ring protons in many other metallocene derivatives.[7] The structure of the dimercurated complex **4** is tentatively assigned on the basis of the nmr spectrum of its corresponding diiodo derivative **14**, which exhibits a low-field, two-proton doublet at τ 5.21, and a higher field, one-proton singlet at τ 5.49.[8,9] The nmr spectra of the cobalt complexes are of additional interest when compared to the spectra of analogous ferrocene derivatives, since the resonances of protons on exocyclic carbon atoms (*e.g.*, the acetyl protons of **9** at τ 8.33, the methylene protons of **11** at τ 5.91, and the trimethylsilyl protons of **8** at τ 10.2) occur at significantly higher fields than do corresponding resonances in the ferrocene series.[7] Molecular models indicate that a substantial shielding effect may be imposed by the phenyl groups of the cyclobutadiene ring, and this effect, together possibly with metal anisotropy differences, may account for the observed chemical shifts.

The ability of **1** to undergo various electrophilic substitution reactions clearly demonstrates the aromatic reactivity of this organocobalt compound. We are currently extending the chemistry of **1** in order to compare the chemical reactivity and physical properties of this complex with other metallocene systems. Research directed toward the synthesis and reactivity of rhodium and iridium analogs of **1** is also in progress, as is the attempted formation of the parent complex, π-cyclopentadienylcyclobutadienecobalt, $(\pi\text{-C}_5\text{H}_5)\text{Co}(\text{C}_4\text{H}_4)$. Reactions of the latter should prove very interesting, since Pettit and co-workers[10] have already shown that cyclobutadieneiron tricarbonyl, like ferrocene, **1**, and certain other metallocenes, also undergoes ring substitution reactions of the electrophilic type.

Acknowledgment. The authors are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this research.

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[7] (a) M. D. Rausch and V. Mark, *J. Org. Chem.*, **28**, 3225 (1963); (b) R. A. Benkeser, Y. Nagai, and J. Hooz, *Bull. Chem. Soc. Japan*, **36**, 482 (1963); (c) G. G. Dvoryantseva, S. L. Portnova, K. I. Grandberg, S. P. Gubin, and Yu. N. Sheinker, *Dokl. Akad. Nauk SSSR*, **160**, 1075 (1965); (d) R. A. Genetti and M. D. Rausch, unpublished studies.

[8] Protons *ortho* to an iodine atom in iodobenzene and diiodobenzenes are known to be substantially deshielded with respect to other ring protons: H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); M. Martin and B. P. Dailey, *ibid.*, 37, 2594 (1962).

[9] The structure of 1,2-dibenzoylruthenocene has been assigned on a similar basis; see ref 7a.

[10] J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3254 (1965).

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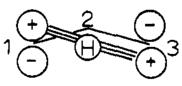
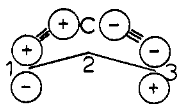
Inversion of Configuration in the Migrating Group of a Thermal 1,3-Sigmatropic Rearrangement[1]

Sir:

When the migrating atom in a concerted thermal 1,3-sigmatropic rearrangement is restricted to the use of a symmetric orbital to form the basis set for the transition state, bonding interactions with both ends (C-1 and C-3) of the allylic system can occur only if the process is antarafacial.[2] For geometric reasons, the requirement is difficult to meet and, consequently, migrations of atoms in this category (*e.g.*, hydrogen, as in I) are rare. Migrating atoms of higher atomic number (*e.g.*, carbon, as in II), however, might use both lobes of an antisymmetric orbital and thereby achieve a suprafacial process.[2] This necessarily would be accompanied by inversion of configuration of the migrating group. The present paper reports the observation that, in a system constructed to force the rearrangement to be suprafacial, such an inversion does occur.

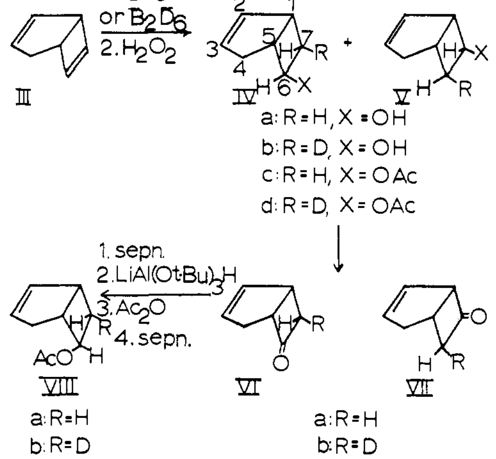


I



II

Deuterioboration–oxidation of 2,6-bicyclo[3.2.0]heptadiene (III)[3a] gives a mixture of bicyclo[3.2.0]-2-hepten-6-*exo*-ol-7-*exo*-*d* (IVb) and the isomeric 7-*exo*-ol-6-*exo*-*d* (Vb). The corresponding acetates IVd and Vd are separable by preparative vapor chromatography (vpc).[4] On a preparative scale, oxidation of the IVb–Vb mixture to the ketones VIb and VIIb, separation of VIb, reduction, and acetylation give bicyclo[3.2.0]-2-hepten-*endo*-6-yl acetate-*exo*-7-*d* (VIIIb) which is separated from a small amount of its *exo*-6-acetoxy isomer by vpc. Compound VIIIb has 0.94 atom of deuterium/molecule, only about 0.02 atom less enrichment than the starting IVb.



The stereochemical relationship of the deuterium and acetoxy groups in VIIIb is established as cleanly *trans* by the method of synthesis (OAc in IVd is *exo*[5-7]

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[1] We are indebted to the Air Force Office of Scientific Research, the Petroleum Research Fund, and the National Science Foundation for support of part of this work.

[2] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

[3] (a) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961); (b) see also M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **83**, 3409 (1961).

[4] Identification of IVb and Vb and their acetates IVd and Vd is by vapor chromatographic retention time comparisons with those of authentic materials prepared in the undeuterated series. In the IV series authentic materials (IVa,c) were available from previous work (ref 5–7 and literature cited there). Confirmation of the structure of the V series is by conversion to bicyclo[3.2.0]-2-hepten-7-one and comparison with a sample kindly provided by Dr. D. I. Schuster.[8]

[5] J. A. Berson and J. W. Patton, *J. Am. Chem. Soc.*, 84, 3406 (1962).

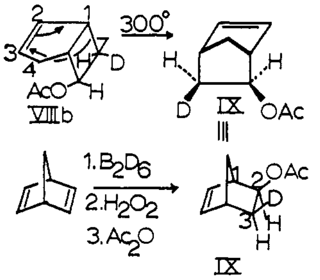
[6] J. A. Berson and R. S. Wood, *ibid.*, **89**, 1043 (1967); (b) R. S. Wood, Ph.D. Dissertation, University of Wisconsin, 1966.

[7] H. L. Goering and T. Beattie, unpublished; T. Beattie, Ph.D. Dissertation, University of Wisconsin, 1965.

[8] D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Letters*, 1911 (1963).

and hydroboration is *cis*[9]) and by the retention of virtually all of the label in the sequence from IV. It is confirmed by the nmr spectra of VIIIb and VIb, which are interpreted with the aid of double- and triple-resonance[10] spectra at 100 Mhz of the undeuterated substances (VIa and VIIIa) and their 5-*d* and 5,7,7-d_3 analogs. The absorptions due to the 7-*exo* protons in VIa and VIIIa disappear in VIb and VIIIb.

Heating VIIIb in decalin solution at 307° under conditions previously shown to cause intramolecular,[5,6] 1,3-sigmatropic[6] rearrangement to *exo*-norbornenyl acetate gives that compound with the deuterium and acetoxy groups both *exo* and hence *cis* (IX). The stereochemistry of IX is established by the nmr spectrum. The spectrum of undeuterated *exo*-norbornenyl acetate shows[6] the absorption of the 3-*exo* proton as a multiplet at δ 1.35 downfield from internal tetramethylsilane. This pattern is missing from the spectrum of the pyrolysis product IX. The geminal coupling (J = 12 cps) in the pattern of the 3-*endo* proton of undeuterated *exo*-norbornenyl acetate disappears in IX, and the doublet of doublets due to the 2-*endo* proton of undeuterated material ($J_{2,3\text{-}exo}$ = 2.8 cps, $J_{2,3\text{-}endo}$ = 7 cps) collapses to a doublet ($J_{2,3\text{-}endo}$ = 7 cps). The entire spectrum is virtually indistinguishable from that of authentic[11] IX, synthesized by deuterioboration–oxidation–acetylation of norbornadiene. From time-averaged repeated-scan observation of the δ 1.35 region of the spectrum and comparison with that of authentic 3-*endo*-deuterio-2-*exo*-norbornenyl acetate independently synthesized,[12] the amount of the latter substance present as contaminant in the pyrolysis product IX can be estimated to be less than 5%. Control experiments show that (1) a mixture of synthetic IX and the undeuterated analog does not fractionate under the pyrolysis conditions; (2) prolonged pyrolysis converts IX to a mixture containing both *endo*- and *exo*-norbornenyl acetate, but the *exo*-acetate recovered is still IX (3-*exo*-*d*); (3) starting material VIIIb recovered from pyrolysis is still exclusively VIIIb (7-*exo*-*d*).



The VIIIb → IX rearrangement, necessarily suprafacial, thus occurs with highly specific inversion of the migrating group, C-7. This result is difficult to rationalize in terms of a stepwise mechanism passing over an intermediate in which the C-7–C-1 bond is broken but no significant bonding of C-7–C-3 exists. Such a process would be expected to result in retention or randomization of configuration. Apparently, the preferred approach to the transition state is by compression of the C-2–C-1–C-7 angle and torsion about the C-5–C-6 and C-6–C-7 bonds until *opposite faces* of C-7 can bond simultaneously to C-1 and C-3, as in II. That progress along the reaction coordinate should consist of this complex set of motions demonstrates the predictive power of orbital symmetry considerations.[13]

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[9] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[10] We are indebted to Professor P. Bender and Mr. L. Sims for expert advice on these techniques and to Miss Martha Petrie for a number of the spectra.

[11] *Cf.* S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2726 (1966).

[12] As the minor component from the sequence: exchange of one (mostly *exo*) deuterium of norbornenone-3,3-d_2, hydride reduction, acetylation, and vpc separation.

[13] Since a transition state with the geometry of II places the migrating group substituents in a plane perpendicular to that of the allyl system, steric repulsions when the substituents are large may be so severe as to prohibit this mechanism.

[14] National Institutes of Health Predoctoral Fellow, 1966–1967.

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β-Styrylnitrene

Sir:

Both β-styryl azide and β-styryl isocyanate undergo photochemical transformation into phenylacetonitrile, a product also obtained from the former by pyrolysis. A previous report that deoxygenation of β-nitrostyrene by triethyl phosphite affords the same nitrile in low yield[1] has been confirmed by glpc analysis. β-Styrylnitrene, a proposed intermediate for the deoxygenation reaction,[1] may be common for all three reactions; however, other mechanisms, such as fragmentation concerted with rearrangement, have not been eliminated.[2] To our knowledge, this is the second recorded example of the probable formation of an organic nitrene from an isocyanate by photolysis.[3]

$$\begin{tikzcd}
 & C_6H_5CH{=}CHN_3 \arrow[d, "\text{heat or } h\nu", "-N_2"'] & C_6H_5CH{=}C{=}NH \arrow[dd] \\
C_6H_5CH{=}CHNCO \arrow[r, "h\nu", "-CO"'] & C_6H_5CH{=}CHN \arrow[ur] \arrow[dr] & \\
 & C_6H_5CH{=}CHNO_2 \arrow[u, "R_3P", "-R_3PO"'] & C_6H_5CH_2C{\equiv}N
\end{tikzcd}$$

Other reactions of β-styrylnitrene have not been elucidated. Cyclization to indole was not observed.[4] Neither abstraction from nor insertion with *n*-heptane C–H bonds during photolysis of either β-styryl azide or isocyanate has been established. By comparison with the formation of 2-phenylazirine from either pyrolysis or photolysis of α-styryl azide,[5] the formation of 3-phenylazirine could be expected from both β-styryl azide and isocyanate. Firm evidence for its presence is not avail-

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[1] R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 165 (1964), reported a private communication from J. Weinstock.

[2] For a discussion of nitrene formation from azides, see P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, p 216; from nitro compounds, see J. I. G. Cadogan and M. J. Todd, *Chem. Commun.*, 178 (1967), and earlier papers.

[3] D. A. Bamford and C. H. Bamford, *J. Chem. Soc.*, 30 (1941), reported $CH_3NCO + h\nu \longrightarrow CH_3N + CO$. After the present paper was submitted for publication, J. S. Swenton, *Tetrahedron Letters*, 2855 (1967), reported the formation of carbazole and phenanthridone during the photolysis of *o*-biphenyl isocyanate.

[4] A positive, but unspecified, indole test was reported for a product from the deoxygenation of β-nitrostyrene.[1]

[5] G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962); L. Horner, A. Christmann, and A. Gross, *Chem. Ber.*, **96**, 399 (1963).