Photochemistry without Light and the Stereochemistry of the Type A Dienone Rearrangement. Organic Photochemistry.[1] XXXVIII[2]

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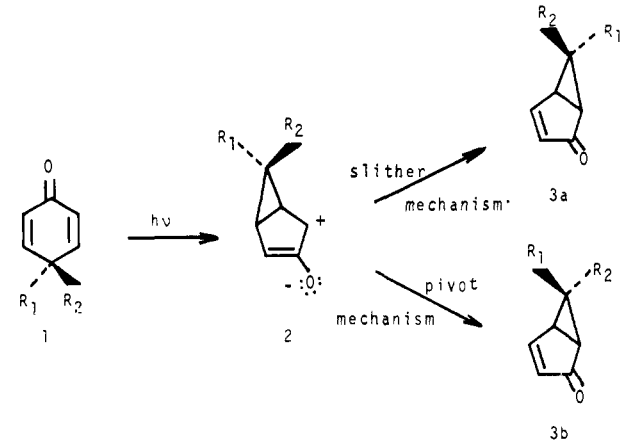
Abstract: A means of generating the zwitterionic species postulated as reaction intermediates in dienone photochemistry was developed. This involved synthesis of 2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one and 2,4-dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one. Treatment of the monobromo ketone with potassium *t*-butoxide or the dibromo ketone with zinc afforded the Type A rearrangement product, 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in a process postulated as proceeding *via* the zwitterionic species of the photochemical process. 6-*endo*-Phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one, 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one, 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one, 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]-hexan-3-one were synthesized and their configurations were interrelated. Reaction of 2-bromo-6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one with potassium *t*-butoxide in *t*-butyl alcohol afforded 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hex-3-en-2-one. Similarly, under these reaction conditions, 2-bromo-6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one gave stereospecifically 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hex-3-en-2-one. In analogy to the stereochemistry of the santonin to lumisantonin rearrangement, the dark reaction of the bromo ketones proceeded with inversion of configuration at the benzhydryl carbon which migrates by a "slither" rather than a pivot mechanism. The stereochemical course is rationalized on a molecular orbital basis.

One of the most intriguing of photochemical rearrangements is the Type A transformation[3] of cross-conjugated cyclohexadienones. Of particular interest is the stereochemistry of the process. *A priori*, the β,β-bridged species **2** formed photochemically from the dienone has two stereochemical courses available to it for rearrangement. This is shown in Chart I.[4]

Chart I. Two Possible Stereochemical Courses for Rearrangement of the β,β-Bridged Species in the Type A Photochemical Dienone Rearrangement



It may be seen that Chart I depicts only one of the two possible stereochemical modes of β,β bonding, namely that with R_2 becoming *endo*. A study of the stereochemistry of the Type A rearrangement is markedly simplified by beginning with the zwitterion itself. Therefore, attention was directed toward methods of generating zwitterions of type **2** both to determine if these species would rearrange as indicated and, if so, to study the stereochemistry of the rearrangement.

Synthetic Details and Stereochemical Assignments. For this study, 6,6-diarylbicyclo[3.1.0]hexan-2-ones, 6,6-diarylbicyclo[3.1.0]hexan-3-ones, and their α-bromo derivatives were required. The 6,6-diphenyl compounds were synthesized first.

6,6-Diphenylbicyclo[3.1.0]hex-2-ene (**4**) was synthesized by photolyzing diphenyldiazomethane in cyclopentadiene. 6,6-Diphenylbicyclo[3.1.0]hex-2-ene (**4**) was then hydroborated to give a mixture of 6,6-diphenylbicyclo[3.1.0]hexan-2-ol (**5**) and 6,6-diphenylbicyclo[3.1.0]hexan-3-ol (**6**) which were separated by silica gel chromatography. 6,6-Diphenylbicyclo[3.1.0]-hexan-2-ol (**5**) was converted by Sarett oxidation to 6,6-diphenylbicyclo[3.1.0]hexan-2-one (**7**); 6,6-diphenylbicyclo[3.1.0]hexan-3-ol (**6**) was similarly oxidized to 6,6-diphenylbicyclo[3.1.0]hexan-3-one (**8**). 2,4-Dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one (**9**) was synthesized by brominating the 3-ketone **8**. The bicyclic skeleton, including the placement of the carbonyl group in the dibromo ketone **9**, was confirmed by treating **9** with dilute hydrogen iodide in acetone[5] which yielded the 3-ketone **8**. 2-Bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one (**11**) was synthesized by brominating the enol acetate (**10**) of **8**. The bicyclic skeleton and carbonyl location of the monobromo ketone **11** was also confirmed by debromination with dilute hydrogen iodide in acetone,[5] which yielded 3-ketone **8**. These syntheses are summarized in Chart II.

(1) Preliminary communications: (a) H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **88**, 5352 (1966); (b) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968).

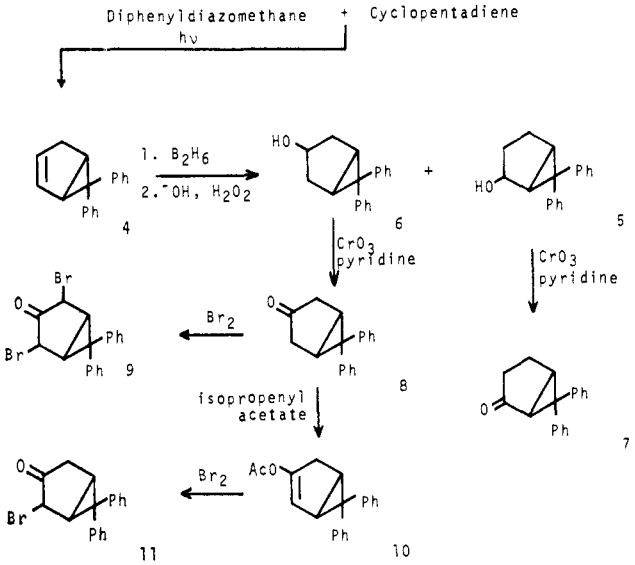
(2) For paper XXXVII of the series, note H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968).

(3) (a) H. E. Zimmerman and D. I. Schuster, *ibid.*, **83**, 4484 (1961); (b) *ibid.*, **84**, 4527 (1962); (c) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 947 (1964); (d) *ibid.*, **89**, 906 (1967); (e) H. E. Zimmerman, 17th National Organic Symposium, Bloomington, Ind., June, 1961, Abstracts, p 31.

(4) In Chart I the first arrow leading from dienone to zwitterion actually represents a series of processes: excitation, intersystem crossing, β,β bonding, and demotion with intersystem crossing.

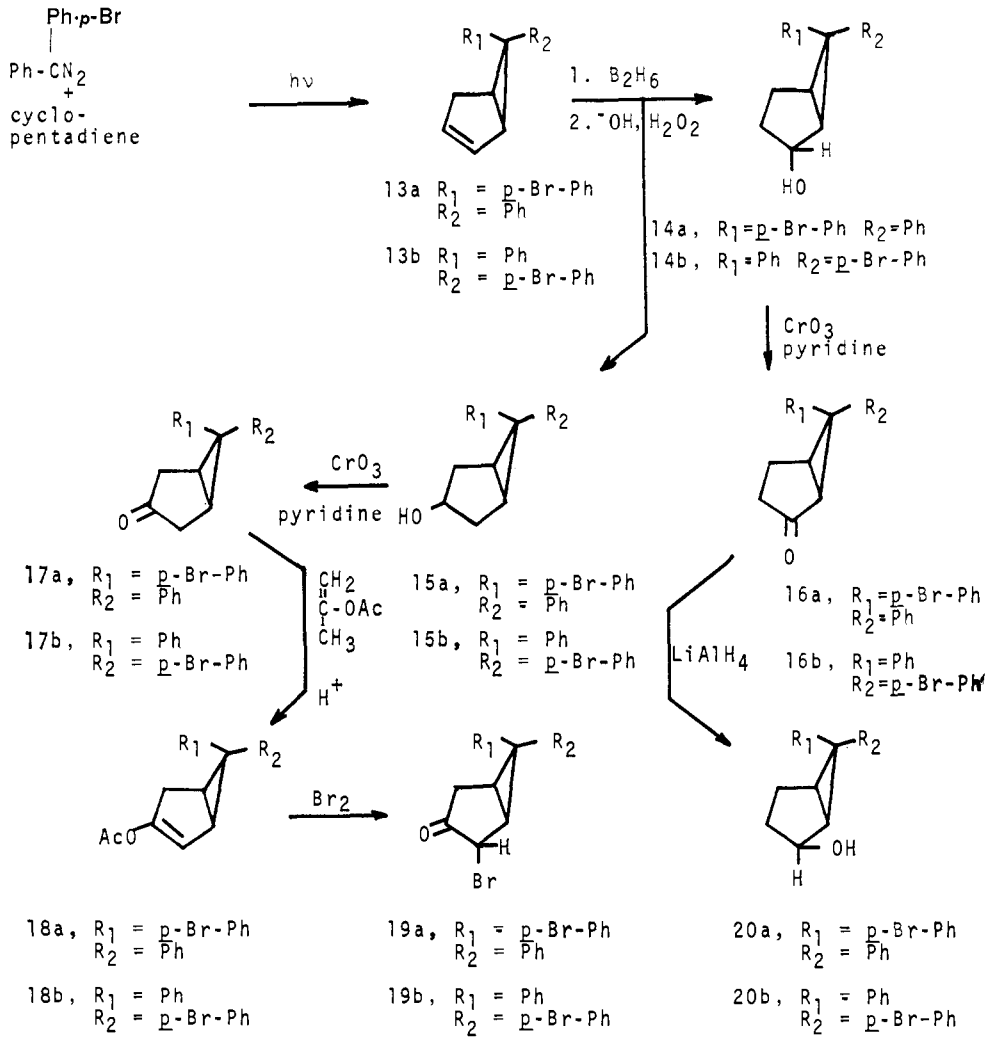
(5) Room temperature, 10 min; this reagent provides a mild method of debromination *via* the enol. *Cf.* H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955).

Chart II. Synthesis of the 6,6-Diphenylbicyclo[3.1.0]hexanones and Their α-Bromo Derivatives



(**12**) in cyclopentadiene yielded the two isomeric alkenes 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo-[3.1.0]hex-2-ene (**13a**) and 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hex-2-ene (**13b**). These were separated by crystallizing **13a** from the mixture and reverse phase liquid–liquid partition chromatography of the residue. Each of the two epimeric bicyclic alkenes was separately subjected to the synthetic sequence shown in Chart III. Thus, **13a** was hydroborated to a mixture of 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*exo*-ol (**14a**) and 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-ol (**15a**) which was then separated by silica gel chromatography. Sarett oxidation of **14a** gave 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one (**16a**); similar oxidation of **15a** gave 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one (**17a**). Bromination of the enol acetate **18a** of the *exo*-phenyl-3-one gave 2-bromo-6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one (**19a**). Lithium aluminum hydride reduction of the *exo*-phenyl-2-one **16a** stereo-

Chart III. Synthetic Aspects of the Phenyl-*p*-bromophenyl Series



Next it was necessary to prepare similar bicyclic ketones with different aryl groups substituted at carbon-6. Photolysis of phenyl-*p*-bromphenyldiazomethane selectively gave 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*endo*-ol (**20a**).

Similarly, **13b** was hydroborated to a mixture of 6-

endo-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*exo*-ol (**14b**) and 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-ol (**15b**) which was separated by silica gel chromatography. Sarett oxidation of **14b** gave 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]-hexan-2-one (**16b**); similar oxidation of **15b** gave 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one (**17b**). Bromination of the enol acetate **18b** of the *endo*-phenyl-3-one gave 2-bromo-6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one (**19b**). Lithium aluminum hydride reduction of the *endo*-phenyl-2-one **16b** stereoselectively gave 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*endo*-ol (**20b**). These synthetic details are summarized in Chart III.

The assignment of the hydroxyl configurations of alcohols **14a**, **14b**, **20a**, and **20b** is based on the assumption of least hindered approach in both the hydroboration and lithium aluminum hydride reactions. Also, since there is evidence in the literature[6] indicating that the bromophenyl moiety hydrogen bonds less strongly than the phenyl group, the OH stretching region of the infrared of the stereoisomeric phenyl-*p*-bromophenylbicyclo[3.1.0]hexan-2-*endo*-ols (**20a** and **20b**) was inspected to help elucidate the configuration at carbon-6 (*i.e.*, which aromatic group was *endo* in each compound). The results are summarized in Table I. We note that

Table I. Hydroxyl Hydrogen Bonding

Compd	Concn, *M*	I_b/I_f[a]
20a	0.032	0.21
20a	0.135	0.16
20b	0.038	0.35
20b	0.113	0.43

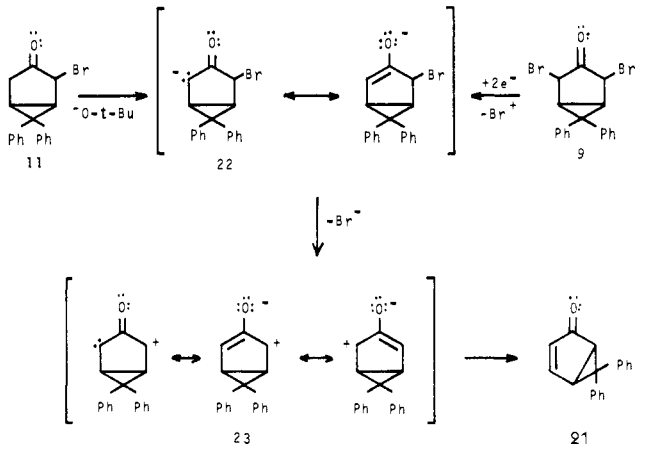
[a] Ratio of integrated intensites.

the stronger hydrogen bond, as revealed by the relative intensities at 3622 (free OH) and 3600 cm^{-1} (internally bonded OH), occurs in **20b**; this should be the isomer with the phenyl *endo*. Still further evidence was available from the nmr of the 2- and 3-ketones. In each of these compounds either the aryl A_2B_2 quartet or the phenyl pseudo singlet was found to be shifted downfield, and it was the group assigned the *endo* configuration which was shifted. The carbonyl group is expected to deshield the hydrogens of the *endo* group.

It is to be noted that although the *endo*–*exo* configurational assignments are convincing, the relative configurations are absolute. Since 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one (**16a**), 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one (**17a**), and 2-bromo-6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one (**19a**) were prepared from the same bicyclic alkene **13a**, these must all have the same configuration at carbon-6. The same is true of the b series ketones. The subsequent mechanistic conclusions depend only on relative configurations rather than absolute assignments.

Generation of Zwitterionic Species from 2-Bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one and 2,4-Dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one. The Favorskii reaction of α-halo ketones with base has been postulated[7] as proceeding in polar solvents *via* a symmetrical zwitterionic intermediate which is quite similar to the zwitterions which we have proposed[3] for many dienone photochemical reactions. It was hoped that the bromobicyclo-3-ones under basic conditions might give rise to the zwitterion which then would undergo the Type A rearrangement so characteristic of dienone photochemistry. Accordingly, 2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one (**11**) was treated with 1 equiv of potassium *t*-butoxide in *t*-butyl alcohol for 7 min at 40° and gave a 74% yield of 6,6-diphenylbicyclo[3.1.0]-hex-3-en-2-one (**21**). This can be viewed as beginning with proton abstraction to form the bromo enolate **22**, followed by loss of bromide ion to give zwitterion **23** which, in turn, then rearranges (*cf.* Chart IV). The

Chart IV. Rearrangement of the Monobromo- and Dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-ones



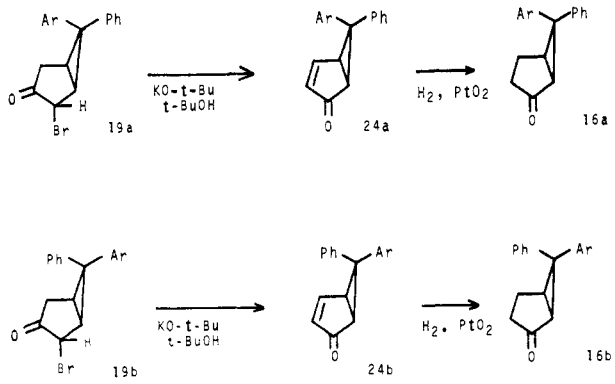
reductive debromination of 2,4-dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one (**9**) with zinc in dry refluxing dioxane gave a 74% yield of photoketone **21**. Similarly the dibromide **9** gave 26% of photoketone **21** on treatment with calcium in tetrahydrofuran at −70° and 14% of **21** on treatment with sodium amalgam in benzene at room temperature. These reactions may be viewed as proceeding by donation of two electrons from the metal to the dibromide which loses bromide ion to form the same bromo enolate **22** as obtained with base from the monobromo ketone **11**. The bromo enolate then proceeds as before to lose bromide ion forming the zwitterion **23** which then rearranges.

Stereochemistry of the Rearrangement of 2-Bromo-6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one and 2-Bromo-6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one. The stereochemistry of this rearrangement is of particular interest. Treating 2-bromo-6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one (**19a**) with 1 equiv of potassium *t*-butoxide in *t*-butyl alcohol for 6 min at 42° gave a 76% yield of 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hex-3-en-2-one (**24a**).[8] Trace amounts of the stereoisomer **24b**, if present, would have been detected from the appropriate chromatographic fractions and crystallization filtrates, but none (<1 to 0.5%) was encountered. Catalytic hydrogenation of **24a** gave the known 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one (**16a**) (note Chart V). Sim-

(6) (a) M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 955 (1959); (b) *ibid.*, **34**, 1395 (1961).

(7) (a) For discussions of the occurrence of such zwitterions in polar media, note H. O. House and W. F. Gilmore, *J. Am. Chem. Soc.*, **83**, 3927, 3980 (1961); (b) J. G. Aston and J. D. Newkirk, *ibid.*, **73**, 3902 (1951); J. G. Burr and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

Chart V. Stereochemical Course of the 2-Bromo-6-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-3-one Isomers

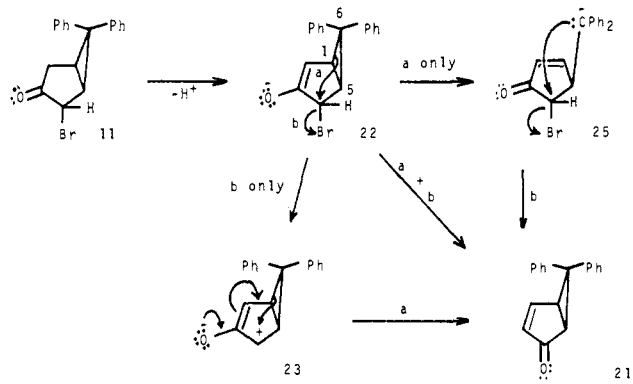


ilarly, 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo-[3.1.0]hexan-3-one (**19b**) on treatment with potassium *t*-butoxide in *t*-butyl alcohol gave a 66% yield of 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hex-3-en-2-one (**24b**)[8] as the sole product of the rearrangement. Catalytic hydrogenation of **24b** gave the known 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one (**16b**).

The simplest statement of these results is that the group that is *endo* to the five-membered ring in the starting material is still *endo* to the five-membered ring in the product; and, equivalently, the group that is *exo* to the five-membered ring in the starting material is still *exo* to the five-membered ring in the product.

Mechanistic Interpretation. Discussion of the Gross Features of the Rearrangement. The rearrangement of 2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one (**11**) into 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**21**) on treatment with potassium *t*-butoxide and the parallel rearrangement of the 2,4-dibromo ketone **9** into the same product on treatment with zinc can reasonably be interpreted, as noted above, as beginning with enolate **22** formation In principle, loss of bromide from this enolate could follow, be concerted with, or precede fission of bond 1,6 (see Chart VI). It is reasoned that

Chart VI. Mechanistic Gradations of the Rearrangement

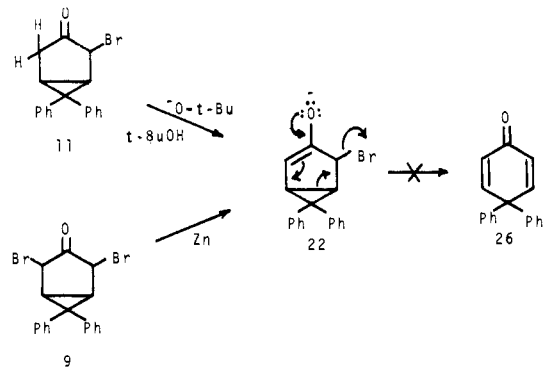


if scission of bond 1,6 occurs as a discrete initial step to afford the free carbanion **25** with any appreciable lifetime,[9] free rotation in the case of the *p*-bromo-substituted compounds **19a** and **19b** would afford a mixture of rotamers and subsequent displacement of bromide would then give a mixture of stereoisomers—a result not observed (*vide supra*). At the other extreme is loss of bromide preceding any 1,6-bond fission. We do note that species **22** is not only an allylic bromide but also a cyclopropyl carbinyl derivative. Additionally, the molecule contains an enolate moiety whose negative charge will facilitate anion expulsion.[10] Loss of bromide from enolate **22** affords zwitterion **23**[11] which is the species postulated by us earlier as an intermediate in the photochemical reaction. The observed rearrangement which gives 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**21**) can then be taken to be necessary and strongly suggestive evidence that a common zwitterionic intermediate actually is involved in both photochemical and nonphotochemical reactions. If this is correct, the present reaction can be stated to provide photochemistry without light.

It is of course possible that two slightly different but related mechanistic pathways could channel to the same product. For example, if bromide departure were concerted with rearrangement of the benzhydryl group, we would be dealing with an "incipient zwitterion" rather than the zwitterion **23** itself.

An interesting facet of the present reaction is that only bicyclic ketone **21** was observed; but no 4,4-diphenylcyclohexadienone (**26**), although the latter is a potential product from the *t*-butoxide and zinc reactions (note Chart VII).

Chart VII. Dienone Formation as a Potential but Unrealized Product



This accords with our previously presented interpretation[3c] based on the "forbiddeness" of the zwitterion (**23**) to dienone **26** conversion and the evidence for absence of appreciable reversion of zwitterion to dienone in the photochemical process.[3c,12]

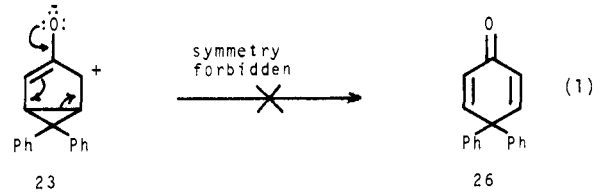
(8) H. E. Zimmerman and J. O. Grunewald, *J. Am. Chem. Soc.*, **89**, 5163 (1967).

(9) If this carbanion is formed with a sufficiently short lifetime due to rapid cyclization relative to free rotation, the observed stereospecificity would be obtained. Such a result could, in principle, be derived from either steric or overlap inhibition of free rotation. Steric hindrance to loss of configuration is not expected since the carbanion is generated in a high-energy conformation with an aryl group *endo* to the five-membered ring. Retardation of rotation due to stabilization by overlap with the backside of the bromine bearing carbon is tantamount to concertedness, the second mechanistic gradation considered in the discussion.

(10) The unshared pair on oxygen and the negative charge are conjugated in a homoallylic way with the carbon bearing the bromide. This may also facilitate bromide expulsion.

(11) This is then a "Favorskii-like" intermediate with the addition of the fused 3-ring. For simple ketones this type of zwitterion has been postulated[7b,c] as an intermediate in the Favorskii reaction and evidence has been advanced that the zwitterion does intervene in polar solvents.[7a] The driving force for ionization here is greater for the reasons cited.

(12) If zwitterion **23** were not a discrete intermediate, then no symmetry exists, and the question arises whether the transformation to afford dienone (as in Chart VII) is still "forbidden." It seems quite certain that even in the nonsymmetrical process, a barrier similar to that of the zwitterion to dienone process would exist, but it most likely would be smaller.



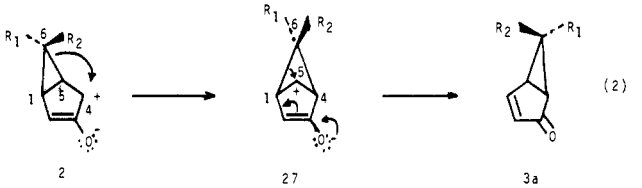
(1)

23 26

Mechanistic Interpretation. Discussion of the Reaction Stereochemistry. With the gross features of the reaction discussed, it is now of special import to explore the implications of the reaction stereochemistry, since stereochemistry seems likely to clarify the precise nature of the molecular details of the rearrangement.

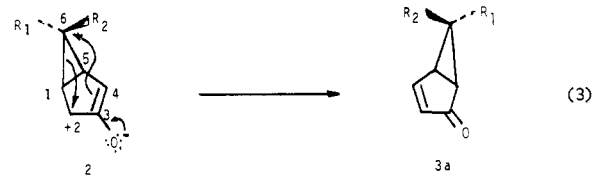
As noted above, the conversion of the *endo*-phenyl bromo ketone **19b** into the *endo*-phenyl bicyclic enone **24b** and the *exo*-phenyl bromo ketone stereoisomer **19a** into the *exo*-phenyl bicyclic enone **24a** may be taken as signifying that in the rearrangement of zwitterions, the *endo* group remains *endo* and the *exo* group remains *exo*. This tells us that the slither mechanism (Chart I) is operative and that the pivot mechanism is inoperative. The question is, why?

One simple formulation of the slither mechanism is that of two sequential 1,2 shifts (eq 2). An alternative view is that as bond 1,6 is weakened and then broken, concerted 4,6 bonding ensues with carbon-4 attacking the reverse face of C-6.[13]



(2)

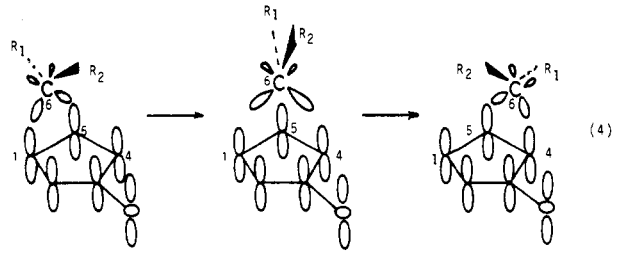
2 27 3a



(3)

2 3a

On looking more closely at these two mechanisms—the double 1,2 shift and the rearside bonding—we note an interesting relationship. In the double 1,2-shift version, a divalent carbon-6 with two hybrid sp^n (*e.g.*, sp^5) orbitals[14] may be pictured as slithering along the five-ring of a cyclopentadienone moiety (note eq 4 and structure **28** for the half-rearranged species). First these sp^5 orbitals are bonded to C-1 and C-5 and then to C-5 and C-4.[14]



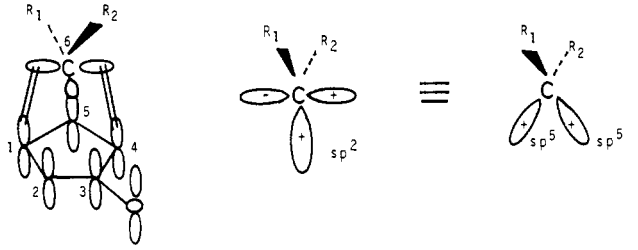
(4)

28 (equiv. to 27)

(13) This might validly be termed an inversion at C-6, except that since the *endo* product is formed from *endo* reactant and *exo* from *exo*, this terminology is confusing.

(14) Since the exact hybridization is unknown, sp^n is meant merely to signify a hybrid with heavier p character than s character.

Alternatively, at the half-way stage of the rearside bonding mechanism, we might picture (note **29**) C-6 being approximately sp^2 hybridized and bonded to C-5 by an sp^2 orbital. Here, one lobe of the p orbital at C-6 would bond to the p orbital at C-1 while the other lobe overlaps with the C-4 p orbital.



29 (equiv. to 27) 30 31

The difference between these formulations is recognized to vary from negligible to nil depending on whether the precise positioning of C-6 with respect to the five-ring is taken as identical in the two structures.[15] Thus the two (*e.g.*) sp^5 orbitals of **31** are merely the normalized linear sum and difference of the p and sp^2 orbitals of **30** and conversely.[15a]

These equivalent formulations lead us to an understanding of the preference for the slither or reverse-side bonding mechanism over the pivot possibility. In looking at the half-rearranged species, we note that **28′** has a cyclic array of six orbitals and six electrons with no sign inversion (*i.e.*, a Hückel-like system[16a]) (Figure 1). Hückel-like systems are known to be "aromatic" with $4n + 2$ electrons. Formulation **29′** has five orbitals and four electrons but a single sign inversion *between* orbitals and constitutes a Möbius system[16a] which is known[18] to be "aromatic" and stable with $4n$ electrons.[16b] Thus either of the equivalent pictures **28′** or **29′** is predicted to be stable. Conversely, species **32′** of the pivot mechanism has five orbitals in a cycle, no sign inversion, and four delocalized electrons and thus represents an antiaromatic system.[16b] The interpretation accords with the facts. In the two representations (*i.e.*, **28′** and **29′**) of the slither intermediate, we have neglected the p orbital at C-5 of **28′** and the σ orbitals χ_5 and χ_6 bonding C-6 to C-5 in **29′**. In the process, we have based our interpretation on a different number of orbitals. Nevertheless, these now nonequivalent interpretations have led to the same prediction of stability. In contrast,

(15) (a) Note J. A. Pople, *Quart. Rev.* (London), 11, 273 (1957); (b) The choice of $sp^2 + p$ in moiety **30**, sp^5 in **31**, and the π system in the 5-ring portion is only representative and approximate with the exact hybridizations being uncertain. The conclusions hold where these are chosen differently but appropriately.

(16) (a) Hückel-like systems have zero or, in general,[17] an even number of sign inversions (*i.e.*, sign changes between orbitals) in a cyclic array of orbitals. Möbius-like systems have one or, in general,[17] an odd number of sign inversions between orbitals constituting a cyclic array. (b) For ground states, it is well known that for Hückel systems $4n + 2$ electrons are needed for aromaticity while $4n$ electrons afford an "antiaromatic" species. Conversely, for Möbius systems, $4n$ is the "magic number" conferring aromaticity while with $4n + 2$ electrons Möbius species are antiaromatic. (c) Sign inversions *within* an atomic or hybrid orbital do not contribute to the odd or even summation.

(17) (a) This depends on the choice of the directionality of the basis set (*i.e.*, definition) set of orbitals chosen. (b) The basis set of AO's should not be confused with the final MO's after mixing. The **28′**, **29′**, and **32′** of Figure 1 give the basis set of orbitals while **29′′** and **32′′** in Figure 2 give the directionality of orbitals in ψ_3 of the oxybutadienyl moiety (*i.e.*, after quantum mechanical mixing).

(18) H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1564, 1566 (1966); *Science*, **153**, 3738 (1966).

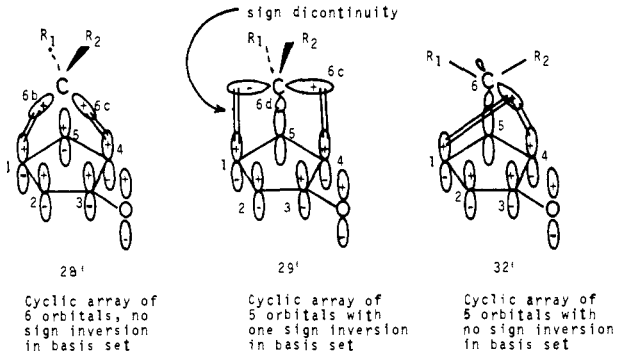


Figure 1. Möbius and Hückel cyclic orbital arrays.

32′, the pivot species, has five orbitals in a Hückel array and four electrons and is antiaromatic. Thus the slither intermediate is preferred.

A second interpretation rests on the symmetry of the highest occupied MO of the 2-oxybutadienyl moiety common to species **28** and **29** and the symmetry of the migrating group. The following symmetry argument is precisely that suggested by Zimmerman[19] in another application.

As was noted, the splitting of two interacting MO's is given by the expression: $E_{\pm} = {}^1/_2(E_U + E_L) \pm ({}^1/_2)\sqrt{(E_U - E_L)^2 + B}$. Here E_+ and E_- are the new MO's resulting from interaction of the two MO's ψ_U and ψ_L, one from each of the two moieties (*i.e.*, carbon-6 and oxybutadienyl). E_U and E_L are the energies of the upper and lower energy MO's mixing, and B is a measure of the extent of the interaction and is given by

$$B = 4\left(\sum_{i}^{\text{orbitals in U}}\sum_{j}^{\text{in L}} C_{iU}C_{jL}h_{ij}\right)^2 \qquad (5)$$

where C_{iU} and C_{jL} and the Hückel MO coefficients for the two MO's ψ_U and ψ_L and the h_{ij}'s are the matrix interaction elements between atomic orbitals in the basis set of the two moieties.

In applying this reasoning to species **29′** and **32′**, we mix the oxybutadienyl highest occupied MO (ψ_3) with the migration group's orbital as shown in **29″** and **32″** (Figure 2).

If $B = 0$, there is no interaction, eq 5 becomes $E_+ = E_U$ and $E_- = E_L$, and there is no electronic stabilization. For both species being compared, **29′** and **32′**, all h_{ij}'s = 0 except for $i = 6$ and $j = 1$ or 4. Also, $C_6 = 1$ since the orbital centered at carbon-6 is the only one present in the single MO of the one-carbon moiety. Hence for either species **29′** or **32′**, $B = 4(C_{1b}h_{16} + C_{4b}h_{46})^2$. Here C_{1b} is the LCAO MO coefficient weighing atomic orbital χ_1 in the highest occupied MO (*i.e.*, ψ_3, note Figure 2, of the oxybutadienyl moiety). Similarly, C_{4b} is the coefficient for AO χ_4 in the same MO. Hückel calculations (see Experimental and Calculation Sections) give $C_{1b} = +0.7357$ and $C_{4b} = -0.2857$.

For a 1,4-suprafacial migration of a single lobe of an orbital at C-6 as in species **32′** (*i.e.*, the pivot mechanism) h_{16} and h_{46} will be positive since positive portions of the orbitals overlap in the basis set as defined (note Figure 1). As a result of the h's both being postive for this stereochemistry and the C's being of opposite sign, the terms $C_{1b}h_{16}$ and $C_{4b}h_{46}$ tend to be self-canceling and B will be small throughout the rearrangement. Were we to use ψ_2 of butadiene as an approximation, at the midpoint of the migration $h_{16} = h_{46}$ and $B = 0$ as a consequence of C_{1b} equaling $-C_{4b}$. In any case throughout the pivot process, B remains small and little energy lowering results.

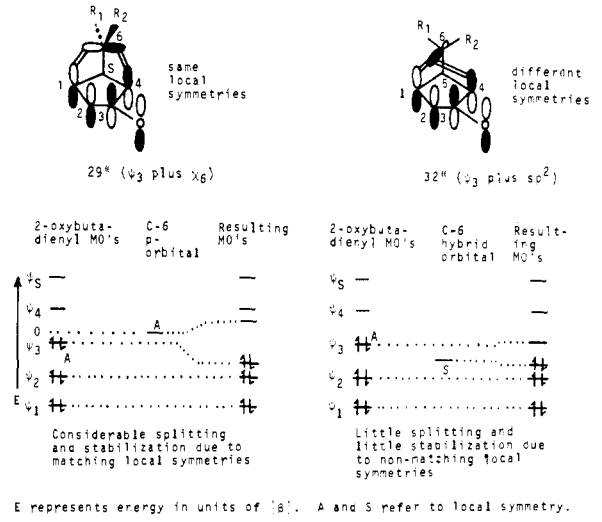


Figure 2.

In contrast, in the slither mechanism utilizing species **29′** the basis set is defined as in Figure 1 and h_{16} is positive while h_{46} is negative. Thus $C_{1b}h_{16}$ and $C_{4b}h_{46}$ are both positive and B is large throughout the slither reaction. This leads to extensive splitting (note Figure 2) and energy lowering.[20] Qualitatively in looking at the overlap of the migrating orbital with the oxybutadienyl highest bonding MO in Figure 2, we see self-canceling of overlap in the pivot process giving a small B. Also we see an additive interaction for the slither process, giving a large B and considerable stabilization. Thus the prediction favors the slither stereochemistry.

This is precisely equivalent to noting qualitatively that in **29″** (*i.e.*, the inversion representation of the slither species) the local symmetry[23] of the p orbital is antisymmetric (labeled A in Figure 2) and MO 3 of the oxybutadienyl moiety is also approximately antisymmetric and labeled A. This leads to the splitting of the p orbital and MO 3 noted above. Conversely, the local symmetry of the hybrid orbital at C-6 in species **32″** is approximately symmetric while the oxybutadiene MO, as noted, is approximately antisymmetric. Little splitting results and lesser stabilization ensues.

(19) H. E. Zimmerman, "Molecular Rearrangements," Vol. 1, Interscience Publishers, New York, N. Y., 1964, p 345, and *errata*.

(20) It should be noted that this approach which follows the method of Zimmerman[19] finds parallel in the frontier MO method of Fukui[21] and that of Woodward and Hoffmann.[22]

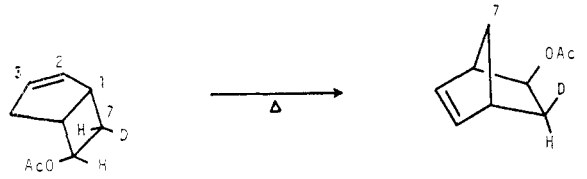
(21) (a) K. Fukui, *Tetrahedron Letters*, 2009 (1965); (b) "Molecular Orbitals in Chemistry, Physics, and Biology," P. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 525.

(22) (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, 87, 2046, 4388, 4389 (1965).

(23) Local symmetry refers to symmetry with respect to a plane perpendicular to the five ring and cutting through C-5 and bisecting bond 2–3 of Figure 2. The symmetry is only approximate since we are dealing with an oxybutadienyl moiety and not butadiene itself. Additionally at only one stage of the reaction is the conformation at C-6 such that the orbital here is precisely symmetric or antisymmetric.

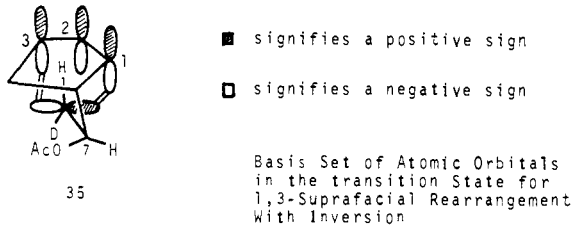
Relationship of the Zwitterion to Bicyclic Ketone Rearrangement of Sigmatropic Rearrangements in General. Completely aside from the relationship of the presently described rearrangement to the type A photochemical transformation, there is intrinsic interest in the rearrangement as an unusual type of sigmatropic rearrangment.[24] It is of interest to consider the relationship of the present transformation to those already known.

The present reaction may be termed a 1,4-suprafacial migration with inversion of configuration of the migrating carbon atom. Closely related to this is the intriguing thermal rearrangement, described by Berson,[25]



33 34

of **33** to give *exo*-norbornenyl acetate-*exo*-3-*d* (**34**). As has been noted by Berson, the reaction must proceed with inversion of configuration at carbon-7 to account for the configuration of the deuterium-bearing carbon in the product. The stereochemistry has been discussed by Berson using the symmetry of the highest occupied MO of the allylic moiety of the transition state comprising atoms 1, 2, and 3. We note that the Möbius–Hückel treatment leads to the same prediction. Thus in structure **35** the basis set of atomic orbitals for the rearrangement transition state is pictured. We have arbitrarily chosen the positive lobes of the allylic moiety up.[26] In counting around the cyclic array of four orbitals at carbons 1, 2, 3, and 7, we note a single (*i.e.*, odd number) sign inversion between orbitals 3 and 7. This means that the transition state is of Möbius type where $4n$ delocalized electrons is the preferred number in the same way the $4n + 2$ is preferred for a Hückel system. Migration with a single lobe overlapping with carbons 1 and 3 (*i.e.*, with retention of configuration) would afford a Hückel system in which $4n$ electrons confers antiaromaticity.



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The remaining examples of sigmatropic rearrangements do not involve inversion of configuration but are equally well treated by the present approach.

Thus, it can be stated in general that for sigmatropic rearrangements, as well as electrocyclic reactions in general, counting the number of sign inversions between adjacent orbitals to categorize the species as Hückel (0 or even number of inversions) or Möbius (odd number of inversions) constitutes a very quick approach to determining "forbiddeness" or "allowedness" of reactions.[27]

Experimental Section[28]

6,6-Diphenylbicyclo[3.1.0]hex-2-ene. A solution of 27.0 g (0.14 mol) of diphenyldiazomethane[29] in 250 ml of freshly cracked cyclopentadiene was purged with vanadous ion purified[30] nitrogen in a 250-ml, water-jacketed photolysis flask for 0.5 hr and then irradiated with a Hanovia 450-W medium-pressure mercury lamp through a Pyrex filter for 5 hr, during which time the purple color faded and a light orange color remained. The solution was concentrated *in vacuo* at 5–10° to remove excess cyclopentadiene.

The residue was filtered to give crystalline 1,1,2,2-tetraphenylethane (average 9.0 g = 0.027 mol, 39% for eight batches), mp 212° after sublimation (760 mm) (lit.[31] mp 211°) and a viscous oil (average 50 g for eight batches). A 150-g portion of this oil was chromatographed on a 6.5 × 100 cm deactivated silica-gel column (Grace, water treated and dried at 70°) slurry packed in 2% ether–petroleum ether (bp 68°); 250-ml fractions were collected using the same solvent. Fractions 9 and 10 gave 33.1 g of impure dicyclopentadiene; fraction 11, 25.1 g of a yellow oil; fractions 12–25, 56.3 g of a yellow viscous oil; subsequent fractions yielded a maximum of 1.0 g each of yellow oil mixed with solid tetraphenylethane. Fractions 11 and 12–25 were diluted with sufficient dry ether and chilled in Dry Ice–acetone to give colorless crystals.

Fraction 11 gave 1.40 g, fractions 12–25 yielded 10.60 g and a second crop of 4.10 g; the melting point was 74–78°. Crystallization from ether gave 13.90 g (14.2% based on diphenyldiazomethane) of 6,6-diphenylbicyclo[3.1.0]hex-2-ene as colorless crystals, mp 77–79°. Recrystallization from pentane gave 6,6-diphenylbicyclo-[3.1.0]hex-2-ene, mp 79–80°.

The spectral data were: ir (CCl_4, CS_2) strong 13.32, 13.60, 13.74, 14.20, 14.36 μ; medium 3.25, 3.26, 3.29, 3.44, 3.52, 6.25, 6.70, 6.91, 14.70 μ; weak 7.01, 7.45, 7.82, 8.61, 9.30, 9.41, 9.64, 9.80, 10.17, 10.74, 10.85, 12.07, 12.74 μ; nmr (CCl_4) τ 2.85 (pseudo s, 5 H, Ph), 2.99 (pseudo s, 5 H, Ph), 4.20 (q, $J_{23} = 5.5$ cps, $J_{12} = 2.0$ cps, 1 H, C-2 vinyl), 4.89 (m, 1 H, C-3 vinyl), 7.60 (broad m, 4 H, CH_2 and cyclopropyl); uv (cyclohexane) max, 276 (700); plateau, 268 (1145); 260 (1560); and plateau, 227 mμ (ϵ 12,800).

Hydroboration of 6,6-Diphenylbicyclo[3.1.0]hex-2-ene. To a solution of 27.54 g (0.118 mol) of 6,6-diphenylbicyclo[3.1.0]hex-2-ene in 70 ml of dry tetrahydrofuran at 0° was added 100 ml of a 1.46 *M* solution of diborane in tetrahydrofuran,[32] and the mixture was stirred at 0° for 1 hr under nitrogen and at room temperature for 1 additional hr. After the excess diborane had been destroyed by careful addition of THF–water (1:1), 160 ml of 3 *N* NaOH and then 110 ml of 30% hydrogen peroxide were added slowly with stirring. After stirring for 1.75 hr at room temperature, the mixture was poured into 600 ml of water, adjusted to pH 7, saturated with sodium sulfate, and ether extracted. Upon concentration, 27.40 g (0.109 mol, 92%) of the crude product mixture was obtained as a fluffy white solid, mp 119–140°. This was chromatographed on a 108 × 6.5 cm deactivated silica gel column slurry packed in 1:1 ether–petroleum ether (bp 68°); using the same solvent 250-ml fractions were collected. Fraction A10, 3.20 g, had mp 145–158°; A11, 6.10 g, had mp 130–150°. A12, 3.70 g, had mp 128–155°; A13, 4.3 g, had mp 125–150°; total weight, 17.3 g. Recrystallization from ether–petroleum ether gave 6.60 g of fine light needles, mp 157–158°. The mother liquors (10.7 g) and the fractions A14–20 (total, 6.98 g) were recycled on the same column. Fractions B13–19 gave 5.76 g of crystals which on recrystallization afforded

(24) For recent reviews note (a) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968); (b) J. A. Berson, *ibid.*, 1, 152 (1968).

(25) J. A. Berson and C. L. Nelson, *J. Am. Chem. Soc.*, **89**, 5503 (1967).

(26) With any different choice of orientation of the atomic orbitals (*i.e.*, a different basis set), we would still have the same even or odd result in counting sign inversions. For example, if orbital 2 is inverted, we would have three inversions rather than one. Each change in orientation of an orbital changes the number of inversions by two and therefore does not affect the even or odd nature of the system.

(27) With a monocyclic array of orbitals the approach is used without ambiguity. Where more than one ring of orbitals can be discerned, it seems to be generally the larger ring which is determining.

(28) All melting points were determined on a hot-stage apparatus calibrated with known substances.

(29) E. C. Horning, Ed., "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, New York, N. Y., 1955, p 351.

(30) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

(31) H. Biltz, *Ann. Chem.*, **296**, 221 (1897).

(32) G. Zweifel and H. C. Brown, *Org. Reactions*, 13, 31 (1963).

4.10 g of product, mp 157–158°. The total yield of 6,6-diphenylbicyclo[3.1.0]hexan-3-ol was 10.7 g (35.8%). Fractions B19–28 gave 12.01 (39%) of oily residues crystallizing on standing to give mp 85–115° and shown by ir to be a mixture of 6,6-diphenylbicyclo-[3.1.0]hexan-3-ol and 6,6-diphenylbicyclo[3.1.0]hexan-2-ol (*vide infra*).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.44, 86.27; H, 7.25, 7.25. The spectral data were: ir (CCl_4, CS_2) OH at 2.74 μ; medium 3.26, 3.29, 3.49, 3.59, 6.25, 6.70, 6.92 μ; intense 9.30, 9.69, 13.40, 14.15, 14.36 μ; nmr ($CDCl_3$) τ 2.70 (s, 5 H, Ph), 2.90 (s, 5 H, Ph), 7.14 (t, J = 7 cps, 1 H, -CHO), 7.56–8.49 (m, 7 H, OH, CH_2 and cyclopropyl); uv (cyclohexane) max 274.7 (480), 267.7 (690), 261.0 (650), 255.0 (500), 233.5 mμ (ϵ 15,400).

6,6-Diphenylbicyclo[3.1.0]hexan-2-ol. Fractions A21–27 from the chromatogram above gave 1.45 g of an oil which crystallized after prolonged standing. Recrystallization from cyclohexane gave 1.21 g (3.9%) of fine needles, mp 99–100.5°.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.27, 86.17; H, 7.19, 7.22. The spectral data were: ir (CCl_4, CS_2) OH at 2.75 μ; strong 9.31, 9.63, 9.75, 9.86, 9.95, 13.41, 14.16, 14.38, 10.17 μ missing in the 3 isomer; medium 3.23, 3.26, 3.29, 3.37, 3.40, 3.48, 6.25, 6.7, 6.92, 7.22, 7.63, 8.26, 8.60, 10.52, 10.93, 11.56, 11.81, 13.00, 13.25 μ; nmr ($CDCl_3$) τ 2.76 (s, 5 H, Ph), 2.92 (s, 5 H, Ph), 5.71 (d, 1 H, J = 5.1 cps); 7.74 (pseudo singlet (4 H); weak broad peaks at 8.03, 8.17 (1 H); weak broad peaks at 8.5, 8.75, and 8.86 (1 H); and a very broad multiplet ($W_{1/2}$ = 39 cps) centered at 9.5 (1 H); uv (cyclohexane): maxima at 274.0 (460), 268 (670), 261 (610), 255 (470), a shoulder at 248 (355), maximum at 223 mμ (ϵ 14,900).

6,6-Diphenylbicyclo[3.1.0]hexan-3-one. A solution of 11.45 g (45.7 mmol) of 6,6-diphenylbicyclo[3.1.0]hexane-3-ol in 10 ml of pyridine was added to Sarrett's reagent prepared from 450 ml of dry pyridine and 27.0 g of chromium trioxide. The mixture was stirred at room temperature for 10 hr. It was poured into 2 l. of 2% sodium sulfate solution and ether extracted; the extracts were washed twice with a mixture of 250 ml of concentrated HCl and 700 g of ice, then once with 200 ml of 10% sodium bicarbonate solution, and finally with 200 ml of saturated sodium sulfate solution, dried over magnesium sulfate, and concentrated *in vacuo*. The residue was taken up in 200 ml of methanol, heated with 1 g of charcoal, filtered, and concentrated to a final volume of 40 ml. Upon chilling, 8.85 g (78.0%) of colorless crystals, mp 96–99°, separated which proved to be pure enough for further work. Upon further concentration to 10 ml, an additional fraction of 0.80 g (7%), mp 99–101°, crystallized. Thus the total yield of 6,6-diphenylbicyclo[3.1.0]hexan-3-one was 85%. A sample crystallized from cyclohexane had mp 100–102 and 101–102° when sublimed at 80° (0.4 mm).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.15, 87.12; H, 6.49, 6.59. The spectral data were: ir (CS_2, CCl_4) 5.73 μ C=O; strong 13.45, 14.14, 14.37; medium 3.22, 3.25, 3.29, 3.43, 6.25, 6.70, 6.92, 7.11, 7.96, 8.72, 12.08, 13.03, 13.18; weak 3.36, 9.24, 9.63, 9.27, 10.44, 10.97, 11.23 μ; nmr ($CDCl_3$) τ 2.73 (s, 5 H, Ph), 2.92, (s, 5 H, Ph), 7.50 (m, 4 H), 7.70 (m, 2 H); uv (cyclohexane) max at 323 (6), 311.0 (15), 300.0 (20), 289.5 (20), 273.5 (460), 266.5 (690), 260.0 (650), 255.0 (520), plateau at 223 mμ (ϵ 14,600).

6,6-Diphenylbicyclo[3.1.0]hexan-2-one. A 918-mg sample of 6,6-diphenylbicyclo[3.1.0]hexane-2-ol was oxidized as described for the 3 isomer with 5.0 g of chromic acid in 80 ml of dry pyridine. Concentration from methanol and chilling gave 592 mg (65.1%) of colorless crystals, mp 104–105°. Two crystallizations from cyclohexane yielded 456 mg of product, mp 104.5–105°.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.05, 87.36; H, 6.47, 6.57. The spectral data were: ir (CS_2, CCl_4) 5.79 μ C=O; strong 8.43, 13.37, 14.15, 14.37; medium 3.24, 3.26, 3.29, 3.39, 3.47, 6.25, 6.69, 6.92, 7.09, 7.65, 7.70, 8.02, 8.71, 9.27, 9.45, 9.63, 10.62, 10.90, 11.12, 11.66, 11.90, 12.09, 12.54, 13.03 μ; nmr ($CDCl_3$) τ 2.65 (pseudo s, 5 H, Ph), 2.84 (s, 5 H, Ph), 7.16–7.53 (m, 3 H), 7.92 (m, 2 H), 8.19–9.39 (multiplets, 1 H); uv (cyclohexane) shoulder at 320 (20), max at 308.8 (49), 289.0 (70), 282.2 (74), 274.6 (500), 267.5 (770), 261.0 (770), plateaus at 254 (700) and 224 mμ (ϵ 15,100).

2,4-Dibromo-6,6-diphenyl-bicyclo[3.1.0]hexan-3-one. To a solution of 3.00 g (12.05 mmol) of 6,6-diphenylbicyclo[3.1.0]hexane-3-one in 10 ml of glacial acetic acid were added 2.0 ml of 48% hydrobromic acid and a solution of 1.29 ml (24.4 mmol) of bromine in 5.0 ml of glacial acetic acid. The mixture was left for 2 hr, during which time the orange color faded and a yellow color remained. The crystalline precipitate formed (4.13 g) was recrystallized from cyclohexane to give 3.99 g (81.2%) of colorless crystals. When placed on a block preheated at 150° the melting point was 161–167° dec. Recrystallization did not raise the melting point.

Anal. Calcd for $C_{18}H_{14}Br_2O$: C, 53.23; H, 3.47; Br, 39.35. Found: C, 53.01, 53.10; H, 3.44, 3.46; Br, 40.11, 40.00. The spectral data were: ir (KBr) 5.70 μ C=O; strong 8.02, 8.13, 8.22, 8.76, 13.02, 13.95, 14.17; medium 3.26 (broad unresolved), 6.26, 6.70, 6.92, 8.57, 9.23, 9.46, 9.63, 10.10, 11.27, 11.38, 11.62, 12.04; weak 7.39, 7.53, 7.58, 8.98 μ; nmr ($CDCl_3$) τ 2.71 (d, 1 cps splitting, 5 H, Ph), 2.80 (d, 1.5 cps splitting, 5 H, Ph), 5.65 (s, 2 H, CHBr), 7.10 (s, 2 H, cyclopropyl); uv (cyclohexane) 353 sh (244), max at 340.0 (281), shoulder at 329 (256), plateaus at 273 (1870), 266.5 (2510), 222 mμ (ϵ 17,000).

3-Acetoxy-6,6-diphenylbicyclo[3.1.0]hex-2-ene. With a very slow stream of nitrogen to remove acetone a mixture of 750 mg (3.02 mmol) of 6,6-diphenylbicyclo[3.1.0]hexane-3-one, 25 ml of isopropenyl acetate, and 300 mg of *p*-toluenesulfonic acid was heated to gentle reflux. During a period of 7 hr, 5 ml of liquid was distilled off through a 10-cm Vigreux column; 5.0 ml of isopropenyl acetate was then added and the mixture refluxed for 5 hr, during which time 5 ml distilled off. The slightly darkened solution was diluted with 40 ml of ether, extracted with 40 ml of saturated sodium bicarbonate solution, and washed with 20 ml of saturated sodium sulfate solution. The partly crystalline residue was three times dissolved in 10 ml of dry benzene and concentrated under vacuum. The slightly brown colored crystalline residue (952 mg, mp 97–110°) was dissolved in 30 ml of ethanol, treated with Norit, and concentrated to a volume of 8.0 ml. After 1 hr of refrigeration, 762 mg (86.7%) of colorless crystals, mp 112–114°, was collected. After a second crystallization from ethanol, 665 mg (75%) of mp 114° was obtained. A sample recrystallized from cyclohexane and dried at 60° (0.2 mm) for 2 hr had mp 115.5–116°.

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.24. Found: C, 82.79, 82.69; H, 6.26, 6.26.

The spectral data were: ir (CS_2, CCl_4) 5.68 μ C=O; strong 8.30, 8.51, 13.38, 14.20, 14.38; medium 3.24, 3.27, 3.30, 6.05, 6.14, 6.25, 6.70, 6.92, 6.99, 7.30, 7.51, 7.74, 9.35, 9.63, 9.95, 10.78, 11.00, 12.15, 13.06, 13.19; weak 3.44, 3.52 μ; nmr ($CDCl_3$) τ 2.74 (s, 5 H, Ph), 2.88 (s, 5 H, Ph), 4.37 (m, 1 H, vinyl), 6.79–7.19 (m, 1 H), 7.62 (m, 3 H), 8.12 (s, 3 H, CH_3); uv (cyclohexane) plateau at 276 (1000), shoulder at 260 (1560), plateau at 228 mμ (ϵ 12,800).

2-Bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one. To a stirred solution of 372 mg (1.28 mmol) of 3-acetoxy-6,6-diphenylbicyclo-[3.1.0]-hex-2-ene in 6.0 ml of carbon tetrachloride were added 0.2 ml of pyridine and 6.50 ml of a solution of 1.0 ml of bromine in 100 ml of carbon tetrachloride dropwise over a period of 1 hr. The reaction mixture was diluted with 10 ml of chloroform, washed with water and twice with 10% sodium sulfate solution, and dried over magnesium sulfate. The residue was concentrated at room temperature *in vacuo*, kept at 0.5 mm for 5 hr to remove residual pyridine, taken up in 25 ml of warm cyclohexane, treated with charcoal, concentrated under nitrogen and gentle heating to a volume of 8 ml, and left standing at room temperature for 10 hr. A 277-mg crop (66.2%) of colorless crystals was collected, mp 116–117° (rapid decomposition above 118°; block preheated to 100°). A 52-mg sample was crystallized from cyclohexane to give 45 mg of mp 117.5–118.5°.

Anal. Calcd for $C_{18}H_{17}OBr$: C, 66.07; H, 4.62; Br, 24.42. Found: C, 66.10; H, 4.67; Br, 24.50. The spectral data were: ir (KBr) 5.73 μ C=O; strong 8.73, 13.08, 13.25, 14.14, 14.32, 14.75; medium 3.30 (unresolved), 6.25, 6.69, 6.93, 7.16, 7.54, 7.93, 8.25, 9.25, 9.32, 9.63, 9.79, 9.96, 10.01, 10.14, 11.53, 12.03, 13.97 μ; nmr ($CDCl_3$) τ 2.77 (s, 5 H, Ph), 2.86 (s, 5 H, Ph), 5.73 (s, 1 H, CHBr), further a complicated pattern from 6.6 to 7.9 (4 H).

Reactions of 2,4-Dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Hydrogen Iodide. A solution of 1.80 g (8.0 mmol) of the azeotropic mixture of HI–water (bp 124.5°, 57% HI) in 10 ml of reagent grade acetone was added to a solution of 406 mg (1.0 mmol) of the dibromo ketone in 3.0 ml of acetone. The mixture immediately darkened and was left standing at room temperature for 10 min. Excess saturated sodium bicarbonate solution was added to remove all acid and then 16 ml of a 5% sodium sulfite solution was added to decolorize the mixture. This was ether extracted, and the extracts were concentrated to give 251 mg of an oil, which crystallized upon standing. Crystallization from methanol gave 221 mg (89%) of colorless crystals, mp 98–99°, whose ir, as well as that of the original oil, was identical with that of 6,6-diphenylbicyclo-[3.1.0]hexane-3-one.

Reaction of 2,4-Dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Sodium Amalgam. A 750-mg sample of sodium was added in

20 portions to 200 g of mercury under dry nitrogen in a 100-ml Morton flask with high speed stirring (*ca.* 15,000 rpm). A solution of 1.016 g (2.5 mmol) of the dibromo ketone in 25 ml of dry benzene distilled from lithium aluminum hydride was added all at once to the amalgam. The mixture was immediately high-speed stirred for 3 min at room temperature and filtered from the amalgam, which was washed twice with dry ether. The solution of the reaction products was washed once with 5% sodium sulfate solution, dried over magnesium sulfate, and concentrated to give 462 mg of an oily residue. The presence of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one was indicated by thin layer chromatography and characteristic bands at 5.94, 6.35, 7.46, and 11.62 μ in the ir of the crude product mixture. The product was subjected to scanning liquid–liquid partition chromatography[33] (using cyclohexane–ethylacetate–dimethylformamide–water: 1000:250:400:30 at 22.5°); 300 ml of lower phase per 600 g of Celite (Eagle Pichler Celatom FW80) on a 4 × 30 cm column; 20-ml fractions were collected. Uv monitoring was at 265 mμ. Fractions 17–21 gave 33 mg of oil (ir bands at 5.78, 5.88, and 6.04 μ, mixture of at least three compounds as shown by thin layer chromatography); 22–23, 162 mg of solid (6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one and starting material); 34–40, 22 mg of amorphous residues which showed no distinct ir bands. Since only 217 mg out of 462 mg were eluted; the packing was washed with chloroform to give 93 mg of an oil, which was shown to be a mixture of carbonyl compounds by its ir spectrum. From the missing 152 mg, 38 mg as brown amorphous material could be recovered by washing with a mixture of 200 ml of acetic acid, 300 ml of methanol, and 500 ml of chloroform. Fractions 86–94 gave 3 mg of yellow oil; 117–130, 30 mg of dibromo ketone; 131–147, 81 mg of crystalline 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, mp 134–136.5°. Taking into account 30 mg of recovered starting material the yield of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one was 13.6%.

Reaction of 2,4-Dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one with Zinc in Dioxane. A solution of 618 mg (1.52 mmol) of dibromo ketone in 30 ml of reagent dioxane was vigorously stirred using a high-speed stirrer in a 100-ml Morton flask with 30 g of zinc dust (reagent, 95% Zn) at reflux under dry nitrogen for 25 min. The slightly yellow solution containing mainly 6,6-diphenylbicyclo-[3.1.0]hex-3-en-2-one as shown by thin layer chromatography was filtered, thoroughly washed with ether, and concentrated. The residue was taken up in 30 ml of ether, washed once with water to remove any zinc bromide, dried over sodium sulfate, and concentrated to give 404 mg of crystalline material which was sublimed at 100° (0.4 mm) to give 284 mg (76.5%) of essentially pure 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, mp 134–136°. Upon crystallization from methanol, 260 mg (70%), mp 138–140°, was obtained (lit.[3] mp 138.5–140.5°). The infrared spectra in carbon tetrachloride, chloroform, and carbon disulfide were identical with those of authentic material. Nmr comparison again showed identity 1 H, nmr ($CDCl_3$): τ 2.65 (q, J_{34} = 5.5 cps, J_{45} = 2.5 cps, C-4 vinyl), 2.80 (s, 5 H, Ph), 2.83 (s, 5 H, Ph), 4.49 (d, 1 H, J_{34} = 5.5 cps, C-3 vinyl), 6.80 (q, 1 H, J_{56} = 4.5 cps, J_{45} = 2.5 cps, CH at C-5), (7.22 d, 1 H, J_{56} = 4 5 cps, CH at C-1).

When 409 mg (1.0 mmol) of this dibromo ketone was allowed to react with 20 g of zinc dust in 30 ml of dioxane under nitrogen at 60°, the reaction was complete after 125 min and yielded 245 mg of crystalline product which gave, upon recrystallization from cyclohexane, 182 mg (74%) of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, mp 134–138°.

Reaction of the Dibromo Ketone with Calcium at −70° in Tetrahydrofuran. A solution of 1.036 g of dibromo ketone in 30 ml of dry tetrahydrofuran was high-speed stirred with 22 g of 2 mm diameter calcium pieces for 10 min under argon at −70° in a 100-ml Morton flask. The mixture assumed an olive color after 3 min and was filtered immediately after 10 min; 0.1 ml of glacial acetic acid was added to the filtrate. Upon addition of 70 ml of ether, a white inorganic precipitate was formed, which was filtered. The filtrate was concentrated, and the residue was treated with water and ether extracted. The ether layer was dried over magnesium sulfate and concentrated and the residue taken up in chloroform. Methanol (5 ml) was added in portions while the chloroform was removed in a nitrogen stream. The 72 mg of amorphous material separating was filtered off. The ir spectrum showed absence of reactant and only bicyclic enone product. The mother liquors were concentrated to give 624 mg of solid containing starting material and 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, which was subjected to liquid–liquid chromatography at 28° in the usual solvent mixture (*vide supra*), 20-ml fractions being taken. Fractions A75–85, 29 mg of resin; A86–94, 115 mg of solid material; A95–118, 284 mg of oil, which was recycled on the same column; B88–96, 77 mg of crystalline starting material; B97–99, 36 mg of a partly crystalline 1:1 mixture of starting material and 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (*i.e.*, nmr and ir analysis); B100–111, 134 mg of oily 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one which crystallized totally upon addition of a few drops of methanol and was crystallized from methanol to give 130 mg, mp 137–138° (26%, based on unrecovered starting material).

Reaction of 2-Bromo-6,6-diphenylbicyclo[3.1.0]hexane-3-one with Hydrogen Iodide. A 33-mg (0.10 mmol) sample treated with 90 mg (0.4 mmol) of 57% HI as described above gave 20.0 mg (81%) of crystalline 6,6-diphenylbicyclo[3.1.0]hexane-3-one, mp 96–99°, identified by ir.

Reaction of 2-Bromo-6-diphenylbicyclo[3.1.0]hexan-3-one with Potassium *t*-Butoxide. To a stirred solution of 46.0 mg (0.14 mmol), in monobromo ketone in 2.0 ml of dry *t*-butyl alcohol (distilled from calcium hydride) at 40° was added 1.16 ml of 0.12 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol during 2 min. After stirring at 40° for an additional 3 min, 5 μl of acetic acid was added; the mixture was concentrated and treated with water and chloroform. The organic phase was concentrated, and the 32-mg residue was taken up in 1.5 ml of methanol and chilled to give 25.6 mg (74%) of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, mp 138–139°, identified by ir.

In another run, 41.0 mg of (0.125 mmol) of the monobromo ketone was allowed to react as above and the residue sublimed at 10° (0.5 mm) to give 20.0 mg of solid, mp 120–135°. This on methanol recrystallization gave 15.8 mg (51%) of bicyclic enone, mp 138–139°. In a control experiment, 47.6 mg of monobromo ketone, mp 116–117°, was kept at 40° in 3.0 ml of *t*-butyl alcohol for 10 min. A 46.0-mg portion of mp 116–117.5° (block preheated to 100°) was recovered unchanged.

Hydrogenation of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one. A 30-mg sample of platinum dioxide was hydrogenated in 5 ml of ethyl acetate containing 10 μl of triethylamine and then a solution of 55.0 mg (0.223 mmol) of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in 50 ml of ethyl acetate was added. Within 5.3 min, 5.7 ml (0.23 mmol, 742 mm, 22°) of hydrogen was taken up. The residue obtained upon concentration had carbonyl absorption at 5.80 μ. Upon recrystallization from 0.5 ml of methanol, 42.0 mg (74%) of 6,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 107–107.5°, was obtained, identical in its ir with the material obtained previously, and the mixture melting point showing no depression.

Phenyl-*p*-bromophenyldiazomethane. An 18-g portion of yellow mercuric oxide followed by 4.0 ml of a saturated ethanolic potassium hydroxide solution was added to a suspension of 10.00 g (36.4 mmol) of *p*-bromobenzophenone hydrazone, 10 g of anhydrous sodium sulfate, and 100 ml of anhydrous ether stirred at room temperature. After stirring for 2 hr the reaction mixture was filtered and concentrated *in vacuo*. The deep red crystalline residue was taken up in pentane, filtered, and reconcentrated *in vacuo* to yield 9.99 g (99%) of phenyl-*p*-bromophenyldiazomethane, mp 39–40°, as deep red crystals. The infrared spectrum (CCl_4) showed a very strong 4.88-μ band. Recrystallization from pentane gave mp 39–40°.

Anal. Calcd for $C_{13}H_9N_2Br$: C, 57.16; H, 3.32; N, 10.26; Br, 29.26. Found: C, 57.07; H, 3.42; N, 10.36; Br, 29.45.

6-*exo*-Phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hex-2-ene and 6-*endo*-Phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hex-2-ene. A 23.57-g (86.1 mmol) sample of phenyl-*p*-bromophenyldiazomethane was dissolved in 250 ml of freshly cracked cyclopentadiene in a 270-ml, water-jacketed photolysis flask with water cooling. The solution was purged for 30 min with pure nitrogen.[30] The solution was then irradiated with a 450-W medium-pressure Hanovia water-cooled immersion lamp with a Pyrex filter for 4.1 hr during which time the theoretical amount of nitrogen (2.14 l.) had evolved. Excess cyclopentadiene was removed *in vacuo*, and 47.59 g of a pale yellow oil remained. This was chromatographed on an 8 × 99 cm deactivated silica gel column slurry packed in 1% ether–hexane (Grace grade 950 60–200 mesh silica gel, deactivated by treating with water, filtering, and drying for 5 hr at 55°). Elution with 29 l. of 1% ether–hexane and collection of 500-ml fractions gave: fractions 1–7, nil; 8–15, 16.65 g of dicyclopentadiene; 16–30, nil; 31–42, 5.75 g of a viscous yellow oil; 43–48, 4.98 g containing decreasing amounts of yellow oil and increasing amounts of a white solid; and 49–58, 7.32 g of white powder. Fractions 49–58 were

(33) Note ref 3b for the general procedure. Later references in the series are also useful.

recrystallized from carbon tetrachloride to give 6.05 g of 1,2-diphenyl-1,2-di-*p*-bromophenylethane, mp 200–201°. Fractions 43–48 were hexane extracted. The extracts were combined with fractions 31–42; on standing at 0°, 3.23 g of one diastereomer of 1,2-diphenyl-1,2-di-*p*-bromophenylethane, mp 197–200°, crystallized. The yellow filtrate was concentrated and kept at 0° to effect further crystallization. The resulting crude material was recrystallized from ether–hexane to give 3.10 g (11.6%) of 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hex-2-ene, mp 105–106°. The filtrates afforded 5.81 g of crude oil which was chromatographed in 2-g lots on a 3.5 × 200 reversed phase liquid–liquid partition column. The column was slurry packed with 100–200 mesh polystyrene–2% divinylbenzene copolymer beads which had been thoroughly leached free of extractable material with chloroform, dried, and then soaked in the upper phase of a two-phase system of 1:1 (v:v) absolute methanol–cyclohexane. The lower phase was used for elution with pumping in a closed thermostated stainless steel column at *ca.* 400 ml per hr; 40-ml cuts gave: fractions 1–11, nil; 12–50, 150 mg of a yellow uncharacterized oil; 50–75, nil; 75–155, 1.26 g of 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]-hex-2-ene isolated as a yellow oil; 156–200, 538 mg of yellow oil which was shown by ir to contain a mixture of both the *exo*-phenylcycloalkene and the *endo*-phenylcycloalkene.

Characterization of 1,2-Diphenyl-1,2-di(*p*-bromophenyl)ethane. Recrystallization from carbon tetrachloride gave a constant melting point of 200–201°. The spectral data were: ir (CS_2) strong 9.30, 9.90, 13.22, 14.39; medium 3.26, 3.29, 8.23, 12.71, 14.05; weak 3.43, 9.09, 9.71; shoulder 13.40 μ; nmr ($CDCl_3$) τ 2.85–3.20 (m, 18 H, aryl and Ph) and 5.41 (s, 2 H, methine).

Anal. Calcd for $C_{26}H_{20}Br_2$: C, 63.49; H, 4.10; Br, 32.47. Found: C, 63.47; H, 4.15; Br, 32.32.

Characterization of 6-*exo*-Phenyl-6-*endo*-*p*-bromophenylbicyclo-[3.1.0]hex-2-ene. Recrystallization from ether–hexane gave a constant melting point 105–106°. The spectral data were: ir (CS_2) strong 9.88, 13.36, 13.68, 14.36; medium 3.27, 3.30, 3.44, 7.17, 7.42, 9.36, 11.97, 12.37, 13.78, 13.95; weak 3.35, 3.52, 7.80, 8.62, 8.98, 9.12, 9.36 μ; nmr ($CDCl_3$) τ 2.67–3.19 (Ph pseudo s centered at 2.77 plus an aryl A_2B_2 quartet, 9 H), 4.19 (q, J_{23} = 5.5 cps, J_{12} = 2.0 cps, 1 H, C-2 vinyl), 4.89 (m, 1 H, C-3 vinyl), 7.60 (m, 4 H, CH_2 and cyclopropyl).

Anal. Calcd for $C_{15}H_{15}Br$: C, 69.50; H, 4.87; Br, 25.70. Found: C, 69.56; H, 4.86; Br, 25.60.

Characterization of 6-*endo*-Phenyl-6-*exo*-*p*-bromophenylbicyclo-[3.1.0]hex-2-ene. Short-path molecular distillation of the material in fractions 75–155 above at 105° (0.005 mm) resulted in a pale yellow oil. The spectral data were: ir (CS_2) strong 9.92, 13.22, 14.22, 14.37; medium 3.27, 3.30, 3.45, 8.62, 9.34, 10.78, 10.89, 12.02, 12.49, 12.80, 14.00, 15.62; weak 3.52, 5.26, 5.30, 7.20, 7.43, 7.82, 8.25, 8.98, 9.20, 9.70, 9.80, 10.19, 11.35, 15.88; shoulder at 11.45 μ; nmr ($CDCl_3$): τ 2.55–3.03 (Ph pseudo s centered at 2.93 plus an aryl A_2B_2 quartet, 9 H), 4.20 (q, J_{23} = 5.5 cps, J_{12} = 2.0 cps, 1 H, C-2 vinyl), 4.89 (m, 1 H, C-3 vinyl), 7.60 (broad m, 4 H, CH_2 and cyclopropyl).

Anal. Calcd for $C_{15}H_{15}Br$: C, 69.50; H, 4.87; Br, 25.70. Found: C, 69.69; H, 5.08; Br, 25.44.

Hydroboration of 6-*exo*-Phenyl-6-*endo*-*p*-bromophenylbicyclo-[3.1.0]hex-2-ene. To a solution of 3.161 g (9.60 mmol) of the 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hex-2-ene in 10 ml of dry tetrahydrofuran at 0° under nitrogen, was added with stirring over 5 min 10 ml of approximately 1 *M* diborane in tetrahydrofuran (Alpha Inorganics). The mixture was stirred at 0° for 1 hr and at room temperature for 1 hr. After the excess diborane had been destroyed by careful addition of 1:1 tetrahydrofuran–water at 0°, 16 ml of 3 *N* sodium hydroxide was added in one portion followed by 11 ml of 30% hydrogen peroxide which was added at room temperature over 5 min. After stirring for 1.75 hr, the mixture was poured into 60 ml of water and adjusted to pH of 7 to give 3.093 g of solid which was filtered. The filtrate was saturated with sodium sulfate and ether extracted; after washing and drying, the ether was removed *in vacuo* to give 113 mg of a light yellow oil. Recrystallization of the solid from chloroform gave 314 mg of 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-ol, mp 185.5–186.5°. The spectral data were: ir (KBr) 3.04 μ broad OH; strong 9.32, 9.73, 9.93, 11.85, 13.31, 14.29; medium 9.10, 10.39, 10.52, 11.35, 12.10, 13.80, 14.02 μ; nmr ($CDCl_3$) τ 2.43–3.17 (Ph, pseudo s centered at 2.94 plus an aryl A_2B_2 quartet, 9 H), 7.05 (t, 1 H, *H*COH), 7.50–8.40 (m, 6 H, CH_2 and cyclopropyl), 8.68 (s, 1 H, OH).

Anal. Calcd for $C_{15}H_{17}OBr$: C, 65.66; H, 5.21; Br, 24.27. Found: C, 65.48; H, 5.19; Br, 24.53.

The filtrate of the crystallization of the *exo*-phenyl-3-ol was concentrated to give 2.675 g of a crude oil. A 1.789-g portion of this oil was combined with the ether extracts of the reaction mixture and then chromatographed on a 3 × 94 cm column slurry packed in 50% ether–hexane with deactivated silica gel (*vide supra*). Elution with 5 l. of 50% ether–hexane collecting 40-ml fractions gave: fractions 1–10, nil; 11–42, 173 mg of a viscous uncharacterizable oil; 43–69, 402 mg, mp 176–180°, isolated as the *exo*-phenyl-3-ol; 70–74, 57 mg of clear oil identified by ir to be a mixture of the *exo*-phenyl-3-ol and the *exo*-phenyl-2-ol; 75–120, 718 mg, mp 138–140°, identified as 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*exo*-*ol*. Recrystallization from methanol gave 337 mg, mp 143–144°. The spectral data were: ir (KBr): 3.02 μ broad OH; strong 9.35, 9.90, 10.18, 13.41, 14.00, 14.28; medium 9.66, 9.78, 10.50, 10.65, 11.45, 11.53, 11.72, 12.31, 13.83, 14.71, 15.72 μ; nmr ($CDCl_3$) τ 2.49–3.00 (Ph pseudo s centered at 2.89 plus an aryl A_2B_2 quartet, 9 H), 5.71 (d, 1 H, J = 5.2 cps, *H*COH), 7.83 (pseudo s, 3 H, CH_2), 8.10–9.00 (broad m, 3 H, CH_2 and one cyclopropyl), 9.17–9.80 (weak broad m, 1 H, cyclopropyl).

Anal. Calcd for $C_{15}H_{17}OBr$: C, 65.66; H, 5.21; Br, 24.27. Found: C, 65.50; H, 5.36; Br, 24.53.

Fractions 70–74 were combined with the mother liquors from the crystallizations of the two alcohols and were chromatographed on the same silica gel column. This afforded 200 mg, of the 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-ol, mp 185–186.5°, and 72 mg of the 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-ol, mp 138–140°.

6-*exo*-Phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one. To 111.0 ml of dry pyridine, was added 7.00 g of chromic acid in portions at 0° with stirring, to give a yellow suspension which was then stirred at room temperature for 2 hr. A solution of 1.346 g (4.0 mmol) of the 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo-[3.1.0]hexan-3-ol dissolved in 4.0 ml of pyridine was added at room temperature in one portion and stirred for 14 hr. The reaction mixture was poured into 500 ml of 2% sodium sulfate solution and ether extracted; the extracts were washed three times with a mixture of 25.0 ml of concentrated HCl in 70 g of ice and once with 10% sodium bicarbonate and then dried. The solvent was removed *in vacuo* to give 793 mg of a yellow oil which was chromatographed on a 2 × 35 cm column slurry packed in 2.5% ether–hexane with 100–200 mesh deactivated (*vide supra*) silica acid (SilicAR CC-7). Elution with 300 ml of 2.5%, 300 ml of 20%, and 1 l. of 50% ether–hexane and collecting 100-ml fractions gave: fractions 1–7, 252 mg of *p*-bromobenzophenone, mp 79–80°; 8–10, nil; 11–20, 499 mg of the 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]-hexan-3-one, mp 108–110°. A 60-mg sample was recrystallized from hexane–methanol to give 21.2 mg, mp 110–111°. The spectral data were: ir (CS_2) 5.72 μ strong C=O; strong 7.12, 8.71, 9.88, 11.96, 12.28, 13.20, 13.46, 13.88, 14.38; medium 3.28, 3.38, 3.45 7.95, 8.24, 9.08, 9.36, 9.63; shoulders 3.22, 3.24 μ; nmr ($CDCl_3$) τ 2.45–2.97 (Ph pseudo s centered at 2.80 plus an aryl A_2B_2 quartet, 9 H), 7.05–7.85 (m, 6 H, CH_2 and cyclopropyl).

Anal. Calcd for $C_{15}H_{15}OBr$: C, 66.07; H, 4.62; Br, 24.42. Found: C, 65.91; H, 4.70; Br, 24.54.

6-*exo*-Phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one. To 23.0 ml of dry pyridine was added 1.40 g of chromic acid in portions at 0° over 15 min with stirring to give a yellow suspension. After stirring at room temperature for 2 hr a solution of 256 mg (0.78 mmol) of the 6-*exo*-phenyl-2-*exo*-ol in 1.5 ml of pyridine was added in one portion and the mixture stirred for 15 hr. The mixture was poured into 125.0 ml of 2% sodium sulfate and ether extracted; the extracts were washed as above with HCl–ice water and sodium bicarbonate solution and then dried. Removal of solvent *in vacuo* afforded 250 mg of a yellow oil which was recrystallized from methanol to give 200 mg of the desired ketone, mp 130–131°. The spectral data were: ir (CS_2) 5.80 μ strong C=O; strong 8.46, 9.35, 9.88, 12.30, 13.22, 13.40, 13.90, 14.40; medium 3.26, 3.29, 3.39, 3.47, 7.12, 7.19, 7.70, 7.76, 9.66, 11.67, 11.81; weak 8.00, 8.72, 10.64, 10.94, 11.17; shoulders at 3.24, 8.30, 9.48, 14.00 μ. nmr ($CDCl_3$) τ 2.41–2.85 (Ph pseudo s centered at 2.82 plus an aryl A_2B_2 quartet, 9 H), 7.14 (m, 2 H, CH_2), 8.00 (m, 3 H, CH_2 and cyclopropyl), 8.90 (m, 1 H, cyclopropyl).

Anal. Calcd for $C_{15}H_{15}OBr$: C, 66.07; H, 4.62; Br, 24.42. Found: C, 65.79; H, 4.52; Br, 24.66.

6-*exo*-Phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*endo*-ol. A solution of 186 mg (0.57 mmol) of the 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one in 10 ml of ether was added to a suspension of 24 mg (0.61 mmol) of lithium aluminum hydride in ether over a period of 5 min. After refluxing for 1 hr, the excess lithium aluminum hydride was destroyed by adding ammonium chloride solution, and the resulting suspension was filtered. The

filtrate was washed with acid, washed with bicarbonate, and dried. Removal of solvent *in vacuo* gave 232 mg of a clear oil which was molecularly distilled at 120° (0.05 mm). The spectral data were: ir (CS_2) 2.95 μ broad OH; strong 9.32, 9.45, 9.62, 9.75, 9.89, 12.30, 13.20, 13.41, 13.92, 14.39; medium 2.87, 3.27, 3.29, 3.38, 3.47, 7.19, 15.19, 15.19; weak 7.50 7.92, 8.35, 11.42, 11.64, 11.83 μ; nmr ($CDCl_3$) τ 2.60 (s, 4 H, aryl protons), 2.91 (s, 5 H, Ph), 5.32 (m, 1 H, *H*COH), 8.15 (broad m, 6 H, CH_2, OH, cyclopropyl), 9.80 (broad weak m, 1 H, cyclopropyl).

Anal. Calcd for $C_{18}H_{17}OBr$: C, 65.66; H, 5.21; Br, 24.27. Found: C, 65.41; H, 5.07; Br, 24.45.

3-Acetoxy-6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]-hex-2-ene. A mixture of 201 mg (0.615 mmol) of the 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one, 7.0 ml of isopropenyl acetate, and 50 mg of *p*-toluenesulfonic acid was heated to gentle reflux. Over a period of 10 hr, 8 ml of distillate was collected; isopropenyl acetate was added every 2 hr to keep the volume constant. The darkened solution was diluted with ether, washed with sodium bicarbonate, and dried. Removal of solvent *in vacuo* and crystallization from ethanol gave 179 mg (78.6%) of the desired enol acetate, mp 169–179°. Recrystallization of an 80-mg sample from ethanol gave 60 mg of the enol acetate, mp 171–171.5°. The spectral data were: ir (KBr) 5.70 μ C=O, 8.32 and 8.50 μ CO; strong 9.90, 12.10, 13.25, 14.25; medium 6.10, 6.14, 6.24, 6.28, 6.68, 6.74, 6.90, 7.00, 7.15, 7.30, 7.49, 10.70, 11.12, 11.25, 11.58, 11.85, 12.38, 13.80, 14.02; weak 3.26, 3.29, 3.44 μ; nmr ($CDCl_3$) τ 2.50–2.98 (Ph pseudo s centered at 2.90 plus an aryl A_2B_2 quartet, 9 H), 4.38 (d, 1 H, vinyl), 6.97 (d of d, J_{22} = 18 cps, J_{12} = 7 cps, plus some smaller coupling, 1 H, HC*H* *exo* to cyclopropane), 7.65 (m, 3 H, *endo* *H*CH and cyclopropyl), 8.09 (s, 3 H, methyl). The assignments are based on spin decoupling and magnitude of coupling constants.

Anal. Calcd for $C_{20}H_{17}O_2Br$: C, 65.05; H, 4.64; Br, 21.64. Found: C, 64.77; H, 4.53; Br, 21.61.

2-Bromo-6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one. To a stirred solution of 182 mg (0.494 mmol) of the *exo*-phenyl enol acetate in 4.0 ml of carbon tetrachloride was added 0.08 ml of pyridine and then 2.54 ml of a solution of 1.0 ml of bromine in 100 ml of carbon tetrachloride over 1 hr. The reaction mixture was diluted with chloroform, washed with water, dried, and concentrated *in vacuo* and the residue kept at 1 mm for 5 hr to remove residual pyridine. Crystallization from ether–hexane gave 19.7 mg of starting material, mp 166–170°, and 62.4 mg (35% based on unrecovered reactant) of the desired 2-bromo-6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one, mp 147–148°. The spectral data were: ir (KBr) 5.72 μ C=O; strong 6.68, 6.75, 7.16, 8.22, 9.39, 9.91, 11.92, 13.24, 14.32; medium 6.26, 6.92, 8.48, 9.08, 9.61, 11.51, 12.27, 12.50, 13.74, 13.93, 14.16, 14.59; weak 3.23, 3.27, 3.32, 3.42, 7.96, 8.21, 10.13 μ; nmr ($CDCl_3$) τ 2.47–3.00 (Ph pseudo s centered at 2.86 plus an aryl A_2B_2 quartet, 9 H), 5.80 (s, 1 H, *H*CBr), 6.86 (d of d, 1 H, J_{44} = 19 cps, J_{54} = 4 cps *exo* H at C-4), 7.43 (d, J_{54} = 5 cps, 2 H plus half of another d, cyclopropyl), 7.69 (d, J_{44} = 19 cps, 1 H, *endo* proton at C-4).

Anal. Calcd for $C_{18}H_{14}OBr_2$: C, 53.22; H, 3.47; Br, 39.36. Found: C, 53.38; H, 3.62; Br, 39.17.

Reaction of 2-Bromo-6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo-[3.1.0]hexan-3-one with Potassium *t*-Butoxide. To a stirred solution of 56.7 mg (0.14 mmol) of the *exo*-phenyl 2-bromo ketone in 3.0 ml of *t*-butyl alcohol (dried over refluxing CaH) at 42°, 1.4 ml of a 0.1 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol was added over 2 min. After stirring at 42° for 4 more min, 8.0 μl of glacial acetic acid was added. Solvent was removed *in vacuo* and the residue was taken up in 10.0 ml of chloroform, the solution washed with water, dried, and concentrated *in vacuo* to leave 58.5 mg of yellow crystalline material. This was then chromatographed on a 2 × 12 cm deactivated silicic acid column slurry packed in 5% ether–hexane. Elution with 125 ml of 5% and 1 l. of 10% ether–hexane and collection of 125-ml fractions gave: fraction 1, nil; 2, 3.3 mg of a yellow oil; 3, nil; 4–8, 42.8 mg of white crystalline product; 9, nil. Fractions 4–8 were recrystallized from hexane to give 34.8 mg (76%) of 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo-[3.1.0]hex-3-en-2-one, mp 123–124° (lit.[8,34] 123–124°), which had nmr and solution ir spectra identical with those of ref 8. The ir spectra of the filtrates showed only additional *exo*-phenyl photoketone and no trace of the *endo*-phenyl photoketone.

Hydrogenation of 6-*exo*-Phenyl-6-*endo*-*p*-bromophenylbicyclo-[3.1.0]hex-3-en-2-one. A 20.3-mg sample of platinum dioxide was hydrogenated in 5.0 ml of ethyl acetate containing 10 μl of triethylamine, and then a solution of 34.8 mg (0.107 mmol) of the *exo*-phenyl photoketone in 2.0 ml of ethyl acetate was added. Within 6 min (738 mm Hg, 23°) 3.0 ml of hydrogen was absorbed. Filtrating and concentration of the filtrate *in vacuo* yielded 34.3 mg of white solid. Recrystallization from methanol gave 29.2 mg (83.5%) of 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one, mp 128.5–129.5°. The mixture melting point with authentic material was undepressed and nmr and solution ir spectra were identical with those of the authentic sample.

Hydroboration of 6-*endo*-Phenyl-6-*exo*-*p*-bromophenylbicyclo-[3.1.0]hex-2-ene. To a solution of 1.337 g (4.06 mmol) of the *endo*-phenylalkene in 5.0 ml of dry tetrahydrofuran at 0° under nitrogen was added with stirring 5.0 ml of approximately 1 *M* diborane in tetrahydrofuran. After stirring at 0° for 1 hr and at room temperature for 1 hr, the excess diborane was destroyed by careful addition at 0° of 1:1 tetrahydrofuran–water. Then 8.0 ml of 3 *N* sodium hydroxide was added in one portion; followed by 5.5 ml of 30% hydrogen peroxide added over 5 min at room temperature. After stirring for 1.75 hr, the mixture was poured into 30 ml of water, adjusted to pH 7, then saturated with sodium sulfate, and ether extracted. The combined extracts were washed, dried, and concentrated *in vacuo* to afford 1.387 g of light yellow oil. This was chromatographed on a 3 × 88 cm deactivated silica gel column slurry packed in 50% ether–hexane. Elution with 5 l. of 50% ether–hexane gave: fractions 1–9, nil; 10–20, 51 mg of an uncharacterized oil; 21–32, nil; 33–49, 123 mg whose ir spectra indicated some *exo*-phenyl-3-ol; 50–66, 393 mg of an oil whose ir spectra showed only 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo-[3.1.0]hexan-3-ol. Crystallization from methanol gave 195 mg, mp 83–87°. Recrystallization from methanol gave 50.8 mg, mp 87–88°. The spectral data were: ir (KBr) 2.92 μ broad OH; strong 9.34, 9.90, 9.98, 12.45, 13.21, 14.26; medium 9.21, 9.69, 9.79, 11.31, 11.90, 14.00; weak 10.48, 11.61 μ; nmr ($CDCl_3$) τ 2.67–3.19 (Ph pseudo s centered at 2.72 plus an aryl A_2B_2 quartet, 9 H), 7.10 (t, 1 H, J = 7 cps, *H*COH), 7.50–8.45 (broad m, 6 H, CH_2 and cyclopropyl), 8.52 (s, 1 H, OH).

Anal. Calcd for $C_{18}H_{17}OBr$: C, 65.66; H, 5.21; Br, 24.27. Found: C, 65.63; H, 5.22; Br, 24.01.

Fractions 67–74, 140 mg of light yellow oil whose ir spectra indicated a mixture of the desired alcohols; and 75–120, 309 mg of an oil whose ir spectra showed only 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*exo*-ol. Recrystallization from pentane of fractions 75–120 gave 295 mg of 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*exo*-ol, mp 96–98°. The spectral data were: ir (KBr) 3.04 μ broad OH; strong 9.31, 9.09, 10.18, 12.33, 13.13, 14.25; medium 9.71, 10.57, 11.54, 11.76; shoulders at 13.32, 13.99, 14.65 μ; nmr ($CDCl_3$) τ 2.63–3.15 (Ph pseudo s centered at 2.80 plus an aryl A_2B_2 quartet, 9 H), 5.68 (d, 1 H, J = 5.5 cps, *H*COH), 7.88–8.98 (m, 6 H, CH_2, OH, one cyclopropyl), 9.27–9.90 (weak broad m, 1 H, cyclopropyl).

Anal. Calcd for $C_{18}H_{17}OBr$: C, 65.66; H, 5.21; Br, 24.27. Found: C, 65.73; H, 5.23; Br, 24.55.

6-*endo*-Phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one. To 30.0 ml of dry pyridine, 1.00 g of chromic acid was added in small portions at 0° during 15 min. After stirring for 2 hr at room temperature, 342 mg (2.56 mmol) of the 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-ol in 4.0 ml of pyridine was added in one portion. After stirring for 11 hr, the mixture was poured into 125 ml of 2% sodium sulfate and ether extracted; the extracts were washed with HCl in ice water, and then in sodium bicarbonate solution. After drying, the solvent was removed *in vacuo* to give 980 mg of light yellow oil which was then chromatographed on a 2 × 12 cm deactivated silicic acid column slurry packed in 5% ether–hexane. Elution with 375 ml of 5% and 625 ml of 10% ether–hexane and collection of 125-ml fractions gave: fraction 1, 74 mg of *p*-bromobenzophenone, mp 79–80° 2, nil; 3–6, 809 mg of the desired ketone as a clear oil; 7–8, 44 mg of recovered starting material, mp 83–85°. Fractions 3–6 were recrystallized from methanol to give 461 mg (55%) of the desired 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one, mp 109–110°, whose spectral data were identical with those of another crystallization modification, mp 98–100°. The spectral data were: ir (CS_2) 5.72 μ C=O; strong 7.12, 8.71, 9.89, 12.32, 13.20, 13.98, 14.22; medium 3.28, 3.37, 3.44, 7.90, 9.07, 9.77, 14.30; shoulders 3.22, 3.24, 12.09, 12.98; weak 10.39, 10.97, 11.91, 11.45 μ; nmr ($CDCl_3$)

(34) The present research confirmed the previously reported[8] isomorphism of this compound in our present study the 111–112° modification was isolated. However, in an earlier preparation nmr and solution ir spectra identical with those of the 123–124° isomer were observed.

τ 2.62–3.12 (Ph pseudo s centered at 2.75 plus an aryl A_2B_2 quartet, 9 H), 7.10–7.85 (m, 6, CH_2 and cyclopropyl).

Anal. Calcd for $C_{18}H_{15}OBr$: C, 66.07; H, 4.62; Br, 24.42. Found: C, 66.10; H, 4.72; Br, 24.64.

6-*endo*-Phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one. To 25.0 ml of dry pyridine was added 1.53 g of chromic acid in portions at 0° over 15 min with stirring. After stirring at room temperature for 2 hr, a solution of 276 mg (0.835 mmol) of the *endo*-phenyl-*exo*-2-ol in 1.5 ml of pyridine was added in one portion. After stirring at room temperature for 15 hr, the reaction mixture was worked up as in the previous preparation to give 180 mg of yellow oil which was then chromatographed on a 2 × 9 cm deactivated silicic acid column slurry packed in 5% ether–hexane. Elution with 375 ml of 5% and 250 ml of 10% ether–hexane and collection of 125-ml fractions gave: fraction 1, nil; 2, 6.5 mg of *p*-bromobenzophenone; 3–4, nil; 5–6, 173 mg of the desired *endo*-phenyl-2-one which was crystallized from cyclohexane to give 102 mg, (37%), mp 119–121°. Recrystallization from methanol gave 68.2 mg of the 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]-hexan-2-one, mp 124–125°. The spectral data were: ir (CS_2) 5.80 μ C=O; strong 8.47, 9.93, 12.31; 13.19, 14.00, 14.21; medium 3.26, 3.29, 3.47, 7.11, 7.68, 7.78, 9.32, 9.72, 10.95, 11.13, 11.90, 12.74; weak 8.00, 8.73, 9.49, 10.70 μ; nmr ($CDCl_3$) τ 2.62–3.12 (Ph pseudo s centered at 2.70 plus an aryl A_2B_2 quartet, 9 H), 7.40 (m, 2 H, CH_2), 7.90 (m, 3 H, CH_2 and cyclopropyl), 8.88 (m, 1 H, cyclopropyl).

Anal. Calcd for $C_{18}H_{15}OBr$: C, 66.07; H, 4.62; Br, 24.42. Found: C, 65.87; H, 4.57; Br, 24.39.

6-*endo*-Phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*endo*-ol. A solution of 163 mg (0.50 mmol) of the *endo*-phenyl-2-one in 15 ml of dry ether was added over a period of 5 min to a suspension of 15 mg (0.39 mmol) of lithium aluminum hydride in 20 ml of ether. After refluxing for 1 hr, a solution of ammonium chloride was added slowly, and the resulting suspension was filtered. The filtrate was washed with acid and bicarbonate, dried, and concentrated *in vacuo* to give 159.9 mg of a clear oil which was molecularly distilled at 140° (0.1 mm) to give 100 mg of 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*endo*-ol. The spectral data were: ir (CS_2) 2.93 μ broad OH; strong 9.10, 9.40, 9.68, 9.75, 9.91, 12.30, 12.59, 13.19, 13.98, 14.29; medium 2.78, 3.27, 3.29, 3.49, 7.19, 11.00; weak 7.55, 8.30, 11.40, 11.65 11.86 μ; nmr ($CDCl_3$) τ 2.44–3.17 (aryl A_2B_2 quartet plus a very broad complex m for Ph, 9 H), 5.16–5.66 (broad m, 1 H, *H*COH), 8.20 (m, 6 H, CH_2, OH, and one cyclopropyl), 9.50–9.95 (weak broad m, 1 H, cyclopropyl).

Anal. Calcd for $C_{18}H_{17}OBr$: C, 65.66; H, 5.21; Br, 24.27 Found: C, 65.83; H, 5.22; Br, 24.23.

Measurement of OH–π Bonding. Carbon tetrachloride solutions of 6-*exo*-phenyl-6-*endo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*endo*-ol and 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-*endo*-ol were run in a 1.0-mm NaCl cell on a Perkin-Elmer 421 machine using single beam mode. Concentrations and results are listed on Table I.

3-Acetoxy-6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hex-2-ene. A solution of 544 mg (1.65 mmol) of the *endo*-phenyl-3-one, 20 ml of isopropenyl acetate, and 150 mg of *p*-toluenesulfonic acid was refluxed gently for 12 hr. During this time 10 ml of distillate was collected; isopropenyl acetate was added every 2 hr to keep the volume constant. The darkened solution was diluted with ether, washed with sodium bicarbonate, dried, and concentrated *in vacuo*. Recrystallization from ethanol gave 222 mg (37%) of the desired *endo*-phenylenol acetate, mp 104.5–105°. The spectral data were: ir (KBr): 5.70 μ C=O; 8.32 and 8.56 μ CO; strong 6.13, 6.73, 7.33, 9.90, 12.20, 12.48, 14.10, 14.23; medium 6.94, 7.02, 7.55, 8.91, 9.32, 11.28, 13.12, 13.48; weak 3.29, 3.31, 3.42, 3.43, 3.55, 7.19, 7.78, 11.85 μ; nmr ($CDCl_3$) τ 2.61–3.15 (Ph pseudo s centered at 2.75 plus an aryl A_2B_2 quartet, 9 H), 4.36 (d, 1 H, vinyl), 7.00 (d of d, 1 H, *exo* *H*CH, J_{22} = 18 cps, J_{12} = 7 cps, ring), 7.65 (m, 3 H, *endo*-HC*H* and cyclopropyl), 8.10 (s, 3 H, methyl).

Anal. Calcd for $C_{20}H_{17}O_2Br$: C, 65.05; H, 4.64; Br, 21.64. Found: C, 65.18; H, 4.65; Br, 21.50.

2-Bromo-6-*endo*-6-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]-hexan-3-one. To a stirred solution of 181 mg (0.493 mmol) of the *endo*-phenylenol acetate in 4.0 ml of carbon tetrachloride was added 79.5 μl of pyridine and then 2.5 ml of a solution of 1.0 ml (0.49 mmol) of bromine in 100 ml of carbon tetrachloride over 1.3 hr. The reaction mixture was diluted in chloroform, washed with water, dried, concentrated *in vacuo*, and kept at 1 mm for 12 hr to remove residual pyridine. Recrystallization from ether–hexane gave 87 mg (43.5%) of the desired 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-3-one, mp 113.5–114.5°. The spectral data were: ir (KBr) 5.72 μ C=O; strong 6.69, 6.74, 8.70, 9.90, 11.15, 12.22, 13.15, 13.90, 14.24, 14.51; medium 3.28, 3.31, 3.38, unresolved at 3.40, 7.91, 7.12, 8.08, 9.38, 11.14 μ; nmr ($CDCl_3$) τ 2.57–3.11 (Ph pseudo s centered at 2.72 plus an aryl A_2B_2 quartet, 9 H), 5.72 (s, 1 H, HCBr), 6.87 (d of d, 1 H, J_{44} = 19 cps, J_{54} = 4 cps, *exo* *H*CH at C-4), 7.50 (d, 2 H plus half of another d, J_{54} = 4 cps, cyclopropyl), 7.61 (d, 1 H, J_{44} = 19 cps, *endo* HC*H* at C-4).

Anal. Calcd for $C_{18}H_{14}OBr_2$: C, 53.22; H, 3.47; Br, 39.36. Found: C, 53.03; H, 3.39; Br, 39.24.

Reaction of 2-Bromo-6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo-[3.1.0]hexan-3-one with Potassium *t*-Butoxide. To a stirred solution of 61 mg (0.15 mmol) of the *endo*-phenyl 2-bromo ketone dissolved in 3.0 ml of *t*-butyl alcohol (dried over refluxing CaH) at 40° was added over 2 min 1.5 ml of a 0.1 *M* solution of potassium *t*-butoxide in *t*-butyl alcohol. After stirring for 4 min more 8.65 μl of glacial acetic acid was added, the solvent was removed *in vacuo*, and the residue was taken up in 10.0 ml of chloroform, washed with water, dried, and concentrated under vacuum to leave 54.3 mg of pale yellow oil. This was chromatographed on a 2 × 11.5 deactivated silicic acid column slurry packed in 5% ether–hexane. Elution with 125 ml of 5% and 1 l. of 10% ether–hexane and collection of 125-ml fractions gave: fractions 1–2, 3.9 mg of an uncharacterized oil; 3–5, 35.3 mg of white crystalline product; 6–9, nil. Fractions 3–5 were collected and recrystallized from ether–hexane to give 32.0 mg (66%) of 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hex-3-en-2-one, mp 110.5–111.5° (lit.[8] 110.1–111.6°), which had nmr and solution ir spectra identical with those of authentic product.[8] The ir spectra of the filtrates showed only additional *endo*-phenyl photoketone and no trace of the *exo*-phenyl photoketone.

Hydrogenation of 6-*endo*-Phenyl-6-*exo*-*p*-bromophenylbicyclo-[3.1.0]hex-3-en-2-one. A 20.4-mg sample of platinum dioxide was hydrogenated in 5.0 ml of ethyl acetate containing 10 μl of triethylamine, and then a solution of 29.6 mg (0.91 mmol) of the *endo*-phenyl photoketone in 2.0 ml of ethyl acetate was added. Within 13 min (741 mm Hg, 24°) 2.30 ml of hydrogen was taken up. Catalyst filtration and solvent concentration *in vacuo* left 30.7 mg of clear oil. Recrystallization from ether–hexane afforded 23.9 mg (81.5%) of 6-*endo*-phenyl-6-*exo*-*p*-bromophenylbicyclo[3.1.0]hexan-2-one, mg 121.5–122°. A mixture melting point with an authentic sample was undepressed and nmr and solution ir spectra were identical with those of the authentic sample.

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