

hexane-1,3,6-triol triacetate (75 mg, 61%), identical in all observed respects with the previously described sample.

Ozonolysis of Compound 28. The diene **28** (12 mg, 0.06 mmol) was dissolved in absolute ethanol (5 ml), ozonized, reduced (0.1 g of NaBH_4), and acetylated (2.5 ml of acetic anhydride) in an identical manner to compound **27**. A mixture of products was obtained, none of which corresponded to hexane-1,3,6-triol triacetate.

Acknowledgments. We thank the Science Research Council, United Kingdom, for an award to K. C. N. We thank Professor R. S. Givens, University of Kansas, for kindly providing us with spectra of compound **18** and the University of London Central Research Fund for the provision of the ozonizer.

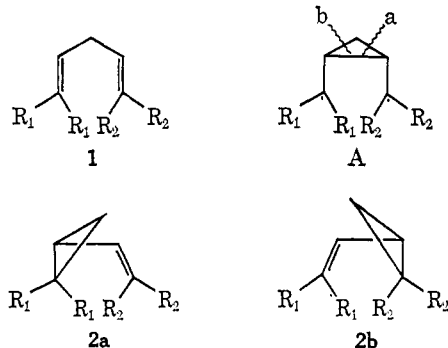
Regiospecificity in Di- π -methane Photoisomerizations

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Abstract: The acetone-sensitized di- π -methane rearrangement of benzobicyclo[2.2.2]octadienes is affected by substituents in the saturated bridge, although these substituents are not bonded to any of the atoms directly involved in the rearrangement. For example, *syn*- and *anti*-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ols **26s** and **26a** rearrange regiospecifically to **27s** and **27a**, respectively. Products arise preferentially from diradicals in which the unpaired electrons are close to (**31p**) rather than remote from (**31d**) the substituents (OH or OAc) on the saturated bridge. Since in several examples (**9**, **12**, **17**) the extent of regioselectivity depends on the geometry of the substituent, being greater when the substituent and aryl ring are *syn*, the interaction between the substituent and the unpaired electrons probably occurs through space, rather than through bonds.

The generality of the di- π -methane photorearrangement was first recognized by Zimmerman.¹ The reaction involves the conversion of a divinylmethane moiety **1** to a vinylcyclopropane **2**.² In cases when $R_1 \neq R_2$, two products (**2a** and/or **2b**) are possible, de-



pending upon whether bond a or bond b is broken when intermediate A is converted to a stable product.³ Several cases are known in which the reaction follows only one of these two possible routes. For example, direct irradiation of **3** gave **4**, not **5**.⁵ Thus the "intermediate" B cleaved exclusively at bond b.

Another type of regiospecificity has been observed in

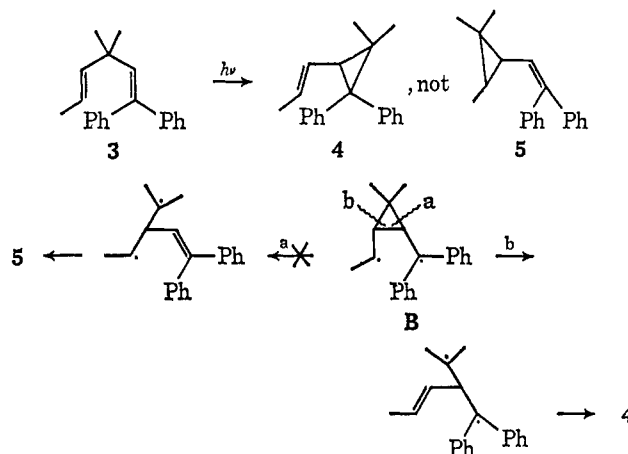
(1) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **89**, 3932 (1967); for a thorough review, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, in press.

(2) The term π is used in the broadest sense, and examples which involve aryl or carbonyl groups as components of the di- π -methane moiety are well known.

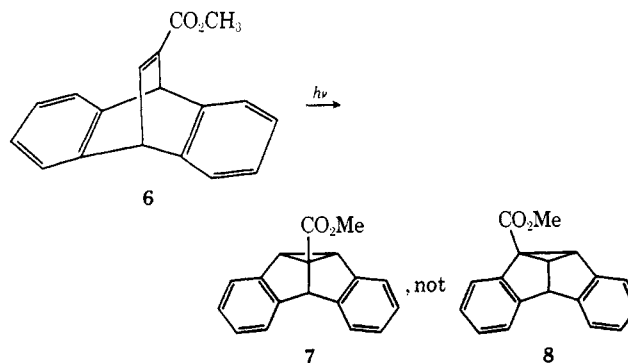
(3) For convenience in the discussion, A-F, etc., are represented as discrete intermediates. In some instances, such discrete diradicals may in fact be involved; in other cases, the reactions may be concerted.⁴

(4) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969); P. S. Mariano and J.-k. Ko, *ibid.*, **94**, 1766 (1972); H. E. Zimmerman, P. Baekstrom, T. Johnson, and D. W. Kurtz, *ibid.*, **94**, 5504 (1972), and leading references therein.

(5) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970).

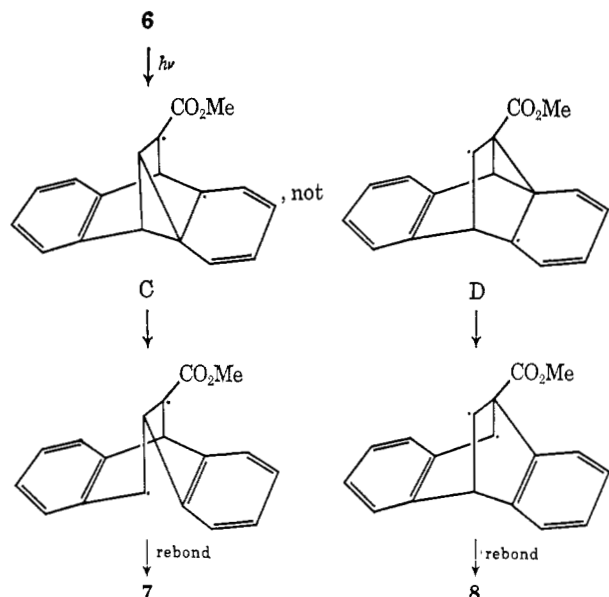


bicyclic systems.⁶ Irradiation of **6** gave **7**, not **8**. In this case, the mode of initial bonding determines the structure of the reaction product. The observed product arose from intermediate C, not D.



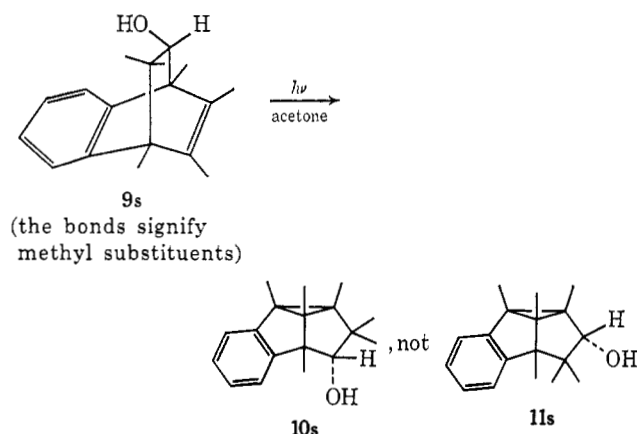
Each of these types of regiospecificity can be easily rationalized. The reactions proceed along routes which

(6) E. Ciganek, *ibid.*, **88**, 2882 (1966).



permit maximum π delocalization. In the first example it is the phenyl groups, and in the second example the carbomethoxy group which is the controlling structural feature. Intermediates with radical sites located so as to permit π delocalization by these substituents are preferred. The substituent effect does not seem to be associated with a particular excited state multiplicity, since the first reaction proceeds from a singlet state, and the second from a triplet.¹

Still a third and less well understood type of regio-specificity has been observed in di- π -methane photoisomerizations, and it is on this problem that we focus attention here. Sensitized irradiation of the secondary alcohol **9s** gave **10s**, not **11s**.^{7,8} Of the two possible di-

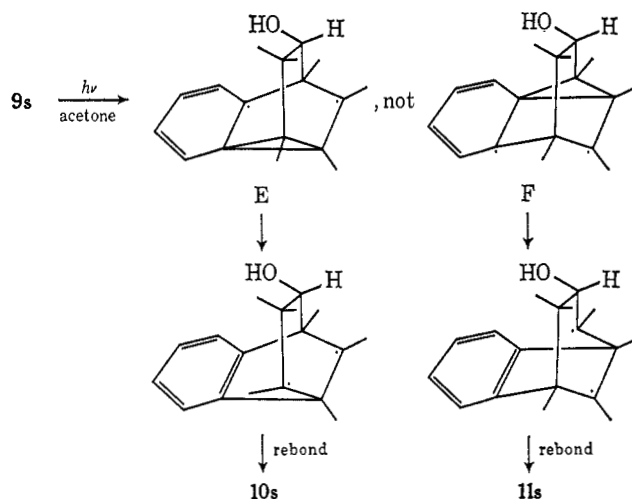


π -methane intermediates E and F, the reaction proceeded only *via* the former. Apparently the hydroxyl group⁹ interacts in some way with the delocalized π -system "beneath" it to stabilize E over F. Since the hydroxyl group is not directly bonded to the π system, the effect may be viewed as a "through space" rather than a "through bond" interaction. It has been suggested that hydrogen bonding and/or charge-transfer interactions may be responsible for the effect. The

(7) H. Hart and R. K. Murray, Jr., *J. Amer. Chem. Soc.*, **91**, 2183 (1969).

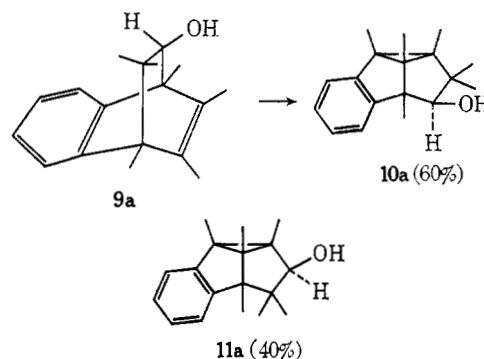
(8) The subscripts s and a are used throughout this paper to designate the syn or anti relationship between the substituent (OH or OAc) and the aryl ring.

(9) It seems unlikely that the *gem*-dimethyl group would be the controlling structural feature; also see the results with **26s** and **26a**.



hydrogen bonding explanation seemed particularly attractive since the ground state of **9s** shows an intramolecular π -bonded OH stretching frequency at 3580 cm^{-1} .

It should be mentioned that irradiation of the epimeric alcohol **9a** was also regioselective, but the directive influence of the hydroxyl group was less dramatic than with the syn isomer.



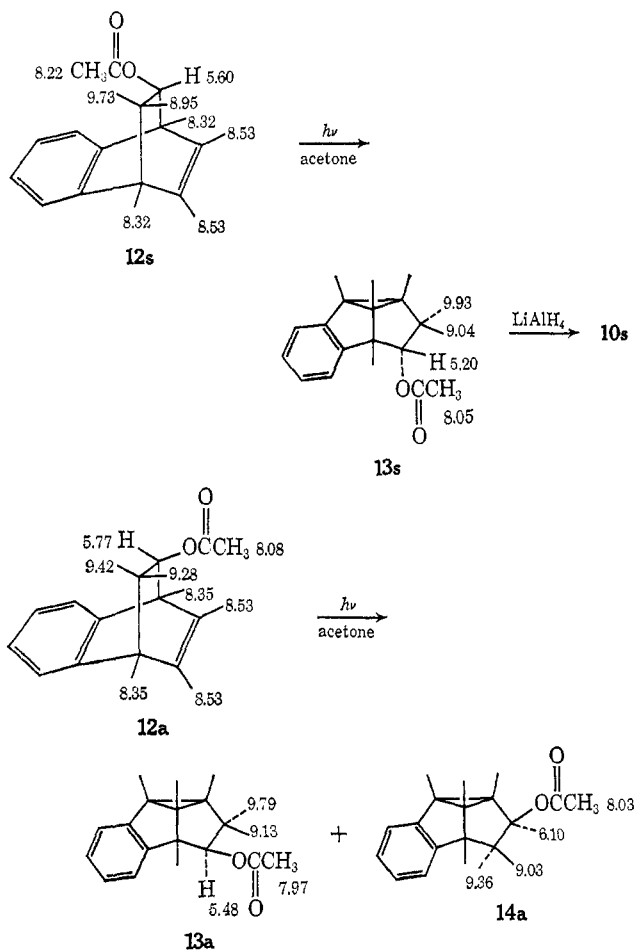
To test the hydrogen bond explanation, we prepared and irradiated the acetates of **9**. To test the generality of the effect, we also prepared and irradiated less methylated analogs of **9**.¹⁰

Results

Alcohol **9s** was converted quantitatively with acetyl chloride to the crystalline acetate **12s**. Acetone-sensitized irradiation of **12s** gave a single crystalline photoproduct **13s**, whose structure was proved by lithium aluminum hydride reduction to the known⁷ alcohol **10s**.

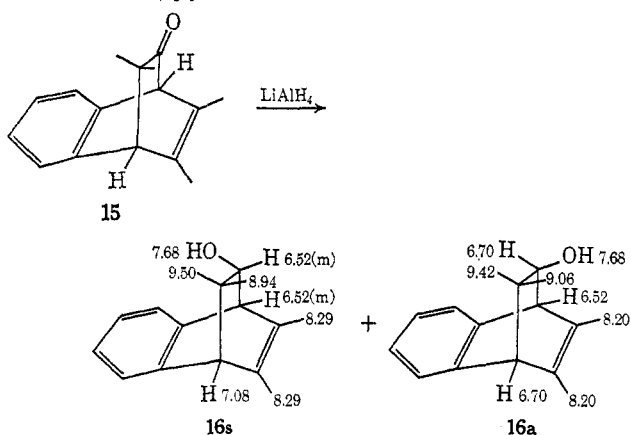
Since it was difficult to obtain the anti alcohol **9a** pure, a mixture of the epimeric alcohols **9** was converted to their acetates **12**. Irradiation of the mixture gave three photoproducts, **13s**, **13a**, and **14a**. The two new products, formed in a 2:1 ratio, presumably arose from the anti acetate **12a**. The structures of **13a** and **14a** were established by lithium aluminum hydride reduction to the known⁷ alcohols **10a** and **11a**, respectively.

(10) There are many ways in which the hydroxyl group could influence the reaction. For example, it could selectively affect various radiationless decay rates. A thorough understanding of the phenomenon may require a detailed kinetic study of the reaction. To determine whether or not such a study would be worthwhile, and to locate a reaction system suitable for detailed study, we decided first to explore the scope of the phenomenon through structural variations in the substituent and in the di- π -methane moiety. The study was limited to sensitized irradiations; direct irradiation of **9**, **16**, and **26** was in general messy, and did not give di- π -methane products.



Since the photoisomerizations of the acetates are as regioselective as those of the alcohols, we conclude that the hydrogen bond explanation for the phenomenon is untenable.

To examine any possible effect of methyl substitution at the bridgehead positions, we synthesized the tetramethyl alcohols **16**.¹¹ Reduction of **15**¹¹ with lithium aluminum hydride gave a 58:42 mixture of **16s**:**16a** in 89% yield. Irradiation of either alcohol, in

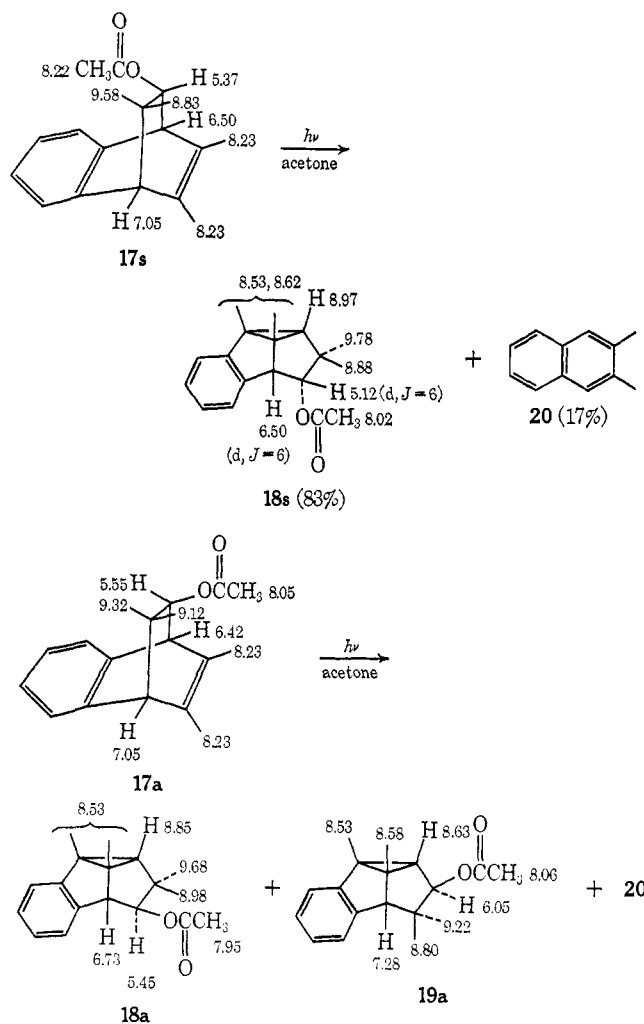


acetone solution, gave only 2,3-dimethylnaphthalene **20** (and presumably isobutyraldehyde), and no di- π -methane photoisomer. Such photoeliminations are well known¹² but the reason for the difference in photochemical behavior of **16** and **9** is not clear.

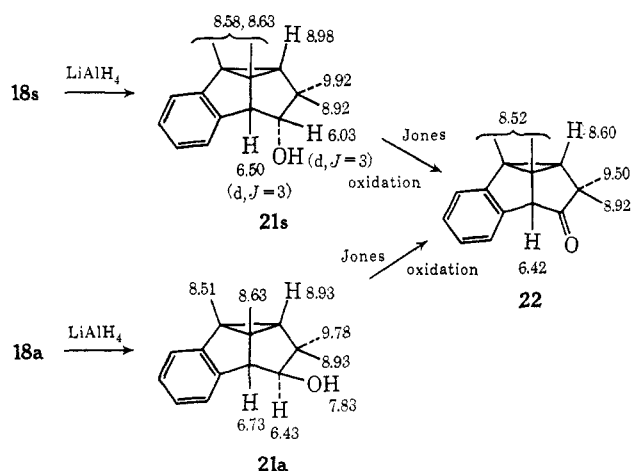
(11) Ketone **15** and alcohols **16** were first prepared by T. Kakihana (M.S. Thesis, Michigan State University, 1966); experimental details are presented here.

(12) R. K. Murray, Jr., and H. Hart, *Tetrahedron Lett.*, 4995 (1968).

The alcohols were converted to their acetates **17** which were separated by preparative vpc. Irradiation of **17s** in acetone afforded two products in the ratio 5:1. The minor product was 2,3-dimethylnaphthalene, and the major product is assigned structure **18s**. Irradiation of an acetone solution of the anti isomer gave three products in the ratio 6:2:1, assigned structures **18a**, **19a**, and **20**, respectively. The structures of **18s** and **18a**

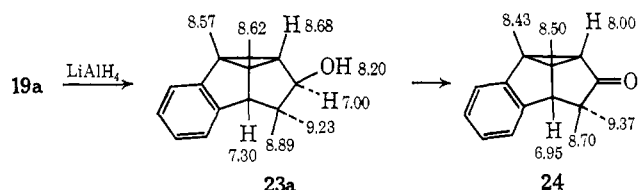


were shown to be related by lithium aluminum hydride reduction to the epimeric alcohols **21s** and **21a**, each of which gave the same ketone **22** on Jones oxidation.



As expected, lithium aluminum hydride reduction of **22**

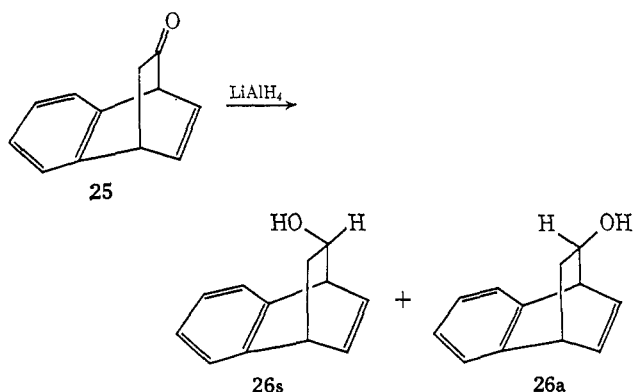
gave a single alcohol, **21s**. Reduction of acetate **19a** gave alcohol **23a** which on Jones oxidation gave **24**,



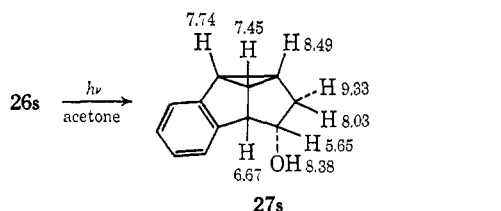
isomeric with **22**. The stereochemical assignments of **18**, **19**, **21**, and **23** not only follow from the stereochemistry of their precursor **17**, but are substantiated by an analysis of their nmr spectra (see Experimental Section).

It is clear from these results that whatever factor is responsible for the regiospecificity of the hexamethyl alcohols and acetates (**9** and **12**) is also operative with the tetramethyl acetates **17**.

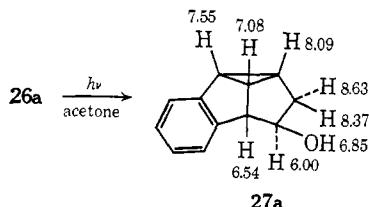
Finally, we examined the photochemistry of the unsubstituted alcohols **26s** and **26a**, prepared by re-



duction of **25**.¹³ The alcohols were separated by preparative gas chromatography, though this caused some thermolysis to naphthalene. Irradiation of **26s** in acetone gave two photoproducts in a ratio of 7:1; the minor product was not identified. The major product is assigned structure **27s** as a consequence of



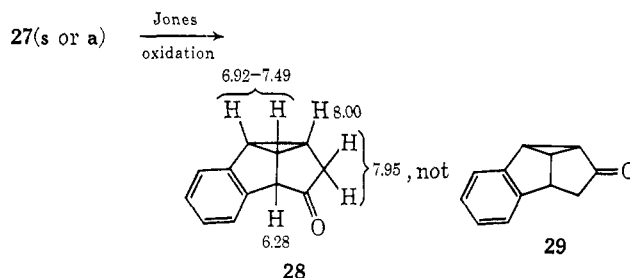
a careful analysis of its nmr spectrum (see Experimental Section).¹⁴ Similar irradiation of **26a** gave a single photoproduct **27a**. Oxidation of **27s** or **27a** afforded



(13) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 6096 (1968).

(14) The methylene protons of **25** were readily replaced by deuterium; advantage was taken of such labeling to simplify the nmr spectra of **26** and **27**.

the same ketone **28** which was different from the known¹⁵ ketone **29**. Finally, reduction of **28** with



lithium aluminum hydride gave a single alcohol, **27s**.

Discussion

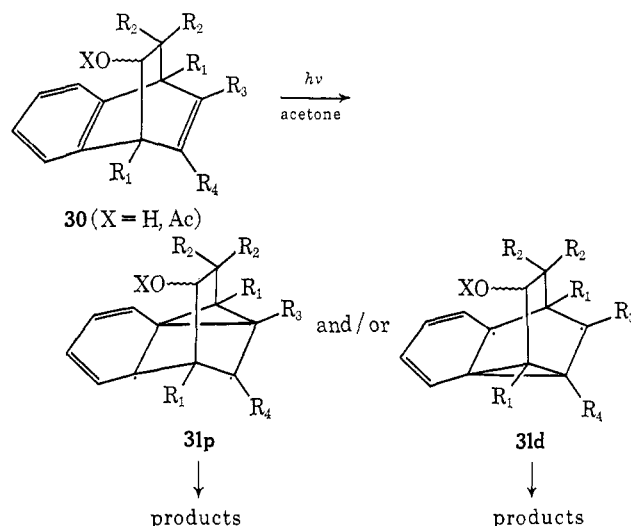
The experiments reported here are summarized in Table I. The acetone-sensitized (*i.e.*, triplet excited

Table I. Photoproducts from **30**

Compd	-OX	Config- uration of OX ^a	R ₁	R ₂	R ₃ = R ₄	% of product from 31p	31d
9s	OH	Syn	CH ₃	CH ₃	CH ₃	100	0
9a	OH	Anti	CH ₃	CH ₃	CH ₃	60	40
12s	OAc	Syn	CH ₃	CH ₃	CH ₃	100	0
12a	OAc	Anti	CH ₃	CH ₃	CH ₃	66	33
17s	OAc	Syn	H	CH ₃	CH ₃	100	0
17a	OAc	Anti	H	CH ₃	CH ₃	75	25
26s	OH	Syn	H	H	H	87-100	13-0
26a	OH	Anti	H	H	H	100	0

^a Relative to the aryl group.

state) di- π -methane photoisomerization of compounds such as **30** proceeded preferentially through intermediate **31p** (the "proximal" diradical, in which the unpaired



electrons are closest in space to the substituent OX). The extent of the preference depended on the relation between OX and the aromatic ring. When OX was syn to the aromatic ring the reaction was regiospecific. When OX was anti to the aromatic ring some product corresponding to the "distal" diradical **31d** was obtained, but the reaction was still regiospecific and in one example (**26a**) regiospecific.

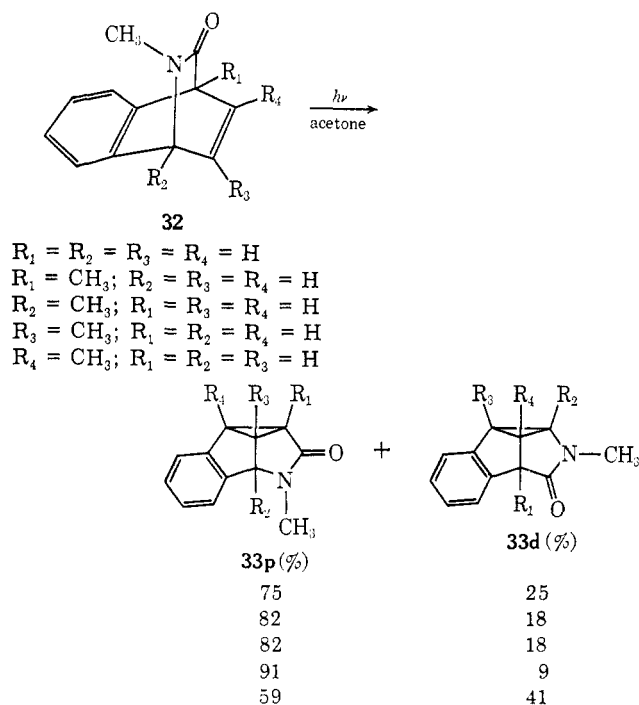
Since the hydroxyl and acetoxy groups behave sim-

(15) J. Ipaktschi, *Tetrahedron Lett.*, 215 (1969).

ilarly, one may conclude that an oxygen atom of the substituent interacts in some manner with the proximal unpaired electrons in **31p** to lower the energy of this intermediate relative to **31d**. If the interaction, whatever its nature, occurred through bonds one might have expected the syn and anti isomers to react similarly. Since they do not, it seems most likely that the interaction occurs through space, rather than through bonds.

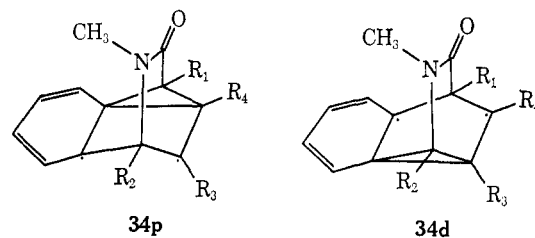
Consider now only the compounds with OX anti to the aryl ring. When the radical at the carbon which bears groups R_3 and R_4 was secondary (**26a**) the regioselectivity was much greater than when these sites were tertiary (**9a**, **12a**, **17a**). Since secondary radicals are less stable and more electrophilic than tertiary radicals, they apparently make greater use of the stabilization which the proximal oxygen can afford. The interaction in the syn compounds is not altered by changing the substituents R_3 and R_4 , and in all these cases the reaction was regioselective.

One can at present only speculate regarding the nature of the stabilizing interaction between OX and the proximal unpaired electrons. A charge-transfer complex (intramolecular triplet exciplex) is one possibility, with some electron density transfer from the nonbonding electrons of the oxygen to the partially filled $p(\pi)$ orbitals of the diradical. Alternatively, the oxygen atom might interact with the proximal unpaired electron in such a way as to promote a change in spin state (*i.e.*, intersystem crossing). This mechanism would imply a photostationary state of **31p** and **31d** intermediates, with enhancement by OX of the rate of conversion of **31p** to products. A third possibility would be that the substituent affects the transfer of triplet energy from the acetone sensitizer. The information available at present does not permit a distinction between these (or other) alternative explanations for the observed regioselectivity of the reactions.



While this work was in progress, a related study was reported by Paquette and Meisinger.¹⁶ They found

that the acetone-sensitized photoisomerization of **32** to **33p** and **33d** was regioselective, the principal product (**33p**) in all cases arising from the diradical in which the unpaired electrons are proximal to the nitrogen atom in the hetero bridge (*i.e.*, **34p**, not **34d**). They at-



tributed this preference to conjugation of the unpaired electrons, through the cyclopropane ring, with the carbonyl group of the amide (possible in **34p**, but not in **34d**). An alternate explanation consistent with our observations would be a stabilizing interaction between the unshared electron pair on nitrogen and the proximal unpaired $p(\pi)$ electrons. These electrons are probably less involved in the usual amide-type resonance in the diradical **34** than they are in ground state **32**. The choice between these alternative explanations can be subjected to experimental test by converting the carbonyl group to a methylene group.

Finally, the results of Paquette and Meisinger show that the proportion of the reaction which proceeds by intermediates **34p** and **34d** can be affected by substituents at R_3 and R_4 . Methyl substitution at R_3 lowers the energy of **34p** relative to **34d** and enhances the regioselectivity of the reaction, whereas methyl substitution at R_4 allows **34d** to compete more favorably with **34p**. This result is consistent with our observation that the photoisomerization of **26a** (secondary diradicals) was more regioselective than the isomerizations of **9a**, **12a**, and **17a** (tertiary diradicals).

Structural Assignments

Although some of the structural assignments in this paper are intermeshed by a web of chemical interconversions, others depend primarily on the interpretation of nmr spectra. This is particularly true of structural assignments of epimeric pairs of compounds. The basis for these assignments is discussed briefly here.

In general, the acetyl methyl singlet in the acetoxy 5,6-benzobicyclo[2.2.2]octa-5,7-dienes appears at higher field when the methyl is syn to and "over" the aromatic π system, than when the methyl has the anti geometry. Thus in **12s**, **17s**, and the acetate of **26s** the acetyl methyl group appears at τ 8.22, whereas in **12a**, **17a**, and the acetate of **26a** it appears at τ 8.05–8.08. In the hexamethyl case (**12s** and **12a**), the structures of the photoproducts of the corresponding alcohols were independently established,⁷ and the photoacetates prepared here were directly related to those alcohols. It does not seem unreasonable, then, to use the same difference in acetate methyl shifts to assign stereochemistry to **17** and **26**, especially since further conversions of the photoproducts in these systems are consistent with the assignments.

Lithium aluminum hydride reduction of the ketone obtained by oxidizing **10** gave a single alcohol, **10s**. Similar reduction of **22** and **28** gave in each case a

(16) L. A. Paquette and R. H. Meisinger, *Tetrahedron Lett.*, 1479 (1970).

single alcohol. It seems reasonable that in all three cases attack of hydride occurs from the convex face of the cupped molecule to produce an alcohol with the hydroxyl group syn to the aromatic ring. Consistent with this assignment, the secondary proton in the resulting alcohol (or its acetate) appears at higher field in the anti alcohol or acetate by about 0.30 ppm than in the corresponding syn isomer.¹⁷ This difference may be caused by shielding of the proton in anti isomers by the aromatic ring. These assignments are further supported in the case of **18** and **21** by the coupling pattern of this proton and the adjacent tertiary bridgehead proton. Models show that the dihedral angle between these protons in the anti isomer is approximately 90°, whereas in the syn isomer it is much smaller (about 25–35°). No coupling between these protons was observed in **18a** and **21a**, whereas in **18s** and **21s** the coupling was 6 and 3 Hz, respectively. A similar argument supports the assignments of **19a** and **23a**. Models show that the dihedral angle between the secondary alcohol (or acetate) proton and the adjacent tertiary cyclopropyl proton is about 95°. No splitting was observed between these protons; if the alcohol or acetoxy function in these compounds had been syn to the aromatic ring, the dihedral angle would have been very small and the coupling substantial.

There is a small but consistent difference in the ir and uv spectra of ketones **22** and **24** which supports the notion that in the latter the carbonyl group is conjugated with the cyclopropane and aromatic rings. Thus the carbonyl frequencies are 1730 and 1715 cm⁻¹, respectively, and the λ_{max} in the uv spectrum of **24** are generally at longer wavelength than those of **22**. A similar comparison can be made between **28** and **29**.

Finally, the spectra of **27s** and **27a** were analyzed carefully *via* decoupling of the 100-MHz spectrum, as well as deuterium labeling. The only unsplit proton in the spectrum of **27s** was the OH proton at τ 8.38. Irradiation at τ 5.65 simplified the splitting patterns at τ 6.67, 8.03, and 9.33 suggesting that protons at these chemical shifts were adjacent to the secondary alcohol function. Consistent with this conclusion, the signals at τ 8.03 and 9.33 were absent from photo-product isolated from **26s-d₂**. In the spectrum of **27s-d₂**, the signal at τ 5.65 simplified to a doublet (J = 6 Hz), now coupled only with the adjacent tertiary bridgehead proton (τ 6.67). This coupling constant is expected (see discussion above for **18s** and **21s**). In the spectrum of **27s-d₂**, the signal at τ 8.49 was also simplified to a triplet, thus locating this cyclopropane proton α to the methylene group. Finally, irradiation at τ 6.67 in unlabeled **27s** simplified the signals at τ 5.65 and 7.45, thus completing the assignment shown in the structure.

As with **27s**, the only unsplit proton signal in the nmr spectrum of **27a** was due to the OH group (τ 6.85). In **27a-d₂**, the signals at τ 8.37 and 8.63 were absent, showing that these signals were due to the methylene group. In this spectrum, the signals at τ 8.09, 6.54, and 6.00 were also simplified. Irradiation

at τ 6.00 (in unlabeled **27a**) simplified the splitting at τ 8.63 and removed a very small perturbation at τ 6.54 to make it a sharp doublet of doublets. Thus coupling between the protons at τ 6.00 and 6.54 is exceedingly small; this is consistent with the assigned geometry (see discussion of the spectra of **19a** and **23a**, above). The long-range coupling between the protons at τ 6.54 and 8.37 is 2.5 Hz; these protons are geometrically fixed in the "W" configuration for coupling through four σ bonds.¹⁸ Irradiation at τ 6.54 sharpened the doublet at τ 6.00 slightly and simplified the signals at τ 8.37 and 7.08, fixing the position of the latter cyclopropyl proton. Thus the spectrum can be completely assigned as shown in the structure.

The nmr spectrum of ketone **28** supports some of the assignments in **27**. The broad two-proton doublet at τ 7.95 was absent from the spectrum of **28-d₂**, fixing these as the methylene protons. Also simplified was the τ 6.28 signal, from a doublet of doublets in **28** to a simple doublet in **28-d₂**. Consequently the same type of four-bond, long-range coupling is present in **28** and **27a**.

Although independent syntheses were not carried out, the chemical and nmr interrelationships seem to place all of the structures on firm ground.

We are continuing to probe the nature of this type of regioselectivity in di- π -methane rearrangements.

Experimental Section

syn-2-Acetoxy-1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]-octa-5,7-diene (12s). A solution of 2 g of the alcohol **9s**¹⁹ in 10 ml of acetyl chloride was refluxed for 15 min. The excess acetyl chloride was distilled under reduced pressure, and the crude residue was dissolved in 20 ml of ether, washed with saturated NaHCO₃ (3 \times 10 ml) and water (3 \times 10 ml), and dried (MgSO₄). Evaporation of the ether gave an essentially quantitative yield of **12s**, which was recrystallized from pentane: mp 85–86°; nmr see structure; ir (neat) 3000, 1720, 1380, 1250, 1230, 1030 cm⁻¹; uv (EtOH) λ_{max} 272 nm (ϵ 852), 264 (1070), 257 (852), 209 (18,800).

Anal.²⁰ Calcd for C₂₀H₂₆O₂: C, 80.54; H, 8.73. Found: C, 80.47; H, 8.78.

Irradiation of 12s. A solution of **12s** (782 mg) in 15 ml of spectral grade acetone, placed in a septum-sealed Pyrex test tube, was deoxygenated by a N₂ stream for 30 min, then irradiated (Hanovia L 450-W lamp). Vpc monitoring (5 ft \times 0.25 in. SE-30 column, 150°, 100 ml/min) indicated the formation of a single photo-product, **syn-4-acetoxy-1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene (13s)**, 92% conversion in 9 hr. The solvent was evaporated, and the residue was recrystallized from pentane: mp 93–94°; ir (neat) 1725 cm⁻¹; nmr in addition to bands shown in the structure, the spectrum showed sharp 3-proton singlets at τ 8.63, 8.76, 8.82, 8.94.

Anal. Calcd for C₂₀H₂₆O₂: C, 80.54; H, 8.73. Found: C, 80.44; H, 8.84.

Reduction of 13s. A solution of **13s** (20 mg) in ether (5 ml) was added at room temperature to a stirred suspension of lithium aluminum hydride (500 mg) in ether (20 ml). After 30 min, water (2 ml) was added dropwise, followed by 1 g of anhydrous MgSO₄. The solution was filtered and evaporated to yield an oil (quantitative) whose ir and nmr spectra were identical with those of **syn-1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-ol (10s)**.⁷

anti-2-Acetoxy-1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]-octa-5,7-diene (12a). A mixture of **9s** and **9a**¹⁹ was fractionally crystallized from pentane to remove as much of the syn isomer as possible. The mixture was acetylated (as in the preparation of **12s**) to give a 2:3 mixture of **12s**:**12a**. The nmr data shown in the

(17) The values of the chemical shifts (τ) are

	10	13	18	21	27
Syn	6.53	5.20	5.12	6.03	5.65
Anti	6.78	5.48	5.45	6.43	6.00
Δ	0.25	0.28	0.32	0.40	0.35

(18) M. Barfield, *J. Chem. Phys.*, **41**, 3825 (1964).

(19) A. C. Gripper-Gray and H. Hart, *J. Amer. Chem. Soc.*, **90**, 2569 (1968).

(20) Microanalyses by Spang Microanalytical Laboratory, Ann Arbor, Mich.

structure of **12a** were determined from this mixture, by subtracting the spectrum of **12s**.

Irradiation of 12. A solution of 1 g of the mixture of **12s** and **12a**, prepared as just described, in 15 ml of acetone was irradiated as described for the irradiation of **12s**. The reaction was monitored by vpc, using a 5 ft \times 0.25 in. 20% SE-30 column, 150°, which did not resolve **12s** from **12a**, and only showed one photoproduct peak. When integration of these peaks showed 92% conversion, the irradiation was stopped. Products were isolated by preparative vpc (10 ft \times $\frac{3}{8}$ in. column, 20% FFAP, 200°); the major products in order of retention time (areas 2:2:1) were **13s** (identified by its nmr spectrum), *anti*-4-acetoxy-1,2,3,3,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene (**13a**), and *anti*-3-acetoxy-1,2,4,4,5,8-hexamethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene (**14a**). The partial nmr spectra of **13a** and **14a** are shown in the text; in addition, **13a** had sharp three-proton singlets at τ 8.62, 8.77, 8.85, and 8.95 and **14a** had bands at τ 8.51, 8.77, 8.84, 9.00 (3 H each, sharp singlets). The ir spectrum (neat) of each had a $\nu_{C=O}$ at 1725 cm⁻¹.

Reduction of 13a and 14a. The entire vpc collected sample of each was reduced with lithium aluminum hydride as described above for **13s**. The products had ir and nmr spectra identical with those of the known⁷ alcohols **10a** and **11a**, respectively.

3,3,7,8-Tetramethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (15).¹¹ To a solution of 3,4,6,6-tetramethyl-2,4-cyclohexadienone²¹ (3.28 g, 21.8 mmol) and isoamyl nitrite (3.87 g, 33 mmol) in methylene chloride (80 ml) was added over 1 hr at reflux a solution of anthranilic acid (4.5 g, 33 mmol) in acetone (40 ml). After 1 hr at reflux, solvent was removed (rotary evaporator) and the residual brown oil was taken up in ether (70 ml), washed (10% sodium hydroxide, then water), dried (Na₂SO₄), and distilled to give 3.18 g (63%) of a pale yellow oil: bp 104–105° (0.5 Torr); nmr (CCl₄) τ 2.88 (br s, 4 H, arom), one-proton singlets at τ 5.98 and 6.60 and three-proton singlets at τ 8.16, 8.23, 8.86, 9.42; uv (EtOH) λ_{max} 300 nm (ϵ 389), 273 (1100), 268 (1200), 216 (8130); ir (CCl₄) 1720, 1675, 1600, 710 cm⁻¹. Treatment of **15** with hydroxylamine hydrochloride in ethanol–pyridine gave a crystalline oxime, mp 175–176° (from ethanol).

Anal. Calcd for C₁₆H₂₀NO: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.90; H, 7.94; N, 5.80.

syn- and *anti*-**3,3,7,8-Tetramethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ols (16s and 16a).**¹¹ A solution of **15** (1.25 g) in ether (5 ml) was added dropwise to a suspension of LiAlH₄ (236 mg) in ether (30 ml) kept at 0°. The mixture was stirred at 0° for 50 min, hydrolyzed, and extracted with ether. The combined extracts were dried (MgSO₄) and solvent was evaporated to leave 1.11 g (89%) of a colorless oil, a 58:42 mixture (nmr analysis) of **16s** and **16a**. Vapor phase chromatography at 210°, 20% Apiezon-L 10 ft \times 0.25 in. column, gave a quantitative conversion to 2,3-dimethylnaphthalene: nmr data are shown in the structures; ir (mixture, CCl₄) 3640, 3520, 1644, 1605, 695 cm⁻¹.

syn and *anti*-**2-Acetoxy-3,3,7,8-tetramethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dienes (17s and 17a).** A solution of **16s** and **16a** prepared as above (6 g) in acetyl chloride (25 ml) was refluxed for 15 min. Excess acetyl chloride was removed by vacuum distillation and the crude esters were dissolved in 50 ml of ether. The ether solution was washed with saturated NaHCO₃ (3 \times 20 ml) and water (3 \times 20 ml), dried (MgSO₄), and evaporated to give an oil which was separated by preparative vpc (10 ft \times $\frac{3}{8}$ in. column, 20% FFAP, 200°): nmr see structure of **17s**; ir (CHCl₃) 2930, 1705, 1375, 1255; uv (EtOH) λ_{max} 288 nm (ϵ 575, sh), 279 (1300, sh), 272 (1900), 265 (1900), 260 (1750), 226 (38,000), 207 (36,000).

Anal. Calcd for C₁₆H₂₀O₂: C, 80.00; H, 8.15. Found: C, 80.38; H, 8.29.

Nmr: see structure of **17a**; ir (CHCl₃) 2940, 1710, 1375, 1250 cm⁻¹; uv (EtOH) λ_{max} 288 nm (ϵ 270, sh), 273 (1300), 266 (1400), 260 (1100, sh), 223 (28,000), 208 (52,000).

Anal. Calcd for C₁₆H₂₀O₂: C, 80.00; H, 8.15. Found: C, 80.08; H, 8.23.

Irradiation of 17s. A solution of **17s** (595 mg) in acetone (15 ml) was irradiated as described for **12s**. Vpc monitoring (10 ft \times $\frac{3}{8}$ in. column, 20% FFAP, 200°) showed the formation of two photoproducts, peak area ratio 5:1, with 82% conversion in 59 hr. The products were isolated by preparative vpc. The minor product had ir and nmr spectra identical with those of 2,3-dimethylnaphthalene. The major product was *syn*-4-acetoxy-1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene (**18s**): nmr see structure; ir (CCl₄) 2950, 1725, 1375, 1240 cm⁻¹.

Anal. Calcd for C₁₆H₂₀O₂: C, 80.00; H, 8.15. Found: C, 80.00; H, 8.16.

syn-**1,3,3,8-Tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-ol (21s).** The entire vpc collected sample of **18s** was reduced with lithium aluminum hydride as described for **13s**, to give the alcohol **21s**: nmr see structure; ir (CCl₄) 3600, 3500, 2950, 1480, 1390, 1080 cm⁻¹.

1,3,3,8-Tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-one (22). The entire sample of **21s** (above) was dissolved in acetone (5 ml) and chilled to 0°. Jones' reagent²² was added dropwise until the solution remained pink for 2 min. Water (50 ml) was added and the mixture was extracted with ether (3 \times 15 ml). The ether extract was dried (MgSO₄) and evaporated to give an essentially quantitative yield of **22**: nmr see structure; ir (neat) 2950, 1730, 1470 cm⁻¹; uv (EtOH) λ_{max} 287 nm (ϵ 9600), 239 (11,000, sh), 210 (12,000); *m/e* 226 (P), 156 (base).

Anal. Calcd for C₁₆H₁₈O: C, 84.96; H, 7.96. Found: C, 84.79; H, 8.00.

Irradiation of 17a. A solution of **17a** (612 mg) in acetone (15 ml) was irradiated as described for **12s**. The photolysis, monitored by vpc (10 ft \times $\frac{3}{8}$ in. column, 20% FFAP, 200°), produced three products in the ratio 6:2:1 with 80% conversion in 25 hr. Removal of the solvent and preparative vpc gave the three products. The product formed in smallest yield was 2,3-dimethylnaphthalene (ir, nmr). The major product was *anti*-4-acetoxy-1,3,3,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene (**18a**): nmr see structure; ir (CCl₄) 2950, 1725, 1375, 1240, 1035 cm⁻¹; *m/e* 270 (P), 156 (base).

Anal. Calcd for C₁₆H₂₀O₂: C, 80.00; H, 8.15. Found: C, 80.07; H, 8.24.

The third product was *anti*-3-acetoxy-1,4,4,8-tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-ene (**19a**): nmr see structure; ir (CCl₄) 2950, 1730, 1375, 1250, 1040 cm⁻¹; *m/e* 270 (P), 156 (base).

Anal. Calcd for C₁₆H₂₀O₂: C, 80.00; H, 8.15. Found: C, 80.18; H, 8.19.

anti-**1,3,3,8-Tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-ol (21a).** Lithium aluminum hydride reduction of **18a**, as described for **13s**, gave a quantitative yield of **21a**: nmr see structure; ir (CCl₄) 3650, 3500, 2950, 1485, 1390, 1050 cm⁻¹. Jones oxidation of **21a**, as described for **21s**, gave a quantitative yield of **22** (identical ir, nmr).

anti-**1,4,4,8-Tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-3-ol (23a).** Lithium aluminum hydride reduction of **19a**, as described for **13s**, gave a quantitative yield of **23a**: nmr see structure; ir (CCl₄) 3650, 3500, 2950, 1485, 1390, 1075 cm⁻¹.

1,4,4,8-Tetramethyl-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-3-one (24). Jones oxidation of **23a**, as described for **21s**, gave a quantitative yield of **24**: nmr see structure; ir (CCl₄) 2920, 1715, 1465, 1380, 1100, and 1060 cm⁻¹; uv (EtOH) λ_{max} 300 nm (ϵ 2400), 289 (2600), 278 (6900), 270 (10,000, sh), 261 (13,000, sh), 251 (17,000, sh), 208 (100,000); *m/e* 226 (P), 156 (base).

Anal. Calcd for C₁₆H₁₈O: C, 84.96; H, 7.96. Found: C, 85.00; H, 8.04.

5,6-Benzobicyclo[2.2.2]octa-5,7-dien-2-one (25) and 25-d₂. A solution of 20 g (77 mmol) of 1,2,3,4-tetrahydro-9-oxo-1,4-ethanonaphthalene-2,3-dicarboxylic acid²³ in a mixture of pyridine (150 ml), triethylamine (12 ml), and water (12 ml) was placed in a rectangular jar which contained two bright Pt electrodes (5 \times 7.5 cm) separated by 4.5 cm, a water cooling coil, and a nitrogen bubbler. A constant unfiltered DC potential (110 V rms) was placed on the electrodes; the initial current was 490 mA. After 15 hr of electrolysis the current had fallen to 200 mA and the solution was black. Evaporation of the solvents (*in vacuo*) left 25 g of a black tar which was extracted with hot ether (10 \times 50 ml). The ether solution was washed with 30% aqueous acetic acid (6 \times 50 ml) and water (10 \times 50 ml), dried (MgSO₄), and evaporated to give 5.5 g (32 mmol, 42%) of a brown oil with an nmr spectrum identical with that reported for **25**.¹³ The oil was crystallized from ethanol–water and recrystallized from hexane to give white needles, mp 53–55° (lit.¹³ 55.7–57°).

Ketone **25-d₂**, deuterated in the methylene group, was prepared by stirring **25** with excess 5 M NaOCH₃ in CH₃OD at room temperature for 6 hr. Its nmr spectrum was identical with that of **25** except that the two-proton multiplet at τ 8.07 was absent.

syn- and *anti*-**5,6-Benzobicyclo[2.2.2]octa-5,7-dien-2-ols (26s and**

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26a). Ketone **25** (or **25-d₂**) was reduced with lithium aluminum hydride as described for the preparation of **16s** and **16a**. Vpc analysis of the product (5 ft \times 0.25 in. column, 30% SE-30, 150°) gave two peaks, area 3:2. The products were collected and identified as **26s** and **26a**, respectively. For **26s**: nmr τ 2.95 (4 H, s, arom), 3.67 (2 H, br m, vinyl), 6.15 (2 H, br m), 7.93 (1 H, br m), 8.63 (1 H, s), 9.10 (1 H, br m); in **26s-d₂**, the signals at τ 7.93 and 8.63 were absent, and the signal at τ 9.10 sharpened to a singlet; ir (CCl₄) 3600, 3100, 2950, 1400, 1250, 1060 cm⁻¹. A small sample of **26s** was converted to its acetate (as in the preparation of **12s**), whose nmr spectrum showed an acetyl methyl peak at τ 8.22. For **26a**: nmr τ 2.95 (4 H, s, arom), 3.42 (2 H, br m, vinyl), 6.05 (2 H, br m), 8.00 (1 H, br m), 8.07 (1 H, s), and 8.75 (1 H, m); in **26a-d₂**, the signals at τ 8.00 and 8.07 were absent, and the signal at τ 8.75 sharpened to a singlet; ir (CCl₄) 3600, 3100, 2950, 1400, 1250, 1050 cm⁻¹. A small sample of **26a** was converted to its acetate (as in the preparation of **12s**), whose nmr spectrum showed an acetyl methyl peak at τ 8.07.

Jones oxidation of the epimeric mixture of **26s** and **26a**, as described for **21s**, gave a quantitative yield of **25**.

Irradiation of 26s. A solution of **26s** (123 mg) in acetone (3 ml) in a Pyrex test tube sealed with a septum was deoxygenated with a N₂ stream for 30 min. An aliquot withdrawn before irradiation, injected into a vpc column (5 ft \times 0.25 in., 20% FFAP, 185°), showed two peaks with retention times 3.5 and 21 min, due to naphthalene and **26s**, respectively. Irradiation was carried out in a Rayonet reactor fitted with 300-nm tubes. Product peaks appeared at retention times 18 and 27 min, area ratio 1:7; conversion was complete in 85 hr. The minor product was not identified. The major product was *syn*-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-ol

(**27s**). For the nmr spectrum, see the structure and the text. Ir (CCl₄): 3590, 3490, 3050, 2950, 1480, 1400 cm⁻¹.

6,7-Benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-one (28). Jones oxidation of **27s**, as described for **21s**, gave a quantitative yield of **28**: nmr see structure; ir (CCl₄) 3080, 2980, 1738, 1480, 1265 cm⁻¹; uv (EtOH) λ_{\max} 285 nm (ϵ 12,000), 235 (33,000, s h), 209 (17,500); *m/e* 170 (P), 128 base).

Anal. Calcd for C₁₂H₁₀O: C, 84.68; H, 5.92. Found: C, 84.75; H, 6.02.

Lithium aluminum hydride reduction of **28**, as described for **16s** and **16a**, gave a quantitative yield of alcohol identical (ir, nmr) with **27s**.

Irradiation of 26a. A solution of **26a** (97 mg) in acetone (3 ml) was irradiated in the same manner as **26s**. A single product with vpc retention time of 34 min was formed. It was identified as *anti*-6,7-benzotricyclo[3.3.0.0^{2,8}]oct-6-en-4-ol (**27a**): nmr spectrum, see structure and the text; ir (CCl₄) 3590, 3400, 3050, 2950, 1480 cm⁻¹. Jones oxidation of **27a**, as described for **21s**, gave a quantitative yield of **28** identical (ir, nmr) with the oxidation product of **27s**.²⁴

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(24) During the time this manuscript was being prepared for publication, another example of a remote group controlling the regioselectivity of the di- π -methane photoisomerization was described by I. Murata and Y. Sugihara, *Tetrahedron Lett.*, 3785 (1972).

Photochemical Reactivity of Some Benzoylthiophenes. I. Electronic Absorption and Emission Spectra¹

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Abstract: The ultraviolet absorption and phosphorescence emission spectra of 2- and 3-benzoylthiophene and their *p*-cyano and *p*-methoxy derivatives have been measured. Partial state diagrams are drawn. The lowest energy absorption in every case is the carbonyl $n \rightarrow \pi^*$ transition. The $\pi \rightarrow \pi^*$ transition associated with the 2-thienoyl chromophore is at considerably longer wavelength than the corresponding transition of the 3-thienoyl chromophore. The lowest triplet of the 2-benzoylthiophene derivatives has π, π^* character and is assigned to the 2-thienoyl moiety. The 3-benzoylthiophene derivatives have an n, π^* triplet.

Photochemistry is one of the most versatile tools available for organic synthesis. However, in order fully to exploit the unusual reactivity of molecules in an excited state there is a need to define the generalizations governing this reactivity. This is a nontrivial matter, more complex than for ground-state molecules, since there are several possible electronic configurations for both singlet and triplet excited states and the rates of internal conversion and intersystem crossing can be competitive with rates of reaction. Furthermore, the same product may arise from more than one state and, in fact, by more than one mechanism involving the same state so that several sets of generalizations may well be necessary.

The most extensively studied functional group in photochemistry is the carbonyl group, and several

generalizations with regard to carbonyl photochemical reactivity have been put forth. For example, hydrogen abstraction, both intra- (*e.g.*, Norrish type II) and intermolecular, is a general reaction of the n, π^* singlet and triplet states of ketones and aldehydes. The carbonyl n, π^* singlet and triplet states also generally add to olefins to form oxetanes. Both of these reactions have been studied with a large number of substituted acetophenone and benzophenone derivatives;³ some limitations to reactivity have been defined and the results are largely, *post facto*, interpretable.

The question should now be asked, can these generalizations be applied to predict the photochemical

(1) Contribution No. 56 from the Photochemistry Unit.

(2) Alfred P. Sloan Fellow, 1972-1974.

(3) Pertinent reviews include: (a) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); (b) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold, New York, N. Y., 1967 Chapter 7; (c) A. Schönberg, "Preparative Organic Photochemistry," Springer-Verlag, New York, N. Y., 1968, Chapters 22 and 41; (d) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).