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Steroid *B*-Ring Lactones: a Reinvestigation

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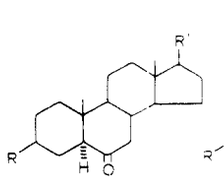
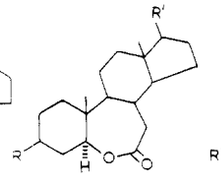
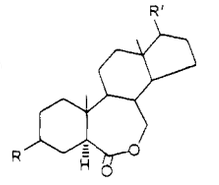
In the Baeyer–Villiger oxidation, the migratory aptitude of alkyl groups decreases in the order tertiary, secondary, primary, and methyl. This tendency is a function of the ability of the migrating group to support a positive charge in the transition state.[1] Accordingly, Fonken and Miles[2] showed that the peracid oxidation of 6-keto steroids is a stereospecific process leading exclusively to 6-oxa steroids by preferential migration of the more substituted C-5. Subsequently, we also reported similar observations.[3] Lately we noted that 6-keto-5α-β-sitostanyl acetate (**1**) on perbenzoic acid (1 molar equiv) oxidation gave the anticipated 6-oxa lactone **2** as well as its 7-oxa isomer **3** arising through migration of the less substituted C-7,[4,5] structures being established spectroscopically beyond doubt. This apparently unusual observation forced us to reexamine the reactions which had led to previous conclusions.[2,3]



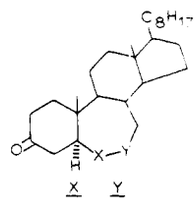
	R	R′
1	OAc	$C_{10}H_{21}$
4	OAc	C_8H_{17}
9	OH	C_8H_{17}
16	H	C_8H_{17}
19	Cl	C_8H_{17}
22	Br	C_8H_{17}



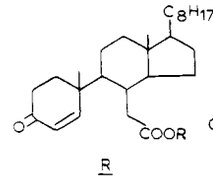
	R	R′
2	OAc	$C_{10}H_{21}$
5	OAc	C_8H_{17}
7	OH	C_8H_{17}
17	H	C_8H_{17}
20	Cl	C_8H_{17}
23	Br	C_8H_{17}



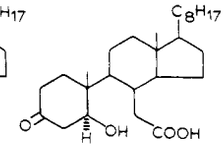
	R	R′
3	OAc	$C_{10}H_{21}$
6	OAc	C_8H_{17}
8	OH	C_8H_{17}
18	H	C_8H_{17}
21	Cl	C_8H_{17}
24	Br	C_8H_{17}



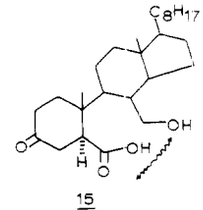
	X	Y
10	O	CO
11	CO	O



	R
12	H
13	CH_3



14



15

Similarly, 5α-cholestan-6-one (**16**) provided the isomeric lactones **17** and **18**, and its 3β-halogen analogues **19** and **22** furnished **20, 21,** and **23, 24,** respectively. On sodium–pentyl alcohol reduction **20** and **23** afforded **17,** while **21** and **24** were transformed into **18.**

An interesting feature of the NMR spectra of both 6- and 7-oxa lactones was the appearance of one of the C-7a protons as a broadened singlet and the other as a doublet with J = 3–5 Hz. Examination of the Dreiding models of the isomeric lactones revealed that the dihedral angle between the planes of C-8–βH (axial) and C-7a–βH (pseudoequatorial) is almost 90°, which may account for its (C-7a–βH) appearance as a broadened singlet, as splitting will be almost negligible. On the other hand, C-8–βH splits C-7a–αH (pseudoaxial) into a doublet.

The point which emerges from this restudy is that a secondary carbon (C-7) competes quite effectively with a tertiary one (C-5) for migration to an electron-deficient oxygen in the Baeyer–Villiger oxidation of 6-keto steroids. In fact, in the presence of C-3 substituents, migration of C-7 is more pronounced than in their absence. Further, the bulk of the C-3 substituent seems to have a pronounced effect on the preferred migratory aptitude of C-7 in relation to C-5, as is evidenced by the behavior of the chloro (**19**) and the bromo (**22**) ketones toward perbenzoic acid.

Experimental Section

All melting points are uncorrected. IR spectra were determined in Nujol with a Perkin-Elmer 237 spectrophotometer. NMR spectra were run in $CDCl_3$ on a Varian A60 instrument with Me_4Si as the internal standard. UV spectra were obtained in methanol with a Beckman DK 2 spectrophotometer. TLC plates were coated with silica gel. A 20% aqueous solution of perchloric acid was used as the spraying agent. Light petroleum refers to a fraction of bp 60–80 °C. Anhydrous sodium sulfate was used as the drying agent. (IR: s, strong; w, weak. NMR: dd, double doublet; d, doublet; br, broad; s, singlet; mc, multiplet centred at; a, axial; e, equatorial.)

6-Oxa-*B*-homo-7-oxo-5α-β-sitostanyl Acetate (*2*) and 7-Oxa-*B*-homo-6-oxo-5α-β-sitostanyl Acetate (3). To a solution of 6-keto-5α-β-sitostanyl acetate (**1**) (obtained by acetylation, nitration, and zinc–acetic acid reduction of β-sitosterol) (2 g) in chloroform (30 mL) was added a chloroform solution of perbenzoic acid (1 molar equiv) and a few crystals of *p*-toluenesulfonic acid monohydrate as catalyst, and the reaction mixture was allowed to stand at room temperature for 1 week. The solvent was removed under reduced pressure and the residue extracted with ether. The ethereal solution was washed successively with water, $NaHCO_3$ solution (5%), and water and dried. Removal of the desiccant and the solvent provided a residue (ca. 2 g) which was chromatographed over silica gel (40 g) (each frac-

tion of about 25 mL was collected). Elution with light petroleum–ether (10:1) gave the unreacted **1** (500 mg), mp and mmp 120 °C. Elution with light petroleum–ether (6:1) afforded **3,** crystallized from light petroleum as shining needles (380 mg): mp 130–131 °C; IR 1740 s (CH_3COO), 1715 s (ε-lactone), 1250 s (acetate), 1210, 1040 cm^{-1} (C–O); NMR δ 4.66 (br, $w_{1/2}$ = 14 Hz, C-3–α*H*), 4.08 (br s, C-7a–β*H*), 3.98 (d, C-7a–α*H*, *J* = 3.5 Hz), 2.91 (dd, C-5–α*H*, $J_{a,a}$ = 11 Hz; $J_{a,e}$ = 5 Hz), 2.01 (s, CH_3COO), 0.9, 0.8, 0.7 (methyl protons). Anal. Calcd for $C_{31}H_{52}O_4$: C, 76.23; H, 10.65. Found: C, 76.37; H, 10.56. Further elution with light petroleum–ether (5:1) furnished **2,** crystallized from light petroleum (365 mg): mp 163–164 °C; IR 1740 s (CH_3COO), 1720 s (ε-lactone), 1240 s (acetate), 1040 cm^{-1} (C–O); NMR δ 4.75 (br, $W_{1/2}$ = 14 Hz, C-3–α*H*), 4.29 (dd, C-5–α*H*, $J_{a,a}$ = 11, $J_{a,e}$ = 5.5 Hz), 2.5 (br s, C-7a–β*H*), 2.43 (d, C-7a–α*H*, *J* = 3.5 Hz), 2.03 (s, CH_3COO), 0.9, 0.8, 0.7 (methyl protons). Anal. Calcd for $C_{31}H_{52}O_4$: C, 76.23; H, 10.65. Found: C, 76.33; H, 10.60.

3β-Acetoxy-6-oxa-*B*-homo-5α-cholestan-7-one (5) and 3β-Acetoxy-7-oxa-*B*-homo-5α-cholestan-6-one (6). Reaction of 3β-acetoxy-5α-cholestan-6-one[7] (**4**) (2 g) with perbenzoic acid was performed in the manner described for **1** to provide a semisolid material which was chromatographed over silica gel. Elution with light petroleum–ether (10:1) gave the unreacted **4** (450 mg), mp[7] and mmp 127 °C. Elution with light petroleum–ether (7:1) afforded **6,** crystallized from light petroleum as needles (460 mg): mp 181 °C; IR 1740 s, 1715 s, 1250 s, 1205, 1035 cm^{-1}; NMR δ 4.66 (br, $W_{1/2}$ = 14 Hz, C-3–α*H*), 4.1 (br s, C-7a–β*H*), 4.0 (d, C-7a–α*H*, *J* = 3.5 Hz), 2.92 (dd, C-5–α*H*, $J_{a,a}$ = 11, $J_{a,e}$ = 5 Hz), 2.03 (s, CH_3COO), 0.9, 0.8, 0.7 (methyl protons). Anal. Calcd for $C_{29}H_{48}O_4$: C, 75.65; H, 10.43. Found: C, 75.75; H, 10.33. Further elution with light petroleum–ether (6:1) gave **5,** crystallized from light petroleum (455 mg): mp 174 °C (lit.[2] mp 162–163 °C);[8] IR 1740 s, 1718 s, 1245 s, 1035 cm^{-1}; NMR δ 4.75 (br, $W_{1/2}$ = 14 Hz, C-3–α*H*), 4.29 (dd, C-5–α*H*, $J_{a,a}$ = 10, $J_{a,e}$ = 5.5 Hz), 2.52 (br s, C-7a–β*H*), 2.42 (d, C-7a–α*H*, *J* = 3.5 Hz), 2.03 (s, C*H*$_3$COO), 0.9, 0.8, 0.7 (methyl protons). Anal. Calcd for $C_{29}H_{48}O_4$: C, 75.65; H, 10.43. Found: C, 75.51; H, 10.47.

3β-Hydroxy-6-oxa-*B*-homo-5α-cholestan-7-one (7). A solution of **5** (250 mg) in 50 mL of methanolic NaOH (2%) was heated under reflux for 1 h. The solution was acidified with HCl and poured into water. The usual workup provided **7,** crystallized from light petroleum–ether (200 mg): mp 202 °C (lit.[2] mp 139–141 °C);[9] IR 3300 br (OH), 1718 s, 1225, 1025 cm^{-1}. Anal. Calcd for $C_{27}H_{46}O_3$: C, 77.51; H, 11.00. Found: C, 77.42; H, 11.07.

3β-Hydroxy-7-oxa-*B*-homo-5α-cholestan-6-one (8). The acetate function in **6** (250 mg) was hydrolyzed in the manner described for **5.** Subsequent workup gave **8,** crystallized from light petroleum (210 mg): mp 124 °C; IR 3430 br, 1715 s, 1195, 1060 cm^{-1}. Anal. Calcd for $C_{27}H_{46}O_3$: C, 77.51; H, 11.00. Found: C, 77.45; H, 10.90.

Baeyer–Villiger Oxidation of 3β-Hydroxy-5α-cholestan-6-one (9). The ketone **9**[7] (2 g) was treated with perbenzoic acid in the usual manner to provide a residue which was chromatographed over silica gel. Elution with chloroform–benzene (8:1) gave the unreacted **9** (345 mg), mp[7] and mmp 143 °C. Elution with chloroform furnished **8** (380 mg), mp and mmp 124 °C. Continued elution with the same solvent provided **7** (370 mg), mp and mmp 202 °C.

6-Oxa-*B*-homo-5α-cholestane-3,7-dione (10). The lactone **7** (300 mg) was dissolved in acetone (40 mL) and cooled below 10 °C in ice bath. Jones' reagent[6] (0.5 mL) was added slowly with continuous stirring. Water (40 mL) was added to it and the precipitate thus obtained was taken in ether. Usual workup provided **10,** crystallized from light petroleum–ether (260 mg): mp 191 °C; IR 1722 s, 1720 s, 1275, 1040 cm^{-1}. Anal. Calcd for $C_{27}H_{44}O_3$: C, 77.88; H, 10.57. Found: C, 77.93; H, 10.46.

Attempted Base-Catalyzed Hydrolysis of 11, 5, and 6. The lactone **11** was subjected to base-catalyzed hydrolysis and worked in the manner described by Fonken and Miles.[2] Immediate TLC of the residue showed two spots of about equal intensity (one lactone **11** and the other probably seco acid **15**). However, on standing the ethereal solution of the mixture at room temperature for some time (3–4 h), relactonization occurred, as was evident from a single spot (TLC) identical with lactone **11.** Efforts were made to separate them by column chromatography over silica gel, but **15** relactonized during the passage through silica gel, as elution afforded only the lactone **11.**

The aforesaid observations were noted for lactones **5** and **6** also, in which relactonized products **7** and **8** were obtained from **5** and **6,** respectively.

7-Oxa-*B*-homo-5α-cholestane-3,6-dione (11). The lactone **8** (300 mg) was treated with Jones' reagent[6] in the manner described for **10.** Subsequent workup afforded **11,** crystallized from light petroleum–ether as needles (250 mg): mp 195 °C; IR 1725 s, 1720 s, 1230, 1185, 1085 cm^{-1}. Anal. Calcd for $C_{27}H_{44}O_3$: C, 77.88; H, 10.57. Found: C, 77.80; H, 10.59.

3-Oxo-5,6-secocholest-4-en-6-oic acid (12). A solution of **10** (200 mg) in 40 mL of methanolic NaOH (5%) was heated under reflux for 2 h. The excess of methanol was removed under reduced pressure, and the residue was poured into water, acidified with dilute HCl, and extracted with ether. Usual workup provided **12** as a noncrystallizable oil (170 mg): UV 230 nm (ε 10 000); IR 3550–3200 br (**COOH**), 1725 s (**COOH**), 1675 s (C=C—C=O), 1610 w (C=C), 1180 cm^{-1}. Anal. Calcd for $C_{27}H_{44}O_3$: C, 77.88; H, 10.57. Found: C, 77.79; H, 10.50.

Methyl 3-Oxo-5,6-secocholest-4-en-6-oate (13). An ethereal solution of **12** (120 mg) was treated with an excess of an ethereal solution of diazomethane and allowed to stand for 10 min in the cold. Usual workup provided **13** as a noncrystallizable oil (110 mg): UV 230 nm (ε 9860); IR 1735 s (**COOCH$_3$**), 1680 s (C=C—**C=O**), 1615 w (C=C), 1190 cm^{-1} (methyl ester); NMR δ 6.75 (d, C-5–H, *J* = 10 Hz), 5.68 (d, C-4–H, *J* = 10 Hz), 3.6 (s, $COOCH_3$), 2.51 (mc, C-2–H_2 and C-7–H_2), 1.2, 0.9, 0.8, 0.66 (methyl protons). Anal. Calcd for $C_{28}H_{46}O_3$: C, 78.13; H, 10.69. Found: C. 78.16; H, 10.68.

6-Oxa-*B*-homo-5α-cholestan-7-one (17) and 7-Oxa-*B*-homo-5α-cholestan-6-one (18). Reaction of 5α-cholestan-6-one[10] (**16**) (2 g) with perbenzoic acid in the usual manner gave a solid residue which was chromatographed over silica gel. Elution with light petroleum–ether (14:1) gave the unreacted **16** (300 mg), mp[10] and mmp 98–99 °C. Elution with light petroleum–ether (11:1) provided **18,** crystallized from light petroleum as needles (250 mg): mp 126 °C; IR 1722 s, 1185, 1135, 1080 cm^{-1}; NMR δ 4.26 (br s, C-7a–β*H*), 4.16 (d, C-7a–α*H*, *J* = 3.5 Hz), 2.66 (dd, C-5–α*H*, $J_{a,a}$ = 10, $J_{a,e}$ = 5 Hz), 0.9, 0.8, 0.7 (methyl protons). Anal. Calcd for $C_{27}H_{46}O_2$: C, 80.59; H, 11.44. Found: C, 80.45; H, 11.39.

Continued elution with the same solvent system furnished **17,** crystallized from light petroleum as needles (760 mg): mp 155 °C (lit.[2] mp 143–144 °C);[11] IR 1720 s, 1275, 1035 cm^{-1}; NMR δ 4.16 (dd, C-5–α*H*, $J_{a,a}$ = 10, $J_{a,e}$ = 5 Hz), 2.5 (br s, C-7a–β*H*), 2.41 (d, C-7a–α*H*, *J* = 3.5 Hz), 0.9, 0.8 (methyl protons). Anal. Calcd for $C_{27}H_{46}O_2$: C, 80.59; H, 11.44. Found: C, 80.47; H, 11.51.

3β-Chloro-6-oxa-*B*-homo-5α-cholestan-7-one (20) and 3β-chloro-7-oxa-*B*-homo-5α-cholestan-6-one (21). 3β-Chloro-5α-cholestan-6-one[12] (**19**) (2 g) on treatment with perbenzoic acid in the usual fashion and subsequent workup gave a residue which was chromatographed over silica gel. Elution with light petroleum–ether (11:1) gave the unreacted **19** (540 mg), mp[12] and mmp 129 °C. Elution with light petroleum–ether (8:1) furnished **21,** crystallized from light petroleum as fine needles (350 mg): mp 145 °C; IR 1715 s, 1195, 1130, 1085, 735 cm^{-1}; NMR δ 4.09 (br s, C-7a–β*H*), 4.0d (C-7a–α*H*, *J* = 5 Hz), 3.70 (br, $W_{1/2}$ = 14 Hz, C-3–α*H*), 2.85 (dd, C-5–α*H*, $J_{a,a}$ = 11, $J_{a,e}$ = 5 Hz), 0.9, 0.8, 0.7 (methyl protons). Anal. Calcd for $C_{27}H_{45}O_2Cl$: C, 74.22; H, 10.30. Found: C, 74.35; H, 10.25. Further elution with light petroleum–ether (7:1) gave **20,** crystallized from light petroleum (345 mg): mp 185 °C (lit.[3] mp 167–168 °C);[13] IR 1718 s, 1280, 1045, 740 cm^{-1}; NMR δ 4.21 (dd, C-5–α*H*, $J_{a,a}$ = 11, $J_{a,e}$ = 5 Hz), 3.66 (br, $W_{1/2}$ = 14 Hz, C-3–α*H*), 2.5 (br s, C-7a–β*H*), 2.41 (d, C-7a–α*H*, J = 5 Hz), 0.9, 0.8, 0.7 (methyl protons). Anal. Calcd for $C_{27}H_{45}O_2Cl$: C, 74.22; H, 10.30. Found: C, 74.20; H, 10.34.

3β-Bromo-6-oxa-*B*-homo-5α-cholestan-7-one (23) and 3β-Bromo-7-oxa-*B*-homo-5α-cholestan-6-one (24). 3β-Bromo-5α-cholestan-6-one[14] (**22**) (2 g) was treated with perbenzoic acid in the usual manner to provide a residue which was chromatographed over silica gel. Elution with light petroleum–ether (12:1) gave the unreacted **22** (620 mg), mp[14] and mmp 124 °C. Elution with light petroleum–ether (8:1) afforded **24,** crystallized from light petroleum as fine needles (460 mg): mp 171 °C; IR 1712 s, 1190, 1130, 1080, 720 cm^{-1}; NMR δ 4.1 (br s, C-7a–β*H*), 4.01 (d, C-7a–α*H*, J = 5 Hz), 3.68 (br, $W_{1/2}$ = 14 Hz, C-3–α*H*), 2.84 (dd, C-5–α*H*, $J_{a,a}$ = 11, $J_{a,e}$ = 5 Hz), 0.9, 0.8, 0.7 (methyl protons). Anal. Calcd for $C_{27}H_{45}O_2Br$: C, 67.35; H, 9.35. Found: C, 67.42; H, 9.32. Further elution with light petroleum–ether (7:1) furnished **23,** crystallized from light petroleum (375 mg): mp 183 °C (lit.[3] mp 179 °C);[15] IR 1715 s, 1280, 1035, 720 cm^{-1}; NMR δ 4.2 (dd, C-5–α*H*, $J_{a,a}$ = 11, $J_{a,e}$ = 5 Hz), 3.70 (br, $W_{1/2}$ = 14 Hz, C-3–α*H*), 2.51 (br s, C-7a–β*H*), 2.41 (d, C-7a–α*H*, *J* = 5 Hz), 0.9, 0.8, 0.7 (methyl protons). Anal. Calcd for $C_{27}H_{45}O_2Br$: C, 67.35; H, 9.35. Found: C. 67.45; H, 9.36.

Sodium–Pentyl Alcohol Reduction of 20 and 23. The lactone **20** (200 mg) was dissolved in warm pentyl alcohol (10 mL) and to this solution was added sodium metal (1 g) in small portions with intermittent heating during 30 min. The solution was kept warm for an additional period of 2 h. When all the metal had dissolved, the reaction mixture was poured into cold water and worked up in the usual manner, followed by column chromatography over silica gel, to provide **17** (120 mg), mp and mmp 155 °C. In similar manner **23** afforded

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**.

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Registry No.—**1**, 63903-45-7; **2**, 63866-15-9; **3**, 63866-16-0; **4**, 1256-83-3; **5**, 20104-89-6; **6**, 20104-90-9; **7**, 20104-95-4; **8**, 20104-91-0; **9**, 1175-06-0; **10**, 20104-96-5; **11**, 20104-92-1; **12**, 63866-17-1; **13**, 63904-21-2; **16**, 570-46-7; **17**, 31239-55-1; **18**, 63866-18-2; **19**, 1056-93-5; **20**, 31239-53-9; **21**, 63866-19-3; **22**, 63866-20-6; **23**, 31239-57-3; **24**, 63866-21-7; diazomethane, 334-88-3.

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(8) An admixture of the isomeric lactones **5** and **6** in the ratio of 1:1 showed the melting point corresponding to the reported[2] melting point of **5**. It obviously indicates that the product obtained by Fonken and Miles[2] was a mixture of **5** and **6**.
(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**.
(10) C. W. Shoppee, R. H. Jenkins, and G. H. R. Summers, *J. Chem. Soc.*, 1657 (1958).
(11) A mixture of **17** and **18** in the ratio of 1:1 melted at 110–121 °C. However, when mixed in the ratio of the yield of **17** and **18**, the melting point was observed at 142–144 °C, corresponding to the melting point reported[2] for **17**.
(12) A. Windaus and O. Dalmer, *Ber.*, **52**, 162 (1919).
(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**.
(14) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 1786 (1952).
(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 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]

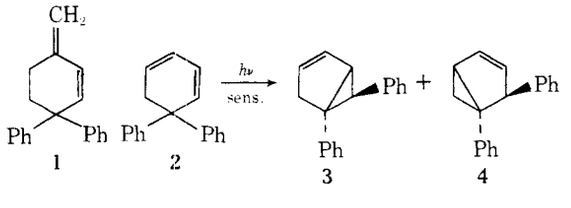
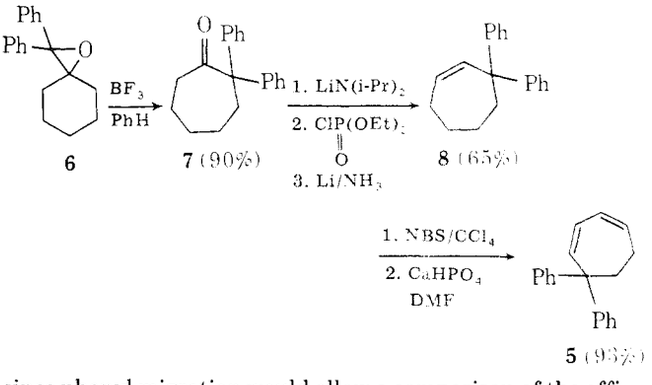


Table I. Quantum Yields for Irradiation of 5,5-Diphenylcyclohepta-1,3-diene (5)

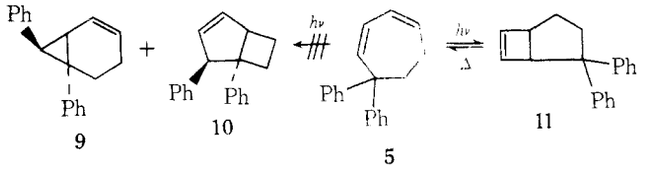
Run	Conc of diene $\times 10^{-3}$ M	Sensitizer	λ (nm)	mE absorbed	Φ_{dis}[b]	Φ_{app}
1[a]	19.6	2-Acetonaphthone	345	0.068	0.30	0.25
2	19.6	Benzophenone	345	0.069	0.30	0.20
3[a]	20.6	None	255	0.039	0.42	0.38

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

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