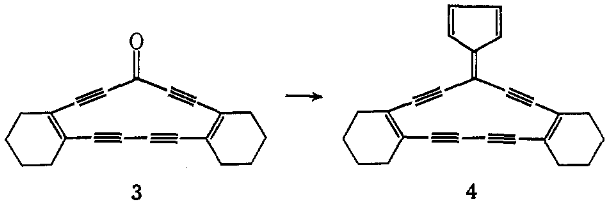
belonging to the second group. Compound **2**, like pentafulvalene (**1**, $x = y = 2$), is made up of two $(4n + 1)$-membered rings.

Substance **4** was obtained simply by the reaction of the ketone **3**[1] with cyclopentadiene in the presence of sodium methoxide.[4] Cyclopentadiene (0.4 ml) was added to an ice-cooled solution of sodium methoxide (from 50 mg of sodium) in methanol (20 ml) under nitrogen, and the ketone **3** (50 mg) in ether (10 ml) was added after stirring for 10 min. An immediate deep red-purple color was formed, and the reaction was quenched by the addition of water. Isolation with ether and chromatography on silicic acid gave **4** in 61% yield as brick-red needles from ether, which decomposed at 135–140° on attempted melting point determination; $\lambda_{max}^{ether}$ 250 m$\mu$ ($\epsilon$ 18,700), 260 (17,900), 273 (14,700), 290 (15,100), 299 (14,900), 383 (36,100), and 401 (43,500); $\nu_{max}^{KBr}$ (cm$^{-1}$) 2185 m, 2155 w (C≡C), and 1567 m (C=C); nmr spectrum (CDCl$_3$, 100 Mcps), four-proton singlet at $\tau$ 3.61 (cyclopentadiene protons),[5] eight-proton multiplet at 7.55–8.00 (allylic protons), and eight-proton multiplet at 8.20–8.50 (methylene protons); mass spectrum (70 eV, direct inlet), molecular ion at *m/e* 332.155 (100%) (calcd 332.156), very little fragmentation. *Anal.* Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 94.05; H, 6.03.



3 4

Compound **4** was more stable than the precursor **3**, but it also gradually decomposed on being allowed to stand in light and air (*ca.* 50% decomposition after 7 days). It was not protonated with trifluoroacetic acid or 70% perchloric acid in ethanol, unlike derivatives of triapentafulvalene[6a] and pentaheptafulvalene.[6b] The normal positions of the allylic[1] and cyclopentadiene[5,7] proton bands in the nmr spectrum of **4** indicate the central double bond not to be greatly polarized, in agreement with expectation.

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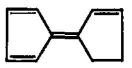
[4] Among others, see E. P. Kohler and J. Kable, *J. Am. Chem. Soc.*, **56**, 2756 (1934); **57**, 917 (1935).

[5] The cyclopentadiene protons in the nmr spectra of other fulvene derivatives have been shown to appear as a singlet. For example, the cyclopentadiene protons in dihydropentafulvalene (i) appear as a singlet at $\tau$ 3.73 (K. V. Scherer, *ibid.*, **85**, 1550 (1963)).



i

[6] See (a) H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, **50**, 1669 (1967); (b) H. Prinzbach, D. Seip, L. Knothe, and W. Faisst, *Ann.*, **698**, 34 (1966).

[7] See G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

[8] Recipient of a Science Research Council Research Studentship (1965–1967) and a New Hall Research Fellowship (1967–1968).

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

*Sir:*

One of the most intriguing of photochemical rearrangements is the type A transformation[2] of 2,5-cyclohexadienones (*e.g.*, **2**). Of particular interest is the stereochemistry of the process. Thus, *a priori*, the zwitterion **4** postulated[3] to be a photochemical reaction intermediate can rearrange by either of two types of stereochemistry (see Chart I). The pivot mechanism is one in which bond 5,6 remains essentially intact with pivoting about this bond and with the orbital at C-6 detaching itself from C-1, then bonding to C-4. The "slither" mechanism can be pictured as involving two 1,2 shifts with C-6 migrating from C-5 to C-4 and then from C-1 to C-5.

The problem is simplified if one begins with zwitterion **4** rather than with its dienone precursor. This we have done, and we now report a stereospecific stereochemical course for the rearrangement of the zwitterion. 6-*exo*-Phenyl-6-*p*-bromophenylbicyclo[3.1.0]hex-2-ene (**6a**), mp 105–106°, and 6-*endo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hex-2-ene (**6b**), bp 105° (0.005 mm), were synthesized[4] from cyclopentadiene and phenyl-*p*-bromophenyldiazomethane. The *exo*-olefin **6a** on hydroboration gave 6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-2-ol (**7a**), mp 143–144°, and 6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-3-ol (**8a**), mp 185–186°. Oxidation of **7a** gave 6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-2-one (**9a**), mp 130–131°, and oxidation of the *exo*-3-alcohol **8a** gave 6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-3-one(**10a**), mp 110–111°. This synthesis rigorously related the configurations of the *exo*-2-one **9a** and the *exo*-3-one **10a**.[5] Similarly, hydroboration of the 6-*endo*-phenyl olefin **6b** and oxidation of the resulting alcohols gave the *endo*-2-one **9b**, mp 124–125°, and *endo*-3-one **10b**, mp 109–110°, whose configurations must then be the same and *endo*,[5] having been derived from the single *endo*-olefin **6b**. Bromination of the enol acetates, mp 170–171° and 104–105, of each of the *exo*- and *endo*-3-ones gave 2-bromo-6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-3-one (**11a**), mp 147–148°, and 2-bromo-6-*endo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hexan-3-one (**11b**), mp 113–114°, respectively.

Previously we reported[6] that treatment of 2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one with potassium *t*-butoxide in *t*-butyl alcohol at 40° gave 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. The reaction was postulated as proceeding *via* zwitterion **4** ($R_1 = R_2 =$

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[1] For paper XXXV of the series, see H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Am. Chem. Soc.*, in press.

[2] The type A dienone transformation is typified by the rearrangement of 4,4-diphenylcyclohexadienone to 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one.[3]

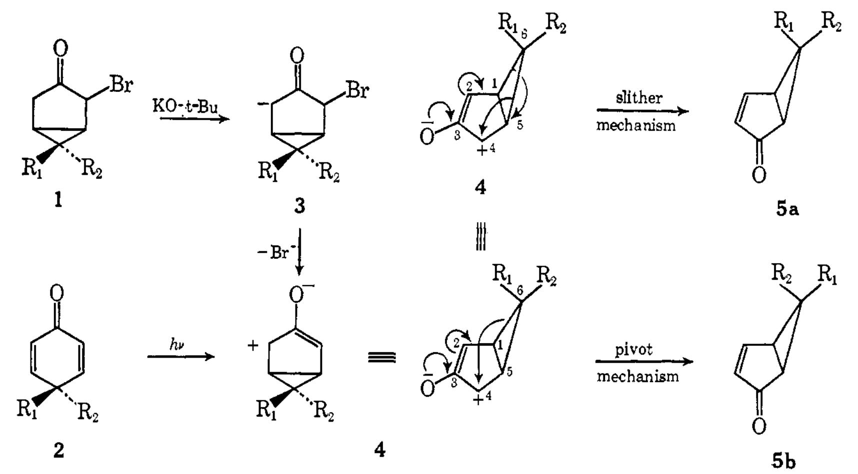
[3] (a) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4484 (1961); (b) *ibid.*, **84**, 4527 (1962); (c) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 947 (1964); (d) *ibid.*, **89**, 906 (1967); (e) H. E. Zimmerman, 17th National Organic Chemistry Symposium, Bloomington, Ind.,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

[4] Synthetic details will be given in our full paper. All compounds were completely characterized and gave satisfactory analyses.

[5] The *exo vs. endo* assignments are based on nmr arguments which are not absolute. However, the stereochemical course is independent of this and relies only on knowing that **9a** and **10a** have the one configuration while **9b** and **10b** have the other configuration.

[6] H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **88**, 5352 (1966).

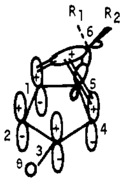
**Chart I**



$C_6H_5$) by a process such as shown in Chart I. Application of the same reaction conditions to the two bromo ketones **11a** and **11b** gave stereospecific reactions, with **11a** (*i.e.*, *exo*) affording only (<2% minor isomer) 6-*exo*-phenyl-6-*p*-bromophenylbicyclo[3.1.0]hex-3-en-2-one (**12a**)[7] and **11b** (*i.e.*, *endo*) leading exclusively (<0.5% minor isomer) to 6-*endo*-6-*p*-bromophenylbicyclo[3.1.0]hex-3-en-2-one (**12b**).[7] **12a** was catalytically hydrogenated to give **9a** and **12b** gave **9b**, thus establishing the configurations of **12a** and **12b**.

Since the rearrangement afforded *endo* product from *endo* zwitterion and *exo* product from *exo* zwitterion, the rearrangement follows the stereochemistry of the slither mechanism of Chart I.[8]

Interestingly, the same stereochemistry[9a] is followed in the santonin to lumisantonin photochemical rearrangement,[9b-d] as has been noted.[3b,e] In the santonin rearrangement, only the slither mechanism is possible. Due to $R_2$ (note Chart I) being part of a six-membered ring attached also to C-5, pivoting is stereochemically precluded. Nevertheless the highly efficient quantum yield,[10] not appreciably different from that of monocyclic dienones (*e.g.*, 4,4-diphenylcyclohexadienone, $\phi = 0.85$[3c]), suggests that this is either the preferred stereochemistry or a highly efficient alternative.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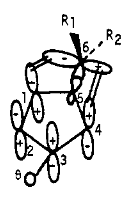
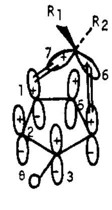
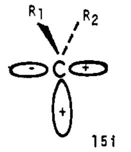

14i


14ii



15i

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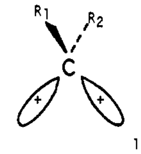

15ii

The preference of the slither over the pivot mechanism is of considerable interest. The pivoting species is depicted as **13**.

If we (a) focus attention on the orbital system comprising $\chi_1$, $\chi_2$, $\chi_3$, $\chi_4$, $\chi_6$ and (b) consider to a first approximation the oxygen charge localized, we find four electrons in a cyclic system of five orbitals with no sign discontinutiy (*i.e.*, Hückel-like with zero or an even number of sign inversions)—a high-energy situation.[11] In contrast, the slither mechanism can be pictured equivalently either as **14i** or **14ii**. In **14i**, we have $\chi_1$, $\chi_2$, $\chi_3$, $\chi_4$, and $\chi_6$ with one sign inversion (*i.e.*, an odd number; Möbius-like[11]) and four electrons—a favorable situation.[11] Alternatively the equivalent orbital representation **14ii** has the cyclic array $\chi_1$, $\chi_2$, $\chi_3$, $\chi_4$, $\chi_6$, $\chi_7$, no sign inversion (*i.e.*, Hückel-like), and six electrons—a favorable combination.[11] Thus the reaction can be considered to use both lobes of $\chi_6$ of **14i** or to involve the motion of the bivalent carbon moiety **15ii**, originally bonded to C-1 and C-5, to C-5 and C-4 by a slithering motion along the five-membered-ring $\pi$ system of **14ii**.[12]

This unusual 1,4-sigmatropic rearrangement is subject to a second interpretation,[13] one based on local symmetry of the highest occupied MO of the 2-oxybutadienyl moiety of **13** and **14i** relative to the symmetries of the C-6 p orbital of **14i** and the C-6 hybrid orbital of **13**. The highest occupied MO, $\psi_3$ of the oxybutadienyl moiety, is approximately antisymmetric with respect to the plane through C-5, C-6, and bond 2,3. The p orbital at C-6 in **14i** is also antisymmetric, and splitting of MO's in **14** leads to considerable stabilization. In contrast, in **13** the $sp^2$-hybrid orbital at C-6 is symmetric and does not mix efficiently with $\psi_3$ of the oxybutadienyl group, and little stabilization results.

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

[8] This result precludes a mechanism in which bond 1,6 of an initial enolate or zwitterion opens to give a free benzhydryl anion. Bromide loss could possibly be concerted with rearrangement, in which case we would be dealing with an incipient zwitterion.

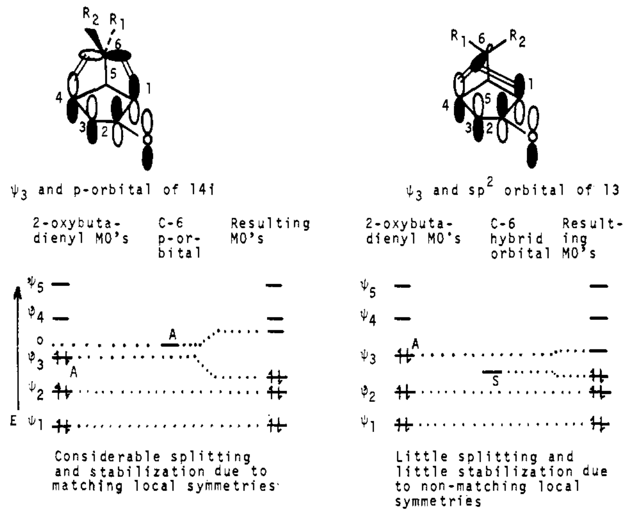
[9] (a) D. H. R. Barton and P. T. Gilham, *J. Chem. Soc.*, 4596 (1960); (b) D. H. R. Barton, P. DeMayo, and M. Shafiq, *ibid.*, 140 (1958); (c) *Proc. Chem. Soc.*, 205 (1957); (d) D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger, and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957).

[10] M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **85**, 3029 (1963).

[11] (a) H. E. Zimmerman *ibid.*, **88**, 1566 (1966); (b) *Science*, **153**, 837 (1966).

[12] (a) Note the parallel case of migration with inversion: by J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **89**, 5503 (1967). (b) The inversion at C-6 contrasts with the retention of configuration in the pivot mechanism. However, these terms are confusing since inversion at C-6 leads *exo* reactant to *exo* product. (c) We note that the reaction when pictured as involving inversion at C-6 proceeds by a novel 1,4-sigmatropic shift.

[13] (a) This is identical with that used by us in another case (H. E. Zimmerman, "Molecular Rearrangements," Vol. 1, Interscience Publishers, New York, N. Y., 1964, p 345, and *errata*). (b) It is, however, easier to use the Möbius-Hückel method in most cases since the odd *vs.* even (or zero) number of sign inversions is quickly counted and corresponds to stability with $4n$ or $4n + 2$ electrons (*i.e.*, Möbius *vs.* Hückel character), respectively.



E represents energy in units of $|\beta|$. S and A refer to local symmetry.

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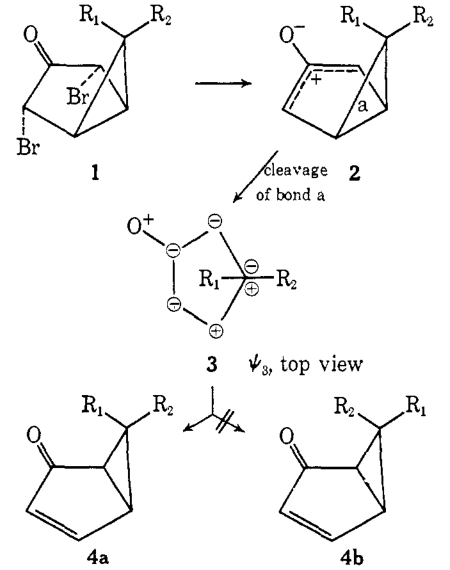
## Stereochemistry of a 1,4-Sigmatropic Rearrangement[1]

*Sir:*

Insight into the mechanism of thermal unimolecular reactions has been enormously increased by the concept of conservation of orbital symmetry, introduced by Woodward and Hoffmann.[2] In one group of reactions, defined as sigmatropic transformations, a $\sigma$-bonded atom or group migrates from one end of a conjugated chain to the other. When the highest occupied molecular orbital of the conjugated system across which migration occurs is antisymmetric, conservation of orbital symmetry in a concerted reaction requires that the migrating group must also undergo an antisymmetric transformation. The group either transverses the nodal plane of the skeleton (antarafacial motion) or suffers an inversion of configuration above the nodal plane (suprafacial motion).[3] No examples of antarafacial migration have yet been observed, but recently Berson and Nelson[4] reported a suprafacial 1,3-sigmatropic rearrangement which proceeded with inversion of configuration in the asymmetric migrating group. We report here a stereochemical study of a 1,4-sigmatropic rearrangement in which migrating carbon also undergoes inversion of configuration.

The system under investigation is the symmetrical Favorskii-like intermediate, usually depicted as the zwitterion **2**, derived from bicyclo[3.1.0]hexan-3-ones (**1**). This species, suggested earlier as an intermediate in the photochemical rearrangement of cyclohexadienones, has been generated recently by nonphotochemical methods (treatment of the bromo ketone with base or of the dibromo ketone with zinc) and shown to rearrange[5] to bicyclo[3.1.0]hex-3-en-2-ones (**4**). The conjugated system over which migration occurs may be considered a 2-oxobutadiene skeleton. Calculation of the symmetry properties of the Hückel molecular orbitals of **3** shows that, whether or not the effect of the oxygen is included, the highest occupied molecular orbital ($\psi_2$ of butadiene or $\psi_3$ of 2-oxobutadiene) is antisymmetric. Thus a concerted suprafacial rearrangement requires *inversion* of configuration of the migrating group, leading to **4a**.

Experimental verification of this predicted mode of rearrangement has been achieved by stereospecific synthesis of one isomer of type **1** ($R_1$ = $CH_2C_6H_5$; $R_2$ = $C_6H_5$) and of reduced derivatives of product **4a**. Diazo ester **5**, prepared by treatment of cyclopent-3-en-1-ol with the *p*-toluenesulfonylhydrazone of phenylglyoxalyl chloride in the presence of triethylamine,[6] was cyclized (by a catalytic mixture of copper, cuprous oxide, and cupric sulfate in refluxing toluene) to lactone **6**, mp 120–121°; $\nu$ 1710 $cm^{-1}$. Reaction with phenyllithium gave hemiketal **7**, mp 152–154°, which was reduced with $LiAlH_4$ to ether **8**, mp 75–78°, and further by sodium–ethanol in liquid ammonia to alcohol **9**, mp 102–105°. Chromic acid oxidation gave the requisite ketone **10**, $\nu$ 1740 $cm^{-1}$, of unambiguous stereochemistry. Bromination in acetic acid gave dibromide **11**,[7] which rearranged almost quantitatively to **12**, $\nu$ 1690 $cm^{-1}$, on treatment with zinc in refluxing dioxane. The product was judged homogeneous by the appearance of only one spot in several tlc systems and particularly by the single sharp benzyl methylene absorption in the nmr spectrum of the total crude product.



**1** **2**

**3** $\psi_3$, top view

**4a** (inversion) **4b** (retention)

To facilitate comparison, **12** was hydrogenated over Raney nickel to the corresponding saturated ketone, $\nu$ 1720 $cm^{-1}$, and then reduced to the crystalline alcohol

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(1) This work was supported in part by a research grant (GP-3811) from the National Science Foundation, to whom the authors express their thanks.

(2) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965). For recent surveys, see (a) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (b) R. B. Woodward, "Aromaticity," Special Publication No. 21, The Chemical Society, London.

(3) For a detailed discussion of this question, see J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

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

(5) H. E. Zimmerman, D. Döpp, and P. S. Huyffer, *ibid.*, **88**, 5352 (1966).

(6) This synthesis was patterned after the method developed by H. O. House and C. J. Blankley, *J. Org. Chem.*, **33**, 53 (1968).

(7) Both bromines are assigned *exo* configurations because of nmr identity of protons at $C_2$ and $C_4$ and the lack of coupling between protons at $C_1$ and $C_2$.