The 3-hydride precursor[3] I was dissolved to the extent of 10% by volume in 50% acetone–50% benzene and treated with increments of purified AgF at room temperature. A smooth reaction at the solid–liquid interface evolved hydrogen and deposited metallic silver, leaving II as the only product in solution. Isolation of II involved the steps: centrifugation and subsequent filtration of the supernatant liquid through Millipore filters; removal of acetone–benzene solvent; and gas–liquid chromatographic separation of the product from any residual solvent. Yields of II uniformly exceeded 95% with the only detectable contaminant being unreacted I.

II is a colorless, volatile liquid possessing a distinctive but not unpleasant odor. The boiling point is 148° at 754.5 mm, which may be compared with the corresponding values for I (141°) and octamethyltrisiloxane (153°). *Anal.* Calcd: C, 34.96; H, 8.80; F, 7.90. Found: C, 32.50; H, 8.47; F, 7.81. The appreciable volatility of II affected the C–H analyses, but not the F analysis in sealed gelatin capsules.

The reaction was monitored throughout by direct measurements of proton magnetic resonance (pmr). The pmr spectrum[4] of I in benzene consists of the hydride quartet centered at 2.21 ppm and the 3-methyl doublet centered at 7.05 ppm with $J_{\mathrm{H-CH_3}} = 1.6$ Hz, and the terminal methyl singlet at 7.03 ppm. (In acetone or benzene, the 3-methyl doublet is partially merged with the terminal methyl absorption; in CCl_4, the doublet appears farther upfield and is clearly observed.) As AgF was added to I in acetone–benzene, the hydride resonance signal diminished until it was no longer detected. The original 3-methyl doublet was progressively replaced by a second 3-methyl doublet of larger splitting.

The pmr spectrum of II in benzene solution consists of the terminal methyl singlet at 7.08 ppm and the 3-methyl doublet centered at 7.12 ppm with $J_{\mathrm{F-CH_3}} = 4$ Hz. The ^{19}F magnetic resonance spectrum[5] of II shows only the expected quartet, centered 9.8 ppm downfield from the CH_3SiF_3 quartet, with a splitting of 4 Hz.

Comparison of the mass spectra of I (calculated molecular weight = 222.510) and II (calculated molecular weight = 240.500) also demonstrates the fluoride-for-hydride substitution. The parent ion of I is observed, and peaks at *m/e* 221 and 207 indicate fragmentation by the competing loss of either H or CH_3, respectively. The parent ion of II is not observed, but peaks at *m/e* 221 (weak) and 225 (intense) indicate fragmentation by the competing loss of either F or CH_3, respectively. Other differences of 18 mass units between fluoride and hydrogen occur at *m/e* 209 and 193 in II *vs.* respective lines at *m/e* 191 and 175 in I. Both compounds show the intense line of the terminal fragment $(CH_3)_3Si^+$ at *m/e* 73, and a basically similar fragmentation pattern.

The infrared and Raman spectra of I and II were obtained and compared. Apart from the conspicuous absence of the strong Si–H stretching frequency at $\Delta\bar{\nu} = 2150\ \mathrm{cm^{-1}}$, II possessed a Raman spectrum virtually identical with that of I. For the infrared spectra also, the principal difference was the presence or absence of the Si–H stretching frequency at 2150 $\mathrm{cm^{-1}}$, the remainder of each spectrum being highly similar. However, II did show new shoulders at 1270 and 1120 $\mathrm{cm^{-1}}$, as well as two new peaks at 875 and 795 $\mathrm{cm^{-1}}$, when compared with I. There were also some apparent differences in the 600–250-$\mathrm{cm^{-1}}$ region. Because such a comparison involves loss of Si–H as well as gain of Si–F, we can only list the above frequencies as likely candidates for Si–F vibrational modes.

We have found that II, in pure form, is inert to either air or moisture for at least 2 months, and appears to be equally stable in neutral or slightly basic media. However, in acid media the fluoride migrates to carbon, forming a C–F bond and leaving behind a Si–H bond at the 3 position. This reversion of Si–F to Si–H at the chain silicon position occurs readily in acetone solutions containing a trace of either HF or HCl. The above process may be observed directly by pmr, or by infrared measurements after removal of acetone solvent. Spectra obtained by either technique are complex, indicating a mixture of several different fluoro derivatives. Fluorine magnetic resonance applied to such mixtures shows several sets of lines. Presumably, AgF treatment followed by fluoride migration under controlled conditions could be employed in repetitive sequence for extensive fluorination at both carbon and silicon.

As the customary synthesis of linear organosiloxanes involves the hydrolysis of organosilicon chlorides,[6] the acidic environment favors such migration of fluoride. For this reason we question the reported presence of chain Si–F bonds in compounds prepared by hydrolysis of organofluorosilicon chlorides.[7,8]

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[3] Obtained through the courtesy of A. N. Pines, Silicones Laboratories, Union Carbide Corp., New York, N. Y.

[4] A Varian HA-100 was employed; the listed chemical shifts are upfield from the benzene signal (≡0).

[5] Measured with a modified Varian HR-60 operating at 56.4 MHz. We are indebted to Dr. Rolf B. Johannesen for the ^{19}F data.

(6) R. J. H. Voorhoeve, "Organohalosilanes. Precursors to Silicones," American Elsevier Publishing Co., New York, N. Y., 1967.

(7) British Patent 627,800 (1949); *Chem. Abstr.*, **44**, 4023 (1950).

(8) M. S. Cohen and D. Graftstein, U. S. Patent 2,981,746 (1961).

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Sodium Borohydride Reduction of Oxymercury Compounds

Sir:

Reduction of 3-acetoxy-5-norbornen-2-ylmercuric chloride or 5-acetoxy-3-nortricyclylmercuric chloride, prepared by the method of Pande and Winstein,[1] gives three acetates: 2-*exo*-acetoxynorborn-5-ene (**1**), 7-*anti*-acetoxynorborn-2-ene (**2**), and 3-acetoxynortricyclene (**3**) in the ratio 6:34:60 (±3%), respectively. The acetates were isolated in high yield (98 and 90%, respectively from the two reductions), separated by preparative gas chromatography,[2] and characterized by comparison with authentic samples prepared by unambiguous synthetic routes.[3] Ir, nmr, mass spectra, and glpc reten-

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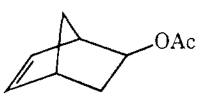
(1) K. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

(2) A Wilkins Autoprep was used for preparative chromatography with a 2-m column packed with DEGS (20% w/w) on Chromosorb W, 30–60 mesh, at 110°.

(3) The 2-*exo*-acetoxy compound (**1**) was prepared by the method of S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Amer. Chem. Soc.*,



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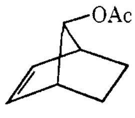

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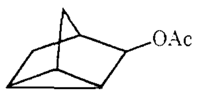
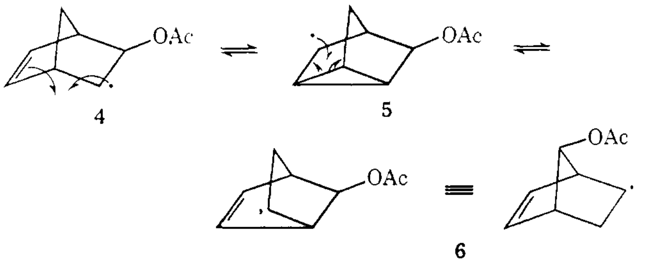


3

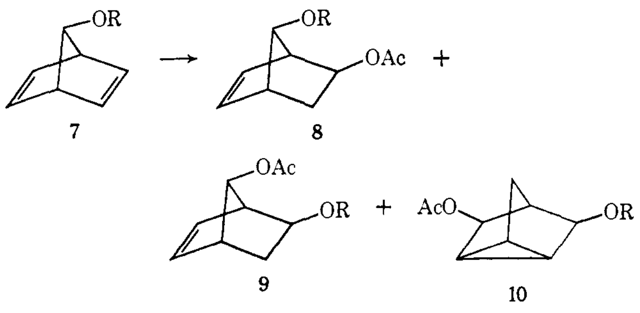
tion times were used for comparison. Hydrolysis and comparison of the resulting alcohols with authentic samples confirmed the above structures. The spectra were also in agreement with previously published values for these compounds.[4] Similar product ratios were obtained when the oxymercuration–sodium borohydride procedure of Brown and Geoghegan[5] was used, *i.e.*, without isolation of the intermediate organomercurials.

The products ratios found in these experiments contrast with those reported recently from a similar study of the mercuration–reduction of norbornadiene.[6] These authors summarize evidence which strongly suggests that a radical mechanism is operating in the borohydride reduction of organomercurials. Our results thus suggest that the radicals **4**, **5**, and **6** are in equilibrium. A similar suggestion has been made recently to account for the product distribution from the photolysis of cyclohex-2-enone and norbornadiene.[7] The product distribution from the addition of trimethyltin hydride to norbornadiene has also been interpreted in a similar manner.[8] These results thus provide support for the radical mechanism proposed by Pasto and Gontarz.[6] However, although the facile interconversion of **4** and **5** has been frequently demonstrated previously, products from the radical **6** have not previously been observed in these equilibria,[9] nor have products from **4** and **5** been observed in systems where the radical **6** has been produced.[10]



A reduction using sodium borodeuteride, followed by preparative glpc, gave small samples of deuterated **2** and **3**. The samples were hydrolyzed and their nmr spectra determined at 220 MHz.[11] The spectrum of the deuterated 7-*anti*-alcohol (in CCl_4) showed that the peak at τ 8.22 had halved in intensity and thus the deuterium had been incorporated into the 4-*exo* position.[4] The spectrum of the deuterated nortricyclanol (in benzene) showed that the absorptions at τ 8.75 (1 H, d, $J = 9.5$ Hz) and 8.88–8.95 (4 H, m) had decreased in intensity. The doublet decreased in intensity by *ca.* one-third and collapsed into a singlet while the multiplet integral decreased from 4 to *ca.* 3.3 H. Double irradiation experiments for spectra at 100 MHz[12] enabled us to assign the positions of deuterium incorporation as 5-*exo* and 5-*endo*, although the spectra do not allow a clear decision to be taken as to the preferred stereochemistry of incorporation. The positions of deuterium incorporation thus provide supporting evidence for the intermediary of the equilibrating radicals **4**, **5**, and **6** but the nonstereospecific reduction of **6** is perhaps somewhat surprising.[13]

Recently the oxymercuration–reduction of 7-acetoxynorbornadiene (**7**, R = Ac) has been reported to give a mixture of 7-*syn*-2-*exo*-diacetoxynorbornene (**8** or **9**, R = Ac) and 3,5-diacetoxynortricyclene (**10**, R = Ac).[14] Rearrangement of the type reported in this paper, *i e.*, **4** $\rightleftharpoons$ **6**, could not be observed as acetoxy-substituted radicals **4** and **6** would give the 7-*syn*-2-*exo*-diacetoxy compound. Reduction of the acetoxymercurial from 7-propionoxynorbornadiene (**7**, R = COEt) gave 3-acetoxy-5-propionoxynortricyclene (**10**, R = COEt) and a norbornene fraction (in the ratio 60:40), yield 62%. The nmr of the acetoxypropionoxynorbornene fraction showed two acetoxy methyl absorptions of almost equal intensity, at τ 8.26 and 8.3, and pairs of overlapping triplets and quartets at τ 9.1 and 7.9 for the methyl and methylene protons in the propionate group. The spectrum thus suggests that unrearranged **8** (R = COEt) and rearranged **9** (R = COEt) were formed in almost equal amounts. Hydrolysis of the mixture gave pure 2-*exo*-7-*syn*-dihydroxynorbornene (80% yield after sublimation).



This work thus suggests that intermediates obtained by sodium borohydride reduction of oxymercurials from

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88, 3087 (1966); the 7-*anti*-acetoxy compound (**2**) by the method of P. R. Story, *J. Org. Chem.*, **26**, 287 (1961); and 3-acetoxynortricyclene (**3**) by the method of J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Syn.*, **45**, 74 (1965).

(4) *E.g.*, (a) nmr of **1**, J. Paasivirta, *Suomen Kemistilehti*, *B*, **38**, 130 (1965); (b) nmr of **2**, E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964); (c) mass spectra of **1** and **3**, S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *J. Org. Chem.*, **31**, 2738 (1966); (d) mass spectrum of **2** as alcohol, T. Goto, A. Tatematsu, Y. Hata, R. Muneyuki, H. Tanida, and K. Tori, *Tetrahedron*, **22**, 2213 (1966).

(5) H. C. Brown and P. Geoghegan Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

(6) D. J. Pasto and J. A. Gontarz, *ibid.*, **91**, 719 (1969). Dr. Pasto has informed us that the structures reported in his paper were incorrectly assigned and that reinvestigation of his work has shown that his results agree with ours.

(7) J. J. McCullough and P. W. W. Rasmussen, *Chem. Commun.*, 387 (1969).

(8) H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968), discussing unpublished observations of O. R. Khan, I. J. Tyminski, F. L. Pelczar, and R. Y. Tien.

(9) S. J. Cristol and R. W. Gleason, *J. Org. Chem.*, **34**, 1762 (1969); S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **90**, 2832 (1968), and references therein.

(10) S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3969 (1969); G. A. Russell and G. W. Holland, *ibid.*, **91**, 3968 (1969).

(11) We thank Drs. J. Becconsall and A. P. McIvor, Imperial Chemical Industries Ltd., P and P Laboratories, for these spectra.

(12) We thank Mr. R. Spratt of this department for these experiments. Full details will be published later.

(13) In a footnote F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966), have previously suggested that the reduction of *exo-cis*-2-hydroxy-3-chloromercurinorbornane with sodium borodeuteride may not be completely stereospecific. We thank a referee for drawing our attention to this footnote.

(14) W. C. Baird and M. Buza, *J. Org. Chem.*, **33**, 4105 (1968).

both norbornadiene and 7-substituted norbornadienes enter into equilibria of the type **4** $\rightleftarrows$ **5** $\rightleftarrows$ **6** and that the position of equilibrium is influenced by the substituents.

Acknowledgment. We acknowledge helpful discussions with Dr. M. A. McKervey of this department and provision of a grant by the Ministry of Education, Northern Ireland (to G. A. G.). We also thank Dr. D. J. Pasto, University of Notre Dame, for helpful information.

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Electrochemical Generation of Stereoisomeric Vinyl Radicals

Sir:

Products isolated from the electrochemical reduction of alkyl halides are generally indicative of carbanion intermediates.[1] A mechanism often suggested for the over-all process involves initial formation of a free radical, which is reduced to the carbanion in a subsequent step (eq 1). Relatively little unambigous evidence has

$$RX + e^- \longrightarrow X^- + R\cdot \xrightarrow{e^-} R^- \longrightarrow \text{products} \qquad (1)$$

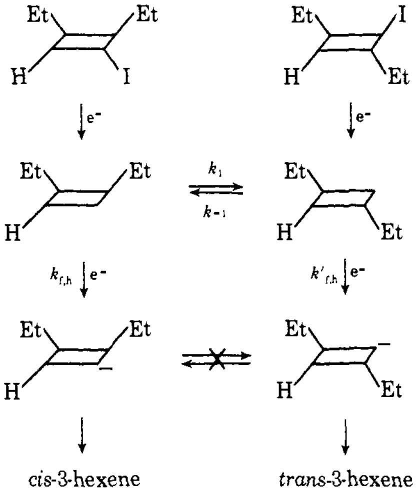
been cited for existence of radical intermediates in these reductions, and at least one investigator[1b] has preferred a concerted two-electron reduction directly to the carbanion. Isolation of alkylmercuric compounds in a few cases[1c,e] would appear, however, to be more consistent with the intermediacy of radicals in such cases. We wish to report direct stereochemical evidence for the existence of vinyl radicals, during the electrochemical reduction of stereoisomeric vinyl iodides, on a time scale sufficiently long to allow partial equilibration before further reduction to the carbanion. Electrochemical reduction of the stereoisomeric 3-iodo-3-hexenes[2] in dimethylformamide (DMF) containing tetraethylammonium bromide (TEAB) affords in each case a mixture of *trans*- and *cis*-3-hexene (total yields 89–92%) (Table I). *trans*-3-Hexene is the predominant product in each case, but it is formed in distinctly higher yields from *trans*-3-iodo-3-hexene than from the *cis*-iodide. Furthermore, electrochemical reduction in the presence of a tenfold excess of phenol (an excellent carbanion trapping agent in DMF)[3] results in exactly the same product ratios as in the absence of phenol. This indicates that isomerization of vinyl carbanions cannot be a significant pathway by which stereochemistry of the starting materials is lost on the way to products. Rates of isomerization of vinyl radicals, on the other hand, are very high[4] and hence the results are consistent with Scheme I involving radical intermediates.

Table I. Stereochemistry of Products from Electrochemical Reduction of the Stereoisomeric 3-Iodo-3-hexenes at 25°[a–d]

Substrate (0.01 *M*)	Phenol concentration, *M*	Relative % products[e] *trans*-3-Hexene	*cis*-3-Hexene
trans-3-Iodo-3-hexene	0	94	6
trans-3-Iodo-3-hexene	0.1	94	6
cis-3-Iodo-3-hexene	0	70	30
cis-3-Iodo-3-hexene	0.1	70	30

[a] The iodides were purified by preparative vpc (1/4 in. by 3 ft column, 20% SF-96 on Fluoropak 80, 110°) immediately before electrochemical experiments. [b] Product analyses were by vpc (1/8 in. by 20 ft column, 25% 1,2,3-tris(β-cyanoethoxy)propane, 30°). [c] Each iodide possesses a single well-developed polarographic wave at −1.35 V *vs.* Ag–AgBr; limiting currents were proportional to the square root of the mercury column height, indicating diffusion control, and values of the diffusion current constant, $I_d = i_d/\text{cm}^{2/3}t^{1/6}$, indicated an over-all two-electron reduction. [d] The stereoisomeric 3-hexenes and 3-iodo-3-hexenes were stable to the reaction conditions. [e] Relative and absolute yields were reproducible to ±2%.

Scheme I



Isolation of partially equilibrated products implies that *isomerization rates are comparable in magnitude to rates of reduction* $(k_{f,h}, k'_{f,h})$ *of the radicals to carbanions.*[5] It is not normally possible to measure high electron-transfer rates under conditions where, as must certainly be true for $k_{f,h}$ and $k'_{f,h}$, mass transport is the rate-limiting step. We wish to point out that when values for the high rates of isomerization of vinyl radicals become available, the data of Table I and similar experiments should allow rather close estimates of the high rates of electron transfer to vinyl radicals. Stereochemical evidence of this sort may be made the basis of a general procedure for indirect measurement of rates of

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(1) (a) R. E. Erickson, R. Annino, M. D. Scanlon, and G. Zon, *J. Amer. Chem. Soc.*, **91**, 1767 (1969); (b) M. R. Rifi, *Tetrahedron Lett.*, 1043 (1969); (c) C. K. Mann, J. L. Webb, and H. M. Walborsky, *ibid.*, 2249 (1966); (d) A. J. Fry and R. H. Moore, *J. Org. Chem.*, **33**, 1283 (1968); (e) J. W. Sease and R. C. Reed, Abstracts, Electrochemical Society Meeting, New York, N. Y., May 1969, No. 134, p 328.

(2) G. Zweifel and R. B. Steele, *J. Amer. Chem. Soc.*, **89**, 5085 (1967).

(3) (a) P. H. Given and M. E. Peover, *J. Chem. Soc.*, 385 (1960); (b) A. J. Fry and M. A. Mitnick, *J. Org. Chem.*, in press; (c) tetraethylammonium bromide is the proton donor, *via* Hoffmann elimination, in the absence of phenol.

(4) (a) R. M. Fantazier and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **88**, 5219 (1966); (b) L. A. Singer and N. P. Kong, *ibid.*, **89**, 6805 (1967).

(5) These results constitute the second unequivocal experimental interception of stereoisomeric vinyl radicals; the first such report[6] utilized a reaction (the isomeric 3-chloro-3-hexenes plus sodium naphthalenide) similar in its gross aspects to the electroreductions reported here. The stereospecific reduction of vinyl halides by dissolving metals[7] may also involve radical intermediates.

(6) G. D. Sargent and M. W. Browne, *J. Amer. Chem. Soc.*, **89**, 2788 (1967).

(7) M. C. Hoff, K. W. Greenlee, and C. E. Boord, *ibid.*, **73**, 3329 (1951).