Tetrahedron. Vol. 28, pp. 2361 to 2367. Pergamon Press 1972. Printed in Great Britain

THE DYE-SENSITIZED PHOTOOXYGENATION OF 2-ETHYLIDENEBICYCLO[2.2.1]HEPT-5-ENE

W. R. ADAMS and D. J. TRECKER

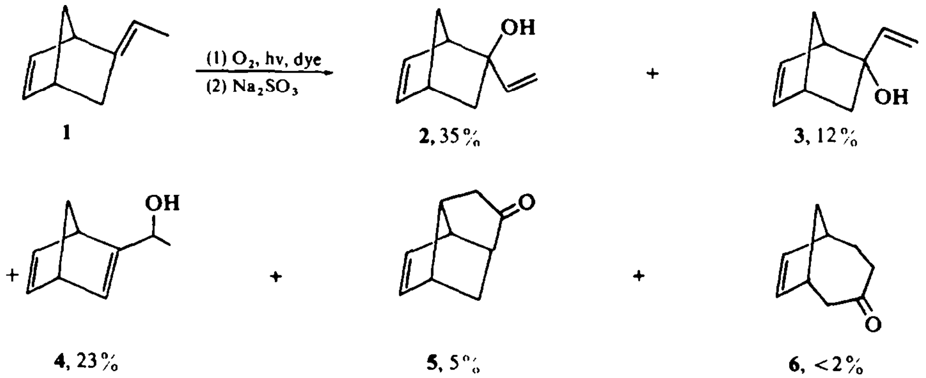
Research and Development Department, Union Carbide Corporation, Chemicals and Plastics Division,
South Charleston, West Virginia 25303

(*Received in the USA* 8 *November* 1971; *Received in the UK for publication* 10 *January* 1972)

Abstract—The mode of singlet oxygen attack on norbornene derivatives was probed *via* a study of the dye-sensitized photooxygenation of 2-ethylidenebicyclo[2.2.1]hept-5-ene (**1**). Reduction of the resulting allylic hydroperoxides provided the epimeric 2-hydroxy-2-vinylbicyclo[2.2.1]hept-5-enes (**2** and **3**) and 2-(1-hydroxyethyl)bicyclo[2.2.1]hept-2,5-diene (**4**), the relative yields of which were apparently controlled by steric factors. Also isolated were two novel multicyclic ketones, **5** and **6**, derived from thermal rearrangements of the primary oxidation products.

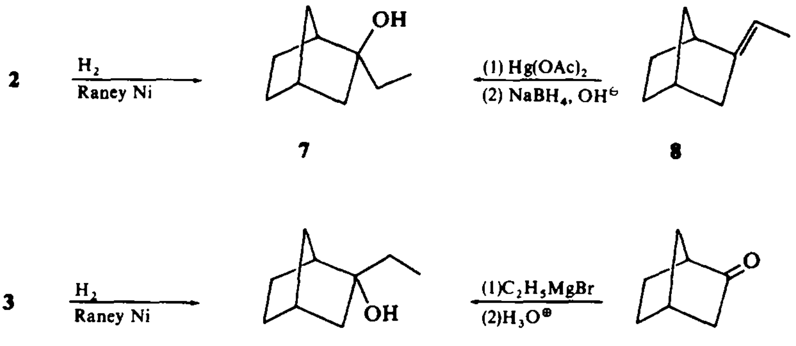
DYE-SENSITIZED PHOTOOXYGENATION of organic compounds represents a facile and selective method for introducing molecular oxygen into organic compounds. Three principal classes of reactions have been reported: (1) oxygenation of cyclic dienes, fused aromatic compounds, and many heterocycles to give cyclic peroxides;[1] (2) oxidation of olefins possessing allylic hydrogen atoms to afford allylic hydroperoxides;[2] (3) oxygenation of certain olefins to carbonyl compounds *via* dioxetane or perepoxide intermediates.[3] In order to ascertain the mode of attack on norbornene compounds, the dye-sensitized photooxygenation of 2-ethylidenebicyclo[2.2.1]hept-5-ene (**1**) was studied in detail.

Irradiation of **1** in an air-purged MeOH solution containing Rose Bengal yielded a mixture of hydroperoxides, which were reduced immediately upon completion of the photooxygenation. The principal products were 2-*exo*-hydroxy-2-*endo*-vinylbicyclo[2.2.1]hept-5-ene (**2**), the *endo*-hydroxy epimer (**3**) (*exo*/*endo* ratio of 3/1), and 2-(1-hydroxyethyl)bicyclo[2.2.1]hepta-2,5-diene (**4**). Also isolated and characterized was the brexane derivative, tricyclo[4.3.0.0^{3,7}]non-4-ene-9-one (**5**). A second ketone, apparently arising from a Cope-like thermal rearrangement of **2** and/or **3** was



isolated and tentatively identified as bicyclo[4.2.1]non-7-en-3-one (**6**) The formation of **5** was found to be temperature-dependent, with photooxygenation at lower temperatures (10–20°) affording little or no ketone.

NMR, IR and mass spectra of **2**, **3**, and **4** were consonant with their assigned structures (Experimental). The stereochemical assignments of **2** and **3** were established by hydrogenating the alcohols to their saturated analogs, **7** and **9**, the structures of which were verified by independent synthesis.



7 **8**

9 **10**

An authentic sample of **3** was provided by the vinyl Grignard treatment of dehydronorcamphor[3] (**11**).

Difficulty encountered in the separation of **5** by distillation or GLC techniques was obviated by the formation of its pyrrolidinium perchlorate salt[4] (**12**). The assignment of **5**, also designated brex-4-en-9-one,[*] was based on the following NMR analysis[†] (Figs 1–3).

The low-field vinyl protons were readily identified by chemical shifts (δ 5·87 and δ 6·35) and by characteristic bicycloheptene coupling patterns.[5] Likewise the bridgehead C-3 and C-6 protons exhibited typically broad signals (δ 2·65 and δ 2·93, respectively) due to coupling with the various vicinal hydrogens. Identification of signals ascribed to the C-2 protons (*exo*, δ 1·65; *endo*, δ 1·25) was based on assignments of C-1 and C-3 interactions and germinal coupling.[5,6] Irradiation of the broad signal centered at δ 2·30 (Figs 2b and 3d) removed the 1·8-Hz splitting due to the "W" configuration[6,7] of bonding between the *anti-C*-7 and *endo-C*-2 protons. Coupling of the *endo*-C-2 and C-1 protons was indicated by a constant of 6·5 Hz, typical of *cis*-2-3 norbornene interactions.[6,8] A measurable coupling constant between the C-3 and *endo*-C-2 hydrogens was not observed because of the unfavorable dihedral angle.[5,8]

Irradiation of the signal assigned to the C-3 proton (δ 2·65) collapsed the *exo*-C-2 resonance to an AB doublet ascribed to the geminal C-2 coupling (Figs 2a and 3c). Assignment of the C-5 vinyl proton to the signal centered at δ 5·87 was verified by

---

[*] Prof. A. Nickon, Johns Hopkins University, converted 5 by Wolff-Kishner reduction to brex-4-ene, thus confirming the assignment of the skeletal structure.

[†] The NMR spectra were obtained on a Varian HA-100 NMR spectrometer.

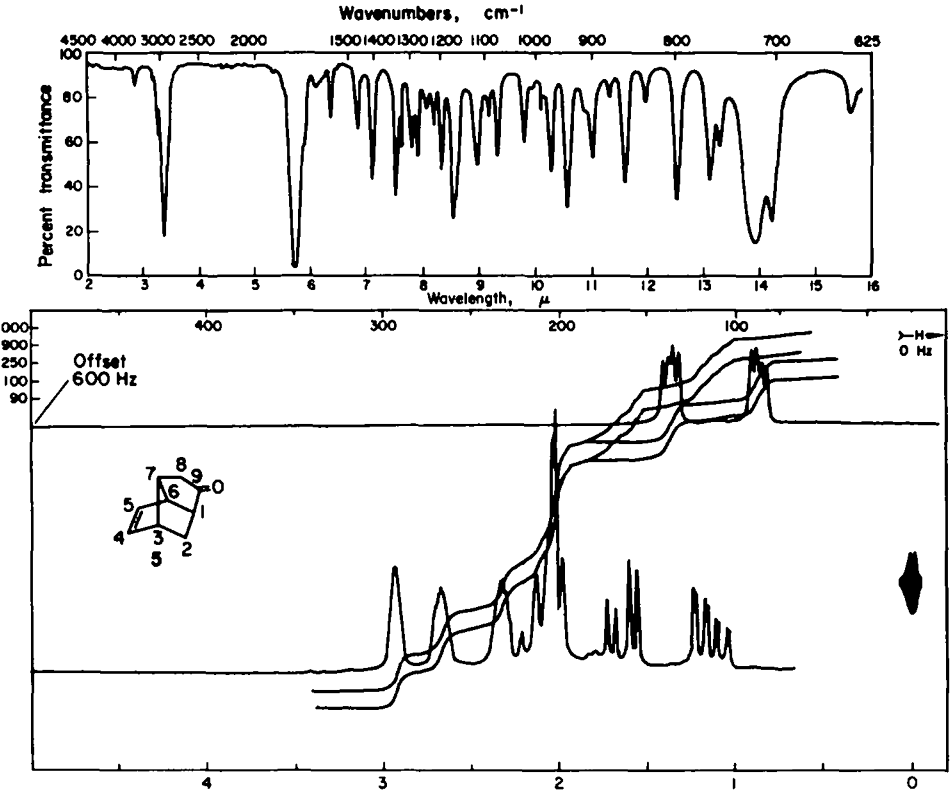


FIG. 1 IR and NMR spectra of tricyclo[4.3.0.0^{3,7}]non-4-en-9-one (5).

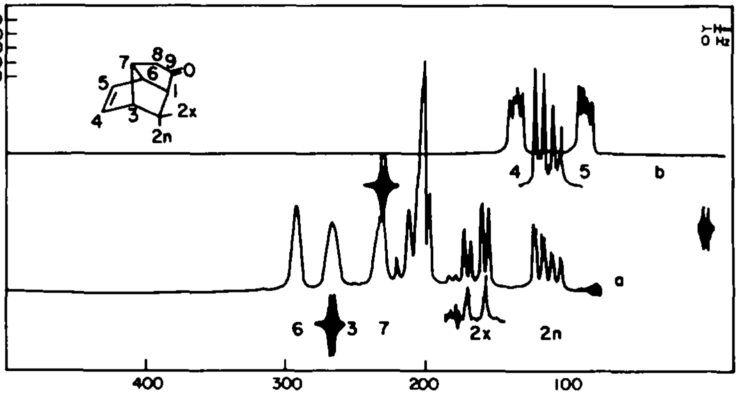


FIG. 2 Decoupled spectra of tricyclo[4.3.0.0^{3,7}]non-4-en-9-one (5): a and b; double irradiation on protons 3 and 7 respectively.

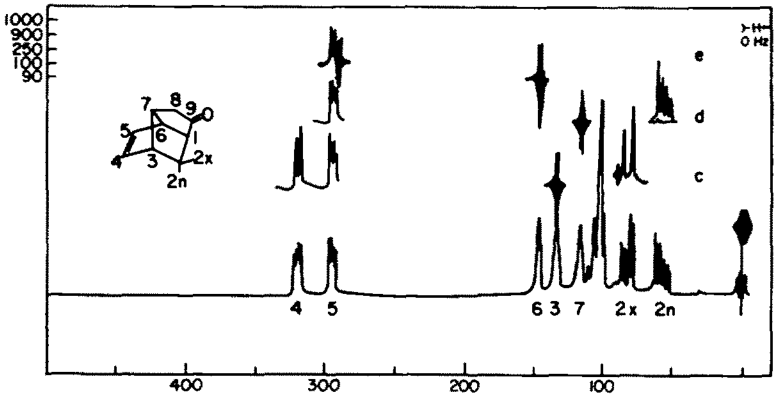


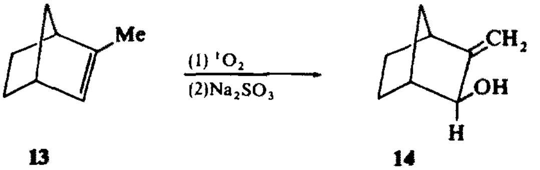
FIG. 3. Decoupled spectra of tricyclo[4.3.0.0^{3,7}]non-4-en-9-one (5): c, d and e; double irradiation on protons 3, 7 and 6 respectively.

double irradiation on the δ 2·93 (C-6) resonance (Fig. 3e). $J_{4,5}$ of 5·5 Hz was confirmed by decoupling the interaction assigned to the C-3 proton (Fig. 3c). The coupling constants are compiled in Table 1.

TABLE 1. NMR COUPLING CONSTANTS (H_2) FOR 5

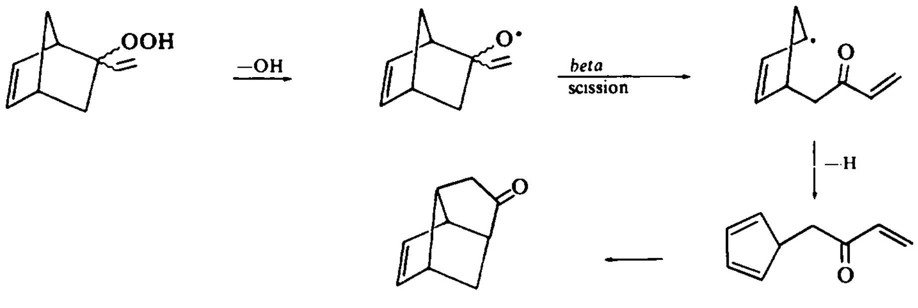
$J_{2n,2x}$	12·9	$J_{2x,3}$	5·0
$J_{2n,7}$	1·8	$J_{4,5}$	5·5
$J_{2n,1}$	6·2	$J_{3,4}$	3·2
$J_{2n,3}$	~0	$J_{5,6}$	3·2
$J_{2x,1}$	~0		

The observed prevalence of the *exo*-hydroxy epimer (**2**) is consistent with approach from the more accessible *exo* direction (steric approach control) by singlet oxygen. This is not surprising in view of the considerable evidence favoring *exo* attack on norbornenyl double bonds.[6, 9] Moreover, in an independent experiment it was shown that the dye-sensitized photooxidation of 2-methylbicyclo[2.2.1]hept-2-ene (**13**) occurred exclusively from the *exo* direction to afford alcohol **14** after reduction.



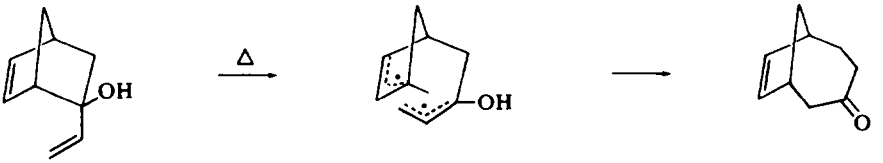
13 **14**

Formation of the novel tricyclic ketone **5** is most reasonably viewed as arising from thermal breakdown of the hydroperoxide precursors of **2** and **3**, followed by intramolecular Diels–Alder reaction of the apparent intermediate (**15**).



5 **15**

Ketone **6**, derived from thermolysis of **2** and **3**, apparently resulted from an oxy-Cope arrangement similar to that reported[10] for 2-vinyl-2-hydroxybicyclo[2.2.2]-octene. That **5** and **6** did not arise from photolysis of primary reaction products was shown by control experiments in which photooxygenation of **1** was conducted with a visible light source and a filter which absorbed all light of wavelength below 450 nm.



3 **6**

EXPERIMENTAL

Apparatus. Irradiations were conducted in an all-Pyrex 2·5-liter immersion assembly described previously.[11] The reactor was fitted with a 450-Watt medium-pressure mercury arc, as indicated and the reaction temperature was maintained at 45 ± 5°C by regulating the water flow through the immersion well. The large volume of the reactor chamber permitted the oxidation of synthetic quantities of substrate with sufficient dilution to retard polymerization and decomposition.

Photooxygenation of 2-ethylidenebicyclo[2.2.1]*hept-5-ene* (**1**). In a typical reaction, a solution of **1**[*] (200 g), Rose Bengal (1·0 g), and MeOH (2 l) was irradiated under conditions of constant air ebullition (flow rate, 0·96 l/min). The abnormally high concentration of dye was required to obtain reasonable conversions of the diene. The reaction, *ca.* 95% complete after eight hr, was followed by GLC analysis (12 ft × $\frac{1}{8}$ in. 10% Carbowax 20M on Chromasorb G column programmed from 100–180°). Immediately following reaction the solution was reduced by dropwise addition of a solution of Na_2SO_3 (200 g) in water (600 ml) and stirred overnight. The resulting solution was then extracted with three 100 ml portions of benzene. The extracts were combined, dried anhyd ($MgSO_4$), and concentrated under reduced pressure. The concentrates from two runs were combined and distilled on a 30-in spinning-band column. Compounds **2** and **3** were separated as a mixture in fractions boiling at 103–107°/40 mm. Analytical samples were isolated by prep. GLC (20 ft. × $\frac{1}{4}$ in. silicone gum rubber on Chromasorb G column at 110°C).

Compound **2**. NMR ($CDCl_3$) δ 1·45 (q, $J_{3n,3x}$ = 12 Hz, $J_{3n,7a}$ = 3 Hz, H-3n), 1·75 (q, $J_{3x,3n}$ = 12 Hz, $J_{3x,4}$ = 4 Hz, H-3x), 2·60 (m, H-4), 2·88 (m, H-1), 3·25 (OH), 5·05 and 5·83 (AMX pattern, J_{AM} = 2, J_{MX} = 17, J_{AX} = 10·5, vinyl protons), 6·08 (m, H-5 and H-6); IR (neat) 2·93, 3·28, 3·36, 6·12, 6·38, 9·07, 10·00, 10·96 and 14·00 μ. (Calc. for $C_9H_{12}O$: C, 79·37; H, 8·88. Found: C, 79·54; H, 9·06%).

Compound **3**: NMR ($CDCl_3$) δ1·15 (broad d, $J_{3n,3x}$ = 12 Hz, H-3n), 1·90 (q, $J_{3x,3n}$ = 12 Hz, $J_{3x,4}$ = 4 Hz, H-3x), 2·46 (OH), 2·68 and 2·83 (H-1 and H-4), 5·12 and 6·10 (AMX pattern, J_{AM} = 2, J_{MX} = 17, J_{AX} = 11,

---

[*] Union Carbide Corporation, Chemicals and Plastics Division.

vinyl protons), 6·22 (m, H-5 and H-6); IR (neat) 2·90, 3·40, 6·09, 7·50, 7·88, 8·39, 8·60, 9·46, 9·92. 10·10, 10·42, 11·95, 11·22, 12·06, 12·98, 13·79 and 14·19 μ. (Calc for $C_9H_{12}O$: C, 79·37; H, 8·88. Found: C, 79·41; H, 8·80%.)

Compound **4** was separated in a fraction boiling at 100–102°/29 mm. An analytical sample was obtained by prep GLC (180°) as described above: NMR ($CDCl_3$) δ1·20 (d, J = 7·0 Hz, Me), 3·48 (m, H-1 and H-4), 3·72 (OH) 4·45 (q, J = 7·0 Hz, CHOH), 6·30 (m, H-3), 6·75 (m, H-5 and H-6); IR (neat) 2·95, 3·40, 6·12, 6·40, 6·90, 7·31, 7·70, 8·82, 9·50, 11·42, 11·92, 12·46, 12·72 and 14·10 μ. Mass spectrum gave a parent ion at *m/e* 136. (Calc for $C_9H_{12}O$: C, 79·37; H, 8·88. Found: C, 79·26; H, 8·92%).

Compound **5** was separated as a 50/50 mixture with **4** in a fraction boiling at 100°/27 mm. To effect complete separation 2·6 g of the mixture was heated gently with pyrrolidinium perchlorate (1·7 g). When a homogeneous solution was achieved, pyrrolidine (1 drop) was added, and upon swirling crystals separated with evolution of heat. Recrystallization from 2-propanol provided the iminium salt (**12**, 2·0 g, m.p. 164–165°). The salt was taken up in water (10 ml) and treated with 0·1N NaOH (2 ml). The solution was extracted with ether, and the ether extract washed successively with 0·1N HCl (5 ml) and water (5 ml). The resulting ether solution was dried over ($MgSO_4$) and concentrated under reduced pressure to yield an analytical sample of **5** (1·1 g); IR (neat) 5·71 (cyclopentanone carbonyl), 6·37 (norbornenyl C=C), 13·9 μ (norbornenyl =C—H deformation); mass spectrum *m/e* 134. (Calc. for $C_9H_{10}O$: C, 80·56; H, 7·51. Found: C, 80·48; H, 7·56%.)

The 2,4-dinitrophenylhydrazone of **5**, recrystallized from 95% EtOH, m.p. 165–166°. (Calc for $C_{15}H_{14}N_4O_4$: C, 57·25; H, 4·27; N, 17·83. Found: C, 57·25; H, 4·37; N, 17·63%.)

Compound **6** was recovered from a high-boiling fraction (b.p. 92–100°/3–12 mm) by prep GLC (12 ft × ⅛ in column of 10% CARBOWAX 20M on Chromasorb G at 200°). An identical sample was obtained from the thermolysis of a mixture of **2** and **3** at 280°. NMR ($CDCl_3$) δ 5·65 (m, vinyl protons). The remainder of the spectra could not be assigned to specific proton absorptions. IR(neat) 3·25 (=C—H), 5·82 (ketone carbonyl), 14·1 μ (norbornenyl-type =C—H deformation); mass spectrum *m/e* 136; 2,4-dinitrophenylhydrazone m.p. 156–157°. (Calc. for $C_9H_{12}O$: C, 79·37; H, 8·88. Found: C, 78·81; H, 8·71%.)

Synthesis of Authentic **3** A solution of dehydronorcamphor[3] (**11**, 105 g, 0·975 mole) in anhyd THF (200 ml) was added gradually to a stirred solution of vinyl magnesium bromide[12] (*ca.* 0·975 mole) in THF. Work-up in the conventional manner provided a solution which, upon fractional distillation, yielded a sample of **3** (b.p. 106–108°/42 mm) which was identical in every manner to the material (**3**) obtained from the photooxygenation of **1**.

Synthesis of **7**. A slurry of 10% Pd/C (3·0 g) in 95% EtOH (50 ml) was placed under a 60 psi hydrogen atmosphere in a Parr hydrogenator and agitated for 15 min. To the activated catalyst mixture was added a solution of **1** (120 g, 1·0 mole) in 95% EtOH (35 ml). and the resulting mixture treated with hydrogen until *ca.* one mole of hydrogen was absorbed (*ca.* 80 psi pressure drop at room temperature). Filtration and distillation yielded 2-ethylidenebicyclo[2.2.1]heptane (**8**, 109 g, 93%, b.p. 70–72°/35 mm). NMR ($CDCl_3$) δ1·50 (2d, Me, J = 4·0 Hz), 2·65 (m, H-3n), 2·08 (m, H-3x), 2·71 (m, H-4), 2·72 (m, H-1), 5·42 (m, vinyl proton). IR (neat) 3·40, 3·49, 6·90, 7·00, 7·28, 10·23, 12·13, 12·61 and 14·13μ. (Calc. for C_9H_{14}: C, 88·45; H, 11·55. Found: 88·56; H, 11·63%).

Oxymercuration-demercuration of **8** in the conventional manner[13] provided 2-*exo*-hydroxy-2-*endo*-ethylbicyclo[2.2.1]heptane (**7**, b.p. 114° at 70 mm). IR (neat) 2·95, 3·39, 3·47, 6·84, 7·28, 9·00, 10·30, 10·43, 11·22, 11·38 and 11·90 μ. (Calc. for $C_9H_{16}O$: C, 77·09, H, 11·50. Found: C, 77·40; H, 11·30%.) The sample of **7** was identical in every respect to the product of exhaustive hydrogenation of **2**.

Synthesis of **9**. Norcamphor was treated with EtMgBr and worked up in conventional fashion to yield 2-*endo*-hydroxy-2-*exo*-ethylbicyclo[2.2.1]heptane (**9**, b.p. 108°/70 mm). IR (neat) 2·95, 3·39, 3·46, 6·83, 7·27, 7·65, 8·54, 10·12, 10·38, 10·70, 11·45 and 11·90 μ. (Calc. for $C_9H_{16}O$: C, 77·09; H, 11·50. Found: C, 77·19; H, 11·32%.) The sample of **9** prepared in this manner was spectroscopically identical to the material obtained from the complete hydrogenation of **3**.

Photooxygenation of 2-methylbicyclo[2.2.1]*hept-2-ene* (**13**). A solution of 2-methylbicyclo[2.2.1]hept-2-ene (20 g, 0·18 mole) and Rose Bengal (0·2 g) in MeOH (500 ml) was irradiated in a Pyrex vessel using a Hanovia Type A 450-watt lamp. The solution was continuously saturated in air (flow rate = 960 cc/min) throughout the irradiation. The uptake of **13** was followed by GLC (12 ft × ⅛ in. 10% Apiezon M on a Chromasorb G column programmed at 140–230°). After 15 hr 90% of the olefin was consumed. The photoreaction product was immediately reduced by dropwise addition of a solution of Na_2SO_3 (25 g) in water (300 ml) and stirred for 2 hr. The solution was extracted with three 100 ml portions of benzene. The extractions were combined and dried ($MgSO_4$) and concentrated under reduced pressure. The residual liquid was distilled giving the alcohol (**14**) (18·2 g, 82%, b.p. 100–104°/40 mm); NMR ($CDCl_3$) δ2·30 (m, H-4), 2·34 (OH), 2·73 (m, H-1), 3·90 (s, H-3n), 5·02 (s, CH_2); IR (neat) 3·00, 3·40, 3·48, 6·00, 6·89, 7·58, 8·95, 9·40, 9·76, 11·25, 13·09 and 13·35 μ (Calc. for $C_8H_{12}O$: C, 77·38; H, 9·74. Found: C, 77·39; H, 9·62%.)

Acknowledgement—The authors are indebted to C. B. Strow, Jr., for his assistance in obtaining and interpreting the NMR spectra.

REFERENCES

[1] K. Gollnick and G. O. Schenck in 1,4-*Cycloaddition Reactions*, Vol. 8, p. 255. J. Hamer, Ed; Academic Press Inc., New York, N.Y. (1967); K. Gollnick in *Advances in Photochemistry* Vol. 6, p. 1. W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Eds., Interscience, New York, N.Y. (1968); K. Gollnick and G. O. Schenck, *Pure Appl. Chem.* **9**, 507 (1964); W. R. Adams in *Oxidation: Techniques and Applications in Organic Synthesis*, Vol. 2, R. L. Augustine and D. J. Trecker, Ed., Marcel Dekker, Inc., New York, N.Y. (1971)

[2] C. S. Foote and J. W.-P. Lin, *Tetrahedron Letters* 3267 (1968); J. E. Huber, *Ibid.* 3271 (1968); W. Fenical, D. R. Kearns and P. Radlick, *J. Am. Chem. Soc.* **91**, 3396, 7771 (1969)

[3] P. K. Freeman, D. M. Balls and D. J. Brown, *J. Org. Chem.* **33**, 2211 (1968)

[4] N. J. Leonard and J. V. Paukstelis, *Ibid.* **28**, 3021 (1963)

[5] J. C. Davis, Jr. and T. V. Van Auken, *J. Am. Chem. Soc.* **87**, 3900 (1965)

[6] C. L. Osborn, T. V. Van Auken and D. J. Trecker, *Ibid.* **90**, 5806 (1968)

[7] S. Sternball, *Rev. Pure Appl. Chem.* **14**, 15 (1964); M. Barfield, *J. Chem. Phys.* **41**, 3825 (1964)

[8] F. A. L. Anet, H. H. Lee and J. L. Sudmeier, *J. Am. Chem. Soc.* **89**, 4431 (1967)

[9] H. C. Brown and J. H. Kawakami, *Ibid.* **92**, 1990 (1970); P. von R. Schleyer, *Ibid.* **89**, 701 (1967)

[10] J. A. Berson and M. Jones, Jr. *Ibid.* **86**, 5017, 5019 (1964)

[11] *Organic Photochemical Syntheses*, p. 14. ed. R. Srinivasan, Wiley–Interscience, N.Y. (1971)

[12] *Organic Syntheses*, IV, 258 (1962)

[13] H. C. Brown and W. J. Hammar, *J. Am. Chem. Soc.* **89**, 1524 (1967)