL) and worked up as usual to afford a solid which was recrystallized from ethanol to yield in two crops 2.23 g (90%) of the desired 2,2-diphenylcycloheptanone (7): mp 92–94 °C (lit.[11] 92–94 °C).

3,3-Diphenylcycloheptene (8). To a lithium diisopropylamide solution [100 mL of THF, 2.05 g (0.020 mol) of diisopropylamine, and 11.55 mL of 1.82 M methyllithium] was added 5.24 g (0.02 mol) of 7 in 25 mL of THF. After 30 min, 30 mL of N,N,N',N'-tetramethylethylenediamine was added followed by 3.79 g (0.02 mol) of diethylchloro phosphate. After stirring for 18 h at room temperature workup in the usual manner afforded a clear colorless oil which was chromatographed on silica gel (2.6 × 40 cm column slurry-packed in 10% ether–hexane). Elution proceeded as follows: 250 mL, 10% ether–hexane, nil; 1000 mL, 10% ether–hexane, 1.1 g of recovered 2,2-diphenylcycloheptanone; 250 mL, 10% ether–hexane, nil; 150 mL, ether, nil; 600 mL of ether, 4.99 g (62% overall, 79% based upon recovered starting material) of the desired product as a colorless oil: IR (neat) 3.45 (s), 6.10 (w), 6.30 (w), 6.78 (m), 6.92 (m), 7.20 (w), 7.32 (w), 7.80 (s, br), 8.50 (s), 8.90 (s), 9.62 (s, br), 10.20–10.60 (s, br), 10.90 (s), 11.13 (s), 11.43 (m), 12.75 (m), 12.40 (m, br), 12.58 (m), 13.35 (s, br), 14.42 (s, br) μm; NMR (CCl₄) δ 7.22 (s, 10 H), 6.15–5.90 (m, 1 H), 3.83–3.30 (pent, 4 H, J = 7 Hz), 2.7–2.4 (m, 2 H), 2.4–2.0 (m, 4 H), 1.65–1.25 (m, 4 H), and 1.06 (t, 6 H, J = 7 Hz).

The phosphate as obtained was dissolved in 45 mL of THF and 175 mL of ammonia and reduced by slow addition of 0.245 g (0.035 mol) of lithium wire. The reaction was quenched with saturated ammonium chloride, diluted with water, and worked up in the standard manner. Molecular distillation (125 °C/0.15 mm) yielded 2.47 g (83%) of 3,3-diphenylcycloheptene as a colorless oil: IR (neat) 3.25 (m), 3.36 (s), 6.23 (m), 6.73 (s), 6.95 (s), 9.63 (m), 13.35 (s), and 14.35 (2) μm; NMR (CCl₄) δ 7.17 (s, 10 H), 5.90 (m, 2 H), 2.57–2.3 (m, 2 H), 2.3–2.0 (m, 2 H), and 1.7–1.4 (m, 4 H).

Exact mass measurement calculated: 248.15649; observed: 248.15691.

5,5-Diphenylcyclohepta-1,3-diene (5). To a solution of 2.47 g (10 mmol) of 8 in 50 mL of carbon tetrachloride was added 1.87 g (10.05 mmol) of N-bromosuccinimide and 3–4 mg of benzoyl peroxide, and the solution was refluxed for 1 h. The original yellow solution that contained the N-bromosuccinimide as an insoluble solid on the bottom of the flask was clear and contained a white solid (succinimide). After filtration and solvent removal in vacuo, a clear oil was isolated and characterized spectrally: IR (neat) 3.28 (w), 3.38 (m), 6,24 (w), 6.76 (m), 6.96 (m), 8.26 (w), 8.48 (w), 8.76 (w), 9.88 (w), 10.06 (w), 11.23 (w), 12.86 (s), 13.36 (s), and 14.46 (s) μm; NMR (CCl₄) δ 7.17 and 7.06 (10 H), 5.95 (s with shoulder at δ 6.0, 2 H), 4.9–4.65 (m, br, 1 H), 3.2–2.3 (m, 2 H), and 2.3–1.4 (m, 4 H).

The mixture of diphenylcycloheptenyl bromides was dissolved in 50 mL of dimethylformamide containing 2.72 g (0.02 mol) of calcium hydrogen phosphate, and the solution was stirred at 80 °C for 12 h. After cooling, the reaction mixture was poured into 200 mL of water and worked up as usual. Molecular distillation (85 °C/1 mmHg) afforded 2.31 g of clear, colorless 5, greater than 99% pure as analyzed

by VPC (25 ft × ⅛ in., 5% SE-30 on 60/80 Chrom G, column temp 200 °C): IR (neat) 3.28 (w), 3.39 (w), 6.24 (w), 6.75 (w), 6.97 (w), 9.75 (w, sh), 9.82 (w), 11.92 (w), 13.44 (s), 14.39 (s), and 14.75 (m, sh) μm; NMR (CCl₄) δ 7.40–7.10 (d, 10 H), 6.0–5.7 (complex q, 4 H, J = 4 Hz), 2.87 (d, 2 H, J = 4 Hz), 2.49 (complex t, J = 7 Hz, 1 H), and 2.00 (complex d, 1 H).

Anal. Calcd for C₁₉H₁₈: C, 92.64; H, 7.36. Found: C, 92.15; H, 7.68.

Sensitized Irradiation of 5,5-Diphenylcyclohepta-1,3-diene (5). A mixture of 0.4635 g (1.88 mmol) of the diene and 1.520 g of 2-acetonaphthone in 225 mL of cyclohexane was irradiated for 1 h in a stirred reactor under nitrogen with Pyrex-filtered light from a 450-W Hanovia medium-pressure source. The reaction was monitored by VPC analysis (13 ft × ⅛ in., 5% SE-30 on 60/80 Chrom G, column temp 200 °C). After solvent removal in vacuo, the resulting oil was chromatographed over neutral alumina (2.5 × 33 cm). Elution proceeded as follows: petroleum ether (30–60 °C), 750 mL, nil; 1825 mL, 0.3160 g (68%) of 2,2-diphenylbicyclo[3.2.0]hept-6-ene (11) 750 mL, 0.0740 g of material consisting of the major photoproduct 11 and an unidentified photoproduct; 750 mL, 0.0802 g of material consisting of a mixture of photoproduct, starting diene, and a high-molecular-weight material. The cyclobutene 11, obtained as white needles (EtOH), showed: mp 56–57 °C; IR (KBr) 3.23 (m), 3.36 (s), 6.25 (m), 6.73 (s), 6.97 (s), 7.73 (m), 9.78 (m), 11.77 (m), 12.08 (m), 12.93 (s), 13.25 (s), 13.46 (s), 13.96 (s), and 14.35 (s) μm; NMR (CCl₄) δ 7.11 (d, 10 H), 5.92 (d, 1 H, J = 3 Hz), 5.52 (m, poorly resolved d, 1 H, J = 3–4 Hz), 3.95 (m, 1 H), 3.30 (m, 1 H), 2.87–2.45 (m, 1 H), 2.15–1.77 (m, 1 H), and 1.65–1.10 (m, 2 H).

Anal. Calcd for C₁₉H₁₈: C, 92.64; H, 7.36. Found: C, 92.50; H, 7.32.

Direct Irradiation of 5,5-Diphenylcyclohepta-1,3-diene (5). A stirred solution of 0.5760 g (2.34 mmol) of 5 in 225 mL of purified cyclohexane was irradiated for 1 h with Vycol-filtered light from a Hanovia 450-W medium-pressure source in a nitrogen atmosphere. The reaction was monitored by VPC analysis (0.125 in. × 13 ft, 5% SE-30 on 60/80 Chrom G, column temp 200 °C). After solvent removal in vacuo, the reaction mixture was chromatographed over neutral alumina (2.0 × 31 cm column slurry packed in petroleum ether). Elution proceeded as follows: 250 mL, 30–60 °C, petroleum ether, nil; 375 mL, petroleum ether, 0.340 g (59%) of crystalline 2,2-diphenylbicyclo[3.2.0]hept-6-ene; 600 mL, 0.0291 g of material consisting of the major photoproduct and an unidentified photoproduct; 375 mL, 0.0486 g of material consisting mainly of starting material and a high-molecular-weight material not characterized. The IR and NMR spectra of the photoproduct were identical with that isolated from the sensitized irradiation of 5,5-diphenylcyclohepta-1,3-diene.

Pyrolysis of 2,2-Diphenylbicyclo[3.2.0]hept-6-ene (11). A solution of 99.4 mg (0.40 mmol) of 11 in 50 mL of benzene was pyrolyzed at 550 °C by the slow addition of the solution (ca. 2 h) to a 3 × 90 cm vertical glass column packed 45 cm with 6-mm glass beads under a stream of nitrogen. Analysis by VPC (6 ft × ⅛ in., 3% SE-30 on 60/80 Chrom G, column temp 200 °C) indicated unreacted starting material and one product which had an identical retention time with 5. After solvent removal in vacuo, the resulting oil was molecularly distilled (90 °C/0.02 mm) to yield 95.8 mg (96%) of a yellow oil consisting of a 7:3 mixture of 5 and 11, as analyzed by NMR. Characterization of the diene was rigorously established by comparison of the IR of material purified by preparative VPC (10 ft × 0.25 in., 5% SE-30 on Chrom W, column temp 200 °C) with that of authentic diene.

Quantum Yields. The measurements were essentially done as previously described using potassium ferrioxalate actinometry.[5a] Analysis of these quantum-yield runs was by VPC (13 ft × ⅛ in., 5% SE-30 Chrom G, column temp 185 °C). The results of the determinations are given in the table.

Registry No.—5, 57304-01-5; 6, 63865-83-8; 7, 50390-71-1; 8, 63865-84-9; 11, 63865-85-0; 7,7-diphenylcyclohept-1-en-1-ol diethyl phosphate, 63904-40-5; 3-bromo-7,7-diphenylcyclohept-1-ene, 63865-86-1; 4-bromo-7,7-diphenylcyclohept-1-ene, 63865-87-2; diethylchloro phosphate, 814-49-3.

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(10) IR spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer. The mass spectra were measured with an AEI MS-9 mass spectrometer. NMR spectra were measured at 60 MHz using tetramethylsilane as internal standard. Elemental analyses were determined by Scandinavian Microanalytical Laboratory, Herlev, Denmark. All irradiations were performed in an atmosphere of purified nitrogen. Workup as usual refers to extraction with ether, washing with dilute acid or base if appropriate, washing with saturated brine solution, drying over calcium sulfate, and removal of solvent in vacuo.

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Photochemistry of Some Pteridine *N*-Oxides[1]

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Purine *N*-oxides, like many heterocyclic aromatic *N*-oxides,[2] undergo deoxygenation and migration of the oxygen to the adjacent carbon under the influence of ultraviolet light.[3-6] 1-Hydroxyxanthine (**1**), which has an *N*-hydroxyimide structure, shows the expected photoreduction, but it also undergoes an unusual 1:3 isomerization of the 1-hydroxyl group to afford 3-hydroxyxanthine[7] (**3**). It was suggested that the isomerization of **1** to **3** proceeds via the enol nitrone (**2**) and two successive oxazirane migrations (Scheme I).

Recently, the pteridine analogues of **1** and **3**, i.e., 3-hydroxy-2,4-dioxo-1,2,3,4-tetrahydropteridine (**4**) and its 1-hydroxy isomer **6**, were reported.[8,9] To investigate whether a pteridine would undergo the unusual *N*-hydroxy rearrangement, we examined the possible photochemical conversion of **4** to **6**. However, the main photoproduct from **4** over the pH range 2 to 12 (Figure 1) was the reduction product **5**, together with a trace of ring-opened compound. Under the same conditions of irradiation, the possible rearrangement product **6** showed little change, although with prolonged ir-
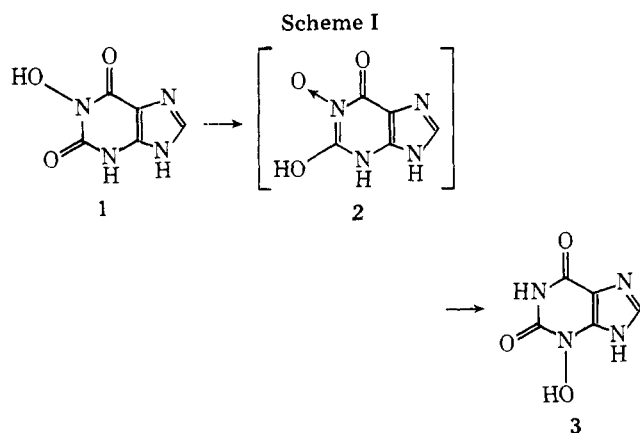
Scheme I

1   **2**

3

Table I. 3-Hydroxy-2,4-dioxo-1,2,3,4-tetrahydropteridine

pH	Species	λ_{max}, nm, $\epsilon \times 10^{-3}$	pK_a
2	0	231 (13.7)	
		322 (7.4)	
			5.61 ± 0.1^a
6.8	−1	217 (15.7)	
		243 (8.7)	
		327 (8.0)	
		338^b (7.5)	
			9.0 ± 0.3
12	−2	217 (17.5)	
		261 (19.0)	
		356 (8.4)	

^{a} pK_as calculated at isosbestic points of isosbestic spectra. ^{b} Shoulder.

radiation it could be slowly reduced to **5** (Φ 5.9 $\times$ 10^{-5} at pH 7.0). The hydroxyl isomerization of **1** was deduced to occur via the singlet state.[5] The lack of *N*-hydroxyl isomerization by the pteridine **4** indicates that the apparent structural similarity of the pyrimidine ring in **1** and **4** is not paralleled by the formation of a tautomer in the excited singlet comparable to **2**. The absence of this tautomer in the excited state precludes *N*-hydroxyl isomerization and the only photoprocess then observed is deoxygenation via the triplet, i.e., **4** to **5**. That process is quite sensitive to change in pH (Figure 1). Changes in pH from 3 to 8 did not affect the quantum yield for the conversion of **4** to **5**. Decreasing the pH from 3 to 1 caused a steep decline in the quantum yield for photoreduction of **4**, and at pH 1 there was no reduction of **4**. This effect of acid is similar to that on the photoreactions of quinoline *N*-oxide[10] and isoquinoline *N*-oxide.[11] Between pH 8 and 10 the quantum yield of reduction of **4** decreased, and then remained unchanged with further increases in pH. Significantly, the inflection in the curve in Figure 1 at pH 9.0 coincides with one of the pK_as of **4**. In contrast to the relatively small spectral changes accompanying the first ionization of **4** (pK 5.6), the second ionization (pK 9.0) is associated with the appearance of a band of high extinction at 261 nm. These data indicate that the sequence of ionization of **4** is N-1 H to **4a**, and then N-3 OH to **4b**. This ionization sequence parallels that of **1**[12,13] (N-3 H, N-1 OH). The close correspondence of the inflection point in Figure 1 with the second ionization pK_a to **4b** would accord with the assignment of positions of ionization and indicates that photoreduction of the *N*-hydroxy species, **4** or **4a**, has a higher quantum efficiency than does that of the enolate anion **4b**. In contrast to the relatively large effects of changes in pH and ionic form on the quantum efficiency for photoreduction observed with **4**, changes in the ionic form of **6** (pK_as 6.50 and 9.35)[9] did not greatly affect the quantum yield for the appearance of **5**.

The photoreactivity of 1-hydroxy-2-oxo-1,2-dihydropteridine (**7**)[9] was also examined. In contrast to the facile photoreduction of 3-hydroxy-2-oxopurine,[14] neither the anion nor the neutral molecule of **7** yielded the anticipated photoreduction product, 1,2-dihydro-2-oxopteridine (**10**). Instead, both produced the C-4 oxidation product **5** in 9 and 38% yields, respectively, as the only UV-absorbing product after irradiation (Corex filter) for 4 h. Irradiation of the neutral molecule of **10** under the same conditions also produced **5** (18%). This indicates that the deoxygenation process at N-1 of **7** is not correlated with oxidation at C-4. Both **7** and **10** form stable hydrates, **8** and **9** (Scheme II), in solution, and air oxidation of **9** is known to yield **5**.[15] These observations suggest that the photochemical formation of **5** probably proceeds via the hydrate **9**. No oxidation of **8** and **9** to **5** occurred under the ex-