(19) J. P. Schaeffer and D. S. Weinberg, *J. Org. Chem.*, **30**, 2635 (1965).
(20) H. C. Brown, S. Ikegami, and J. Kawakami, *J. Org. Chem.*, **35**, 3243 (1970).
(21) A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Amer. Chem. Soc.*, **89**, 68 (1967).
(22) We thank Dr. L. M. Leichter for performing this experiment.
(23) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **92**, 1765 (1970); **93**, 5128 (1971).
(24) The following library of crystallographic programs was used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFT and FRIEDEL," USAEC Report IS-2625, Iowa State University Institute for Atomic Research, Ames, Iowa, 1971; W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least Squares Program," USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Tenn., 1965; C. Johnson, "ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," USAEC Report ORNL-3794, Oak Ridge National Laboratory, Tenn., 1965; W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program," USAEC Report ORNL-TM-306, Oak Ridge National Laboratory, Tenn., 1964.
(25) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. IV, Table 2.2A, in press.
(26) See paragraph at end of paper regarding supplementary material.

The Reduction of 2-Substituted 2-Halonorbornanes by Tri-*n*-butyltin Hydride[1]

Joseph San Filippo, Jr.,* and George M. Anderson

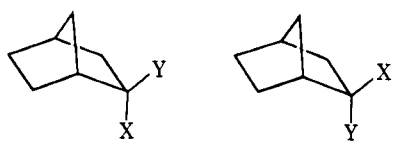
School of Chemistry, Rutgers University, The State University of New Jersey, New Brunswick, New Jersey 08903

Received September 7, 1973

The reduction of a series of 2-substituted 2-halonorbornanes by tri-*n*-butyltin hydride has been carried out. Product analysis revealed that complete loss of stereochemistry had taken place, demonstrating that, unlike similarly substituted vinyl and cyclopropyl radicals, the presence of an electronegative substituent is not sufficient to permit a monosubstituted alkyl radical to retain configurational integrity on the time scale of most nongeminate reactions. The moderate stereoselectivity of the 2-norbornyl radical in atom abstraction reactions is contrasted by the only slight selectivity (k_{exo}/k_{endo} = 1.4) which 2-chloronorbornane exhibits as a halogen donor toward tri-*n*-butyltin radical.

There is considerable spectroscopic evidence in support of the contention[2-4] that the configuration of free radicals is strongly influenced by the difference in electronegativity between the radical center and its substituents. Thus, studies of tri- and difluoromethyl radicals by esr[5] and of trifluoromethyl radicals by infrared spectroscopy[6] and photoionization[7] indicate that these intermediates have a distinctly nonplanar geometry, while the balance of evidence from electronic[8] and electron spin resonance spectra[9] favors a planar structure for the methyl and unsubstituted alkyl radicals. Fluoro- and hydroxymethyl radicals may also persist in a nonplanar configuration.[10] In contrast to the weight of spectroscopic evidence, there exists only scattered chemical information about the nature and, in particular, the configurational integrity of α-substituted alkyl radicals.[11]

We have explored the relationship between substituent electronegativity and the configurational stability of α-substituted alkyl radicals by examining the stereochemistry of the 2-substituted norbornanes obtained from the tri-*n*-butyltin hydride reduction of 2-substituted 2-halonorbornanes of known stereochemistry. In each of the reductions studied the result was that, within our limits of detection, the reduction proceeded with complete *loss* of configuration at the 2 position. A summary of these stereochemical results is presented in Table I.



1 2

X = Cl, Br
Y = F, OCH_3, Cl, CH_3, H

The stereoselectivity of the 2-norbornyl radical in atom-capture reactions has been examined extensively;[15] however, the degree of stereoselectivity involved in atom transfer from a norbornyl ring remains unknown. In an effort to determine the relative selectivity of atom transfer from the 2 position of the norbornyl ring we have examined the competitive reduction of *exo*- and *endo*-2-chloronorbornane using a limiting amount of tri-*n*-butyltin hydride.[16] The observed relative rate constant[17] (k_{exo}/k_{endo} = 1.4 ± 0.1) reveals that only a slight preference exists for exo chlorine abstraction.

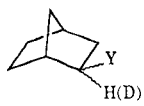
The stereospecific synthesis of 1 and 2 (X = Br; Y = F) was achieved by treating 2-bromonorborn-2-ene and 2-fluoronorborn-2-ene with, respectively, anhydrous hydrogen fluoride and anhydrous hydrogen bromide in methylene chloride at −78°. *exo*-2-Chloro-*endo*-2-methoxynorbornane was prepared by treating 2-methoxynorborn-2-ene with anhydrous hydrogen chloride in pentane at −120°. The absence of CHX (X = F, Cl, Br) resonances in the nmr spectra of these compounds, taken together with their other spectral characteristics and their method of preparation,[18] provides convincing evidence for the assigned stereochemistries. The remaining compounds were synthesized using unexceptional adaptations of literature procedures.

Discussion

Organotin hydrides are among the most active of all hydrogen atom donors known.[19] Thus, if the difference in electronegativity between an alkyl carbon and its α substituents is important in determining the configuration of the carbon radical, it is apparent from these stereochemical results that electronegativity differences alone are not sufficient to permit monosubstituted alkyl radicals to retain configurational integrity on the time scale of most nongeminate reactions.

These stereochemical results do not provide an adequate basis for conclusions concerning the geometry of the intermediate radicals; in particular they do not indicate whether the 2-fluoronorborn-2-yl radical has a planar or a shallow or rapidly inverting pyramidal configuration. It is noteworthy in this regard that the reduction of 2-bromo-2-fluoronorbornane proceeds with loss of stereochemistry

Table I
Stereochemistry of the Mixtures of 2-Substituted Norbornanes Obtained on Reduction of 1 and 2 with Tri-*n*-butyltin Hydride[a]



Registry no.	1	exo:endo	Registry no.	2
49689-61-4	Y = F X = Br	10:90[b,h]	49633-57-0	X = Br Y = F
	Y = OCH_3[d] X = Cl	10:90[c]	49633-58-1	X = Cl Y = OCH_3
21690-95-9	Y = Cl X = Br	4:96[e]	21690-94-8	X = Br Y = Cl
6196-86-7	Y = CH_3 X = Cl	6:94[e]	19138-54-6	X = Cl[f] Y = CH_3
	Y = H X = Cl	16:84[g]		X = Cl Y = H

[a] Reductions were carried out neat (~1:1) at room temperature using AIBN as an initiator. [b] Determined from an examination of the relative areas of ^{19}F nmr signals; estimated accuracy is ±5%. [c] Determined from an examination of the relative areas of the $-OCH_3$ nmr resonances performed in the presence of Eu(fod)$_3$; estimated accuracy is ±5%. [d] Various attempts to prepare this isomer were unsuccessful. [e] Based on glpc analysis; estimated accuracy of these ratios is ±1%. [f] An epimeric mixture of *endo*-2-chloro-*exo*-2-methyl- and *exo*-2-methyl-*endo*-2-chloronorbornane (~20:80) was employed. [g] Taken from ref 22. [h] This ratio remained unchanged when reduction was performed at −78°.

at the 2 position while similar reductions of *gem*-halofluorocyclopropanes occur with complete retention at 130° and predominant retention at 165°.[13] If it is assumed that k_2, the rate constant for hydrogen abstraction from tri-*n*-butyltin hydride by the intermediate α-fluorocyclopropyl radical, is approximately the same as that for abstraction by a primary alkyl radical at 30° and will probably[20] be $2.6 \times 10^8\ M^{-1}\ sec^{-1}$ at 165°, the rate constant for the inversion of the intermediate and presumably pyramidal α-fluorocyclopropyl radical is given[20] by

$$[Bu_3SnH]\frac{[R'F]}{[RF]}k_2 \approx 3 \times 10^7\ sec^{-1}$$

at 165°. Here, R and R′ represent the configurationally unaltered and isomerized carbon skeleton, respectively.

The intermediacy of a pyramidal radical in the reduction of 2-bromo-2-fluoronorbornane requires that the rate of inversion must be at least 10^2 faster than the rate of hydrogen atom transfer in order to be consistent with the observed stereochemical results. Hence

$$k_{inversion}[R\cdot] > 10^2\ k_2\ [R\cdot][Bu_3SnH]$$

In these reactions the product stereochemistry showed no dependence on the extent of reaction and at 1 half-life $[Bu_3SnH] \approx 1\ M$; thus, if inversion is occurring, $k_{inversion}$ must be greater than $5 \times 10^8\ sec^{-1}$ at 30°. The difference between the rate of inversion of an α-fluorocyclopropyl radical and that of a 2-fluoronorborn-2-yl radical is seen to be considerable in view of the substantial difference in reaction temperatures employed.

Stereoselectivity in the reactions of the norbornyl radical is well known: regardless of the position of equilibrium between endo and exo products, there is a preference for atom capture from the exo side. Several factors, including steric effects, polar contributions, and the nature of the donor molecule, appear to control the degree of selectivity.[15] Although the stereochemical results in Table I are consistent with the direction and range of magnitude of exo/endo selectivities arising from the torsional interaction[21] of the bridgehead hydrogen and the substituent on the adjacent 2 carbon, these results cannot be interpreted as favoring one particular geometry for the 2-fluoronorborn-2-yl radical, since the transition state for hydrogen abstraction and the point of maximum torsional barrier do not necessarily coincide.

An appreciable body of chemical and physical evidence suggests that the hybridization of a carbon radical center strongly influences the configurational stability of the radical. This fact is reflected in the observed order of configurational stability of radical centers, *i.e.*, vinyl > cyclopropyl > alkyl. The influence which substituent electronegativity has on the geometry of carbon radicals can be qualitatively rationalized in this light, since to a first approximation[22] the more electronegative a substituent is the more diminished will be the s character of the carbon valence electrons involved in the carbon–substituent bond.[3,4] It follows, therefore, that a planar, sp^2-hybridized alkyl radical center will tend to adopt the pyramidal geometry characteristic of sp^3 hybridization as the electronegativity of the α substituent(s) increases. Similarly, bent sp^2-hybridized vinyl radicals[23] could be expected to have, and in fact do reveal, increased preference for sp^2 hybridization, *i.e.*, retention of configuration, as the electronegativity of the α substituent is increased.[11] Viewed in this manner, it is reasonable to expect that the enhanced configurational stability which an electronegative substituent imparts to a vinyl radical is greater than that imparted by the same substituent to an alkyl radical center, since a greater change in fractional s character is required during the inversion of a vinyl radical center ($sp^2 \rightarrow sp \rightarrow sp^2$) than would be experienced during the inversion of a pyramidal alkyl radical ($sp^3 \rightarrow sp^2 \rightarrow sp^3$).

Experimental Section[24]

2,2-Dichloronorbornane, bp 58–61° (11 Torr) [lit.[25] bp 65–68° (12 Torr)], was obtained from norcamphor and phosphorous pentachloride in 75% yield following the procedure of Bixler and Niemann.[25]

2-Chloronorborn-2-ene was isolated in 86% yield following the procedure of McDonald and Steppel,[26] bp 54–55° (28 Torr) [lit.[26] bp 72–75° (69 Torr)].

2-Bromonorborn-2-ene was synthesized in 25% yield, bp 50–51° (13 Torr) [lit.[27] bp 57–58° (16 Torr)], following the procedure of Kwart and Kaplan with the modifications described by LeBel.[28]

***exo*-2-Bromo-*endo*-2-chloronorbornane and *exo*-2-chloro-*endo*-2-bromonorbornane,** bp 41–42 (1.0 Torr) and 83–85° (9.0 Torr), respectively [lit.[29] bp 42–49° (0.06 Torr)], were prepared by treating 2-chloronorborn-2-ene and 2-bromonorborn-2-ene with anhydrous hydrogen bromide and hydrogen chloride, respectively, as described by Fry.[29]

***endo*-2-Chloro-*exo*-2-fluoronorbornane.** A solution of 2-chloronorborn-2-ene (7.0 g, 54 mmol) in 50 ml of methylene chlo-

ride was placed in a 250-ml polyethylene bottle equipped with a Teflon-coated stirring bar. Under a nitrogen atmosphere the vessel was chilled to −78°. Anhydrous hydrogen fluoride (~20 ml) was condensed into the stirred reaction mixture. After 10 min the organic layer was removed through a polyethylene cannula and neutralized by the addition of a saturated aqueous solution of potassium carbonate in ice water. The organic layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. Distillation yielded 5.1 g (63%) of *endo*-2-chloro-*exo*-2-fluoronorbornane: bp 62–65° (30 Torr); ^{1}H nmr (CCl_4) δ 3.0–1.0 (complex multiplet); ir (CS_2) 2950 (vs), 1310 (s), 1145 (s), 1090 (vs), 1020 (vs), 910 (w), 840 (s), 800 (m), 780 cm^{-1} (s).

Anal. Calcd for $C_7H_{10}ClF$: C, 56.57; H, 6.78; Cl 23.86; F, 12.79. Found: C, 56.37; H, 6.73; Cl, 23.66; F, 12.96.

***endo*-2-Bromo-*exo*-2-fluoronorbornane** was prepared from 2-bromonorborn-2-ene in 90% yield by a procedure analogous to that described for the preparation of *endo*-2-chloro-*exo*-2-fluoronorbornane: bp 62–64° (15 Torr); ^{1}H nmr (CCl_4) δ 3.0–1.0 (complex multiplet); ir (CS_2) 2950 (vs), 1310 (s), 1195 (s), 1090 (vs), 905 (m), 865 (vs), 835 (s), 800 cm^{-1} (m).

Anal. Calcd for $C_7H_{10}BrF$: C, 43.55; H, 5.22; Br, 41.39; F, 9.84. Found: C, 43.63; H, 5.28; Br, 41.34; F, 9.70.

2,2-Difluoronorbornane. A solution of 2-norbornanone (110 g, 1.00 mol) in methylene chloride (450 ml) was added dropwise under a nitrogen atmosphere to a mechanically stirred solution of molybdenum hexafluoride[30] (210 g, 1.00 mol) in methylene chloride (1 l.). Following completion of addition, during which time a reaction temperature of −15° was maintained, the resulting mixture was allowed to warm to room temperature and stirring was maintained for an additional 3 hr before the solution was poured into 600 ml of ice water. The organic layer was separated, filtered through diatomaceous earth, and dried over magnesium sulfate. Distillation of this solution yielded 2,2-difluoronorbornane (60 g, 45%): bp 120–124°; mp 64–66°; ^{1}H nmr (CCl_4) δ 3.0–1.0 (complex multiplet); ir (CS_2) 2990 (s), 1350 (vs), 1060 (s), 985 (vs), 900 (s), 850 (m), 820 (w), 760 (m), 690 cm^{-1} (w).

Anal. Calcd for $C_7H_{10}F_2$: C, 63.60; H, 7.57; F, 28.83. Found: C, 63.21; H, 7.42; F, 28.90.

2-Fluoronorborn-2-ene. A solution of 2,2-difluoronorbornane (32.5 g, 250 mmol) in 75 ml of cyclohexanol was added to a solution of potassium (20.0 g, 500 mmol) dissolved in 400 ml of cyclohexanol. After refluxing under nitrogen for 14 days, the crude product (bp 85–115°) was distilled directly from the reaction mixture. Refractionation on a 90-cm Teflon spinning band yielded 10 g (39%) of 2-fluoronorborn-2-ene: bp 94–98°; ^{1}H nmr (CCl_4) δ 4.97 (1 H, d, J = 3.9 Hz, FC=CH), 2.77 (2 H, bridgehead), 2.0–0.8 (6 H, complex multiplets); ^{19}F nmr (neat) δ (downfield relative to C_4F_8) 3.70; ir (CS_2) 2970 (vs), 1640 (vs), 1340 (vs), 1105 (m), 960 (w), 915 (w), 865 (m), 845 (w), 800 (vs), 760 (m), 710 cm^{-1} (m).

Anal. Calcd for C_7H_9F: C, 75.05; H, 8.05; F, 16.10. Found: C, 74.85; H, 7.60; F, 16.08.

***exo*-2-Bromo-*endo*-2-fluoronorborane** was prepared by treating 2-fluoronorborn-2-ene (1.8 g, 16 mmol) with anhydrous hydrogen bromide similar to the procedure outlined for the preparation of *endo*-2-chloro-*exo*-2-fluoronorbornane: yield 1.8 g (58%); bp 55–59° (14 Torr); ^{1}H nmr (CCl_4) δ 3.0–1.0 (complex multiplet); ir $(CS)_2$ 2910 (s), 1310 (m), 1200 (w), 1155 (s), 1080 (s), 1040 (vs), 940 (vs), 845 (w), 815 (vs), 765 (s), 745 cm^{-1} (s).

Anal. Calcd for $C_7H_{10}BrF$: C, 43.55; H, 5.22; Br, 41.39; F, 9.84. Found: C, 43.60; H, 5.31; Br, 41.44; F, 9.81.

***exo*-2-Chloro-*endo*-2-fluoronorbornane** was prepared in 66% yield from 2-fluoronorborn-2-ene (2.16 g, 19 mmol) and anhydrous hydrogen chloride, by a procedure similar to that described for the preparation of *endo*-2-chloro-*exo*-2-fluoronorbornane: bp 66–69° (40 Torr); ^{1}H nmr (CCl_4) δ 2.8–1.0 (complex multiplet); ir (CS_2) 2950 (s), 1315 (s), 1210 (m), 1160 (s), 1120 (w), 1090 (s), 1050 (vs), 950 (vs), 850 (m), 825 (vs), 770 (m), 750 cm^{-1} (m).

Anal. Calcd for $C_7H_{10}ClF$: C, 56.57; H, 6.78; Cl, 23.86; F, 12.79. Found: C, 56.77; H, 6.91; Cl, 23.74; F, 12.57.

2-Methylnorborn-2-ene was prepared by the reaction of methyllithium with 2-chloronorborn-2-ene.[31] A solution of methyllithium in ether (24 ml, 40 mmol) was added to a stirred solution of 2-chloronorborn-2-ene (5.0 g, 39 mmol) in 20 ml of ether. The mixture was stirred at room temperature under nitrogen for 8 days before it was carefully hydrolyzed with a saturated solution of aqueous ammonium chloride. The organic layer was washed with water and dried over magnesium sulfate. Careful fractionation on a 90-cm Teflon spinning band yielded 2-methylnorborn-2-ene (2.0 g, 50%): bp 115–116° (lit.[32] bp 104–125°); nmr (CCl_4) δ 5.47 (1 H, C=CH), 2.68 (2 H, br, bridgehead), 1.73 (3 H, s, CH_3), 1.7–0.7 (multiplet); ir (CS_2) 2960 (vs), 1440 (s), 1310 (m), 1275 (m), 1120 (m), 1015 (w), 990 (m), 870 (s), 800 (s), 775 cm^{-1} (m).

***exo*-2-Chloro-*endo*-2-methylnorbornane.** A solution of 2-methylnorborn-2-ene (2.20 g, 20 mmol) in methylene chloride (40 ml) was chilled to −78° under an atmosphere of dry nitrogen. Anhydrous hydrogen chloride was bubbled through the stirred solution for 3 min. The solution was purged with nitrogen for 15 min while warming to room temperature, then treated with a saturated solution (20 ml) of aqueous potassium carbonate. The organic layer was separated, washed with water, and dried over magnesium sulfate. Distillation yielded 1.50 g (51%) of *exo*-2-chloro-*endo*-2-methylnorbornane: bp 32–34° (4.4 Torr); nmr (CCl_4) δ 2.40 (2 H, br, bridgehead), 1.65 (3 H, s, CH_3), 2.0–0.9 (8 H, complex multiplet); ir (CS_2) 2900 (vs), 1445 (s), 1230 (w), 1105 (s), 1005 (m), 980 (w), 835 (w), 800 (m), 765 (w), 730 cm^{-1} (m).

Anal. Calcd for $C_8H_{13}Cl$: C, 66.05; H, 9.00; Cl, 24.55. Found: C, 65.60; H, 8.53; Cl, 24.37.

2-Chloro-2-methylnorbornane. *endo*-2-Hydroxy-*exo*-2-methylnorbornane[33] (10.0 g, 79.5 mmol) was dissolved in 1,2-dimethoxyethane (100 ml, freshly distilled from sodium benzophenone ketyl) containing 1.0 g of potassium carbonate. To this solution was added, dropwise with cooling to −10°, 10 ml of freshly distilled thionyl chloride. The mixture was allowed to warm to room temperature, then stirred overnight before filtering and concentrating under reduced pressure. Distillation of the concentrate yielded 2-chloro-2-methylnorbornane (6.5 g, 46%), bp 33–34° (4.4 Torr). Glpc analysis on a 50 ft × 0.125 in. Teflon column of 20% Carbowax M on silynated Chromosorb W indicated an epimeric mixture consisting of approximately 20% *endo*-2-chloro-*exo*-2-methylnorbornane and 80% *exo*-2-chloro-*endo*-methylnorbornane. Examination of the nmr revealed no -CHCl resonance. Because of its instability this mixture was used without further purification.

2,2-Dimethoxynorbornane. 2-Norbornanone (25.0 g, 228 mmol), trimethyl orthoformate (35 g), and *p*-toluenesulfonic acid (0.5 g) were placed in a 250-ml flask containing 100 ml of methanol and the mixture was refluxed for 12 hr. After cooling to room temperature, a solution of 1 g of sodium dissolved in 10 ml of methanol was added and the methanol and trimethyl orthoformate were removed by distillation. Distillation of the concentrate at reduced pressure yielded 2,2-dimethoxynorbornane (33 g, 90%): bp 65–68° (15 Torr) [lit.[34] bp 73° (20 Torr)]; nmr (CCl_4) δ 3.08 (6 H, s, $-OCH_3$), 2.28 (br, bridgehead), 2.0–0.9 (8 H, complex multiplet); ir (neat) 2990 (s), 1335 (m), 1190 (m), 1175 (m), 1140 (s), 1110 (vs), 1035 (m), 970 (m), 875 (w), 850 cm^{-1} (w).

2-Methoxynorborn-2-ene. A mixture of 2,2-dimethoxynorbornane (30 g, 193 mmol) and ammonium dihydrogen phosphate (1.5 g) was placed in a 100-ml flask equipped with a 6-in. fractionating column and condenser. The flask was immersed in oil bath which was gradually heated to 230°. The fraction boiling over the range 163–174° was collected. Careful refractionation on a 90-cm Teflon spinning band from a pot containing 0.5 g of potassium carbonate yielded 1.3 g (5.5%) of 2-methoxynorborn-2-ene: bp 153–155° [lit.[35] bp 77–79° (75 Torr)]; nmr (CCl_4) δ 4.47 (1 H, d, C=CH), 3.43 (3, H, s, $-OCH_3$), 2.78 (2 H, br, bridgehead), 2.0–0.9 (6 H, complex multiplet); ir (neat) 2970 (vs), 1610 (vs), 1345 (s), 1275 (m), 1240 (vs), 1145 (m), 1020 (s), 870 (w), 720 cm^{-1} (m).

***exo*-2-Chloro-*endo*-2-methoxynorbornane.** A solution of 2-methoxynorborn-2-ene (4.0 g, 32 mmol) in pentane (100 ml) was cooled under an atmosphere of nitrogen to −120°. Anhydrous hydrogen chloride was bubbled through the stirred solution for 2–3 min. While warming to room temperature the mixture was purged with dry nitrogen. The product, which was too unstable to permit distillation or elemental analysis, was obtained by removing the pentane at reduced pressure at 0°: ir (neat) 2990 (vs), 1775 (m) (2-norbornanone impurity), 1450 (m), 1325 (s), 1205 (s), 1000 (m), 945 (m), 850 (w), 800 (s), 730 cm^{-1} (s); nmr (CCl_4) δ 3.40 (3 H, s, OCH_3), 3.72 (2 H, br, bridgehead), 2.0–0.9 (~8 H, complex multiplet).

2-Methylnorbornane. A 90:10 endo:exo mixture of 2-methylnorbornane was prepared by hydrogenation of 2-methylnorborn-2-ene over platinum oxide.[36]

***exo*-2-Methoxynorbornane** was prepared by the acid-catalyzed addition of methanol to norbornene,[34] bp 153–154° (lit.[37] bp 151–152°).

***endo*-2-Methoxynorbornane** was obtained by treating *endo*-2-hydroxynorbornane with sodium hydride and methyl iodide in ether as described by Traylor and Perrin,[34] bp 153–154° (lit.[37] bp 152–153°).

Tri-*n*-butyltin hydride was prepared by a modification[38] of the literature procedure.[39]

Procedures for Reductions. Similar procedures were used to carry out the reduction of all compounds. Representative procedures are given below.

Reduction of *exo*-Bromo-*endo*-2-chloronorbornane. *exo*-2-Bromo-*endo*-2-chloronorbornane (0.114 g, 5.44 mmol) was placed in a 20-nm (5-mm o.d.) test tube which was then capped with a rubber septum and flushed with nitrogen before cooling to 0° and adding 0.174 g (5.92 mmol) of the tri-*n*-butyltin hydride by syringe. After the reaction mixture was allowed to stand with warming to room temperature for 2 hr with occasional swirling, carbon tetrachloride (0.5 ml) was added and the reduction products were isolated by total collection from preparative glpc using a 6 ft × 0.25 in. aluminum column of 20% SE-30 on Chromosorb W. Detailed analysis was carried out by reinjection of the collected material onto a 50 ft × 0.125 in. aluminum column of Zonyl E-7. Glpc analysis of the crude reaction mixture indicated <5% unreacted starting halide.

Reduction of *exo*-2-Bromo-*endo*-2-fluoronorbornane. Into a capped, nitrogen-flushed nmr tube cooled to 0° was injected *exo*-2-bromo-*endo*-2-fluoronorbornane (0.103 g, 5.35 mmol) and tri-*n*-butyltin hydride (0.178 g, 6.05 mmol). The tube was shaken periodically over a 2-hr period while allowing it to warm to room temperature. The reduction product ratios were determined directly by planimeter integration of the characteristic ^{19}F nmr resonance. The ^{19}F spectrum provided no evidence (<5%) of any unreacted starting halide.

Reduction of *exo*-2-Chloro-*endo*-2-methylnorbornane. A mixture of *exo*-2-chloro-*endo*-2-methylnorbornane (0.077 g, 0.53 mmol) and AIBN (~1 mg) was placed in a test tube which was then capped with a rubber septum and flushed with nitrogen before injecting by syringe 0.192 g (0.654 mmol) of tri-*n*-butyltin hydride at 0°. The reaction mixture was subsequently photolyzed at ~10° for 2 hr with a short-wavelength uv hand scanner. After 0.5 ml of carbon tetrachloride was added to destroy any excess tri-*n*-butyltin hydride, the reduction products were collected by preparative glpc from a 6 ft × 0.25 in. SE-30 on Chromosorb W column. Analytical analysis of product ratios was achieved by reinjection onto a 24 ft × 0.125 in., Hi-Pak SE-30 column. Product yield as determined in an independent experiment by glpc using an internal standard was approximately 75%.

Reduction of *exo*-2-Chloro-*endo*-2-methoxynorbornane. Into a capped, nitrogen-flushed nmr tube which had been cooled to 0° was injected *exo*-2-chloro-*endo*-2-methoxynorbornane (0.200 g, 1.24 mmol) and tri-*n*-butyltin hydride (0.390 g, 1.33 mmol). While at 0° the tube was shaken occasionally over a 2-hr period before 0.1 ml of carbon tetrachloride was added. A similar experiment carried out with an internal standard indicated a product yield of approximately 60%. The product isomers were collected by preparative glpc and the ratio of *exo*- to *endo*-2-methoxynorbornane was determined by integrating the relative $-OCH_3$ peak areas in the nmr spectrum. The separation of the two resonances was achieved by the addition of the chemical shift reagent [tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)europium (III)].

***endo*-2-Fluoronorbornane** was prepared by hydrogenating 2-fluoronorborn-2-ene (1.5 g) in diethyl ether (10 ml) over platinum oxide (40 mg) under 80 psi of hydrogen for 5 min. Following filtration the ether was removed under reduced pressure at room temperature. The resulting product mixture contained a 90:10 epimeric mixture of *endo*- to *exo*-2-fluoronorbornane as determined by ^{19}F nmr. Both epimers were observed to undergo substantial decomposition when subjected to glpc analysis.

Configurational Stability of *exo*-2-Bromo-*endo*-2-fluoronorbornane and *endo*-2-Fluoronorbornane in the Presence of Tri-*n*-butyltin Bromide. The configurational stability of *exo*-2-bromo-*endo*-2-fluoronorbornane and *endo*-2-fluoronorbornane to reaction conditions was determined in separate experiments by mixing equal quantities of reagents in an nmr tube and allowing the mixture to stand for 2 hr. Examination of the ^{19}F nmr spectra revealed that within the limits of detection (±5%) no isomerism had taken place.

Acknowledgment. The experimental assistance of Mr. Alan Sowinski is gratefully acknowledged.

Registry No. *endo*-2-Chloro-*exo*-2-fluoronorbornane, 49633-61-6; 2-chloronorborn-2-ene, 694-93-9; 2-bromonorborn-2-ene, 694-90-6; 2,2-difluoronorbornane, 22847-05-8; 2-norbornanone, 497-38-1; 2-fluoronorborn-2-ene, 49633-63-8; *exo*-2-chloro-*endo*-2-fluoronorbornane, 49633-64-9; 2-methylnorborn-2-ene, 694-92-8; *endo*-2-hydroxy-*exo*-2-methylnorbornane, 3212-16-6; 2,2-dimethoxynorbornane, 10395-51-4; 2-methoxynorborn-2-ene, 17190-90-8.

Table II
^{19}F Chemical Shifts of Some 2-Substituted 2-Fluoronorbornanes[a]

X	F_{exo}	F_{endo}
H	+6.55[b]	+14.10[b]
F	+86.2[c]	+109.3[c]
Cl	+21.05	−7.05[b]
Br	+19.60	+25.80

[a] Unless otherwise indicated chemical shifts are in parts per million relative to $CFCl_3$ and are considered accurate to ±0.05 ppm. Upfield chemical shifts are denoted as (+). [b] Chemical shift relative to C_4F_8. [c] Taken from J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7107 (1970).

References and Notes

(1) Supported by the Research Corporation, Uniroyal Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.
(2) L. Pauling, *J. Chem. Phys.*, **51**, 2767 (1969).
(3) A. D. Walsh, *J. Chem. Soc.*, 2306 (1953); A. D. Walsh, *Discuss. Faraday Soc.*, **2**, 18 (1947).
(4) H. A. Bent, *Can. J. Chem.*, **38**, 1235 (1960).
(5) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).
(6) G. A. Carlson and G. C. Pimental, *J. Chem. Phys.*, **44**, 4053 (1966); D. E. Milligan, M. E. Jacox, and J. J. Comeford, *ibid.*, **44**, 4058 (1966).
(7) C. Lifshitz and W. A. Chupka, *J. Chem. Phys.*, **47**, 3439 (1967).
(8) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956); G. Herzberg, *Annu. Rev. Phys. Chem.*, **9**, 357 (1958); G. Herzberg, *Proc. Chem. Soc. (London)*, 116 (1959).
(9) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
(10) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).
(11) Chemical studies of 1-substituted vinyl radicals indicate that the configurational stability of these radicals is strongly dependent on the nature of this substituent and that the difference in rates of inversion vary according to the series.[12] A similar order, *viz.*, $CH_3 > Cl > OCH_3$ and $CH_3 > Cl > F$, has been observed in the rates of inversion of α-substituted cyclopropyl radicals.[13,14]
(12) D. K. Wedegaertner, R. M. Kopchik, and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **93**, 6890 (1971), and references cited therein.
(13) T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970).
(14) L. J. Altman and R. C. Baldwin, *Tetrahedron Lett.*, 2531 (1971).
(15) P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, *Accounts Chem. Res.*, **3**, 177 (1970), and references cited therein.
(16) Kuivila and coworkers have carried out a detailed investigation of the relative rates of reduction of a variety of organic halides by organotin hydrides: L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).
(17) Calculated by the method of C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).
(18) H. L. Goering and J. V. Clevenger, *J. Amer. Chem. Soc.*, **94**, 1010 (1972); J. K. Stille and R. D. Hughes, *J. Org. Chem.*, **36**, 340 (1971).
(19) Typically, the second-order rate constant for hydrogen abstraction from tri-*n*-butyltin hydride by a number of alkyl radicals is 5×10^6 at 30°.[20]
(20) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).
(21) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699, 701 (1967).
(22) In particular, substituent lone pair–odd electron effects (*i.e.*, p–p π bonding) are neglected.
(23) For a review of the stereochemistry of vinyl radicals, see O. Simamura, *Top. in Stereochem.*, **4**, 1 (1969).
(24) All melting points and boiling points are uncorrected. Infrared spectra were determined within sodium chloride cells on a Perkin-Elmer Model 225 grating spectrophotometer. Nmr (^1H and ^{19}F) spectra were determined with a Varian T-60 nmr spectrometer at 60 and 56.4 MHz, respectively. ^1H chemical shifts are reported in parts per million relative to internal tetramethylsilane. The internal standard for ^{19}F chemical shifts is as noted. All coupling constants are in hertz. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7E mass spectrometer. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Samples for spectral and elemental analyses were purified on a Hewlett-Packard Model 700 thermal conductivity gas chromatograph. Analytical glpc analyses were performed on a Hewlett-Packard Model 5750 flame ionization instrument. Absolute yields of products were calculated from peak areas using internal standard techniques with response factors obtained from authentic samples. For convenience of comparison, ^{19}F chemical shift data are summarized in Table II.
(25) R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958).
(26) R. N. McDonald and R. N. Steppel, *J. Amer. Chem. Soc.*, **92**, 5664 (1970).
(27) H. Kwart and W. G. Kaplan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).
(28) N. A. LeBel, *J. Amer. Chem. Soc.*, **82**, 623 (1960).

(29) A. J. Fry, *et al.*, *J. Org. Chem.*, **34**, 4195 (1969).
(30) Molybdenum hexafluoride was obtained commercially from PCR, Inc., and used directly.
(31) P. G. Gassman, J. P. Andrews, Jr., and D. S. Patton, *Chem. Comm.*, 437 (1969).
(32) H. E. Fritz and K. E. Atkins, U. S. Patent 3,240,828 (1966); *Chem. Abstr.*, **64**, 17451*d* (1966).
(33) R. R. Sauers, *J. Amer. Chem. Soc.*, **81**, 4873 (1959).
(34) T. G. Traylor and C. L. Perrin, *J. Amer. Chem. Soc.*, **88**, 4934 (1966).
(35) J. S. McConaghy, Jr., and J. J. Bloomfield, *J. Org. Chem.*, **33**, 3425 (1968).
(36) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).
(37) W. Hückel and O. Vogt, *Justus Liebigs Ann. Chem.*, **695**, 16 (1966).
(38) G. M. Whitesides and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 6611 (1970).
(39) K. Kuhlein, W. P. Neumann, and H. Mohring, *Angew. Chem., Int. Ed. Engl.*, **7**, 455 (1968).

The Reaction of Vinylferrocenes with Tetracyanoethylene

Kenneth R. Berger, Edward R. Biehl, and Perry C. Reeves*

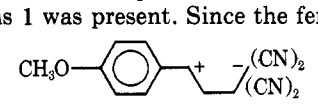
Department of Chemistry, Southern Methodist University, Dallas, Texas 75275

Received July 16, 1973

Tetracyanoethylene has been found to react readily with several substituted vinylferrocenes to produce cyclobutane derivatives. This facile reaction appears to be a two-step reaction involving the development of a charged center which can be effectively stabilized by the ferrocene system. Reaction of the cis and trans isomers of 1-ferrocenylpropene with tetracyanoethylene yields a single product. This indicates that the dipolar intermediate is sufficiently stable to allow rotation to occur prior to the product-forming step.

Tetracyanoethylene (TCNE) is one of the most reactive dienophiles known in Diels–Alder reactions.[1] However, Stewart[2] noticed that 4-methyl-1,3-pentadiene reacted with TCNE to produce not only a cyclohexene product but also a cyclobutane product. McKusick[3] and coworkers observed that a diene system was not essential for these reactions because the cyclobutane products were also readily formed by cycloaddition of TCNE to electron-rich alkenes such as methyl vinyl ether and *p*-methoxystyrene. These reactions are remarkable in that the products, obtained in high yields, are rapidly formed in tetrahydrofuran solution at 0–30°.

Woodward–Hofmann rules suggest that a concerted [2_s + 2_s] addition is symmetry forbidden; however, the ease with which these reactions proceed is reminiscent of the concerted [2 + 4] symmetry allowed Diels–Alder additions. McKusick[3] found the reaction rates of these [2_s + 2_s] reactions to be very sensitive to changes in solvent polarity, and this led him to postulate that a charged intermediate such as **1** was present. Since the ferrocene system

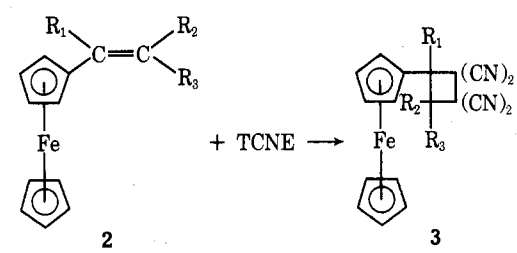


1

is known to be strongly electron releasing[4] and its ability to stabilize adjacent carbonium ions has been established,[5] it appeared that vinylferrocenes should be electron-rich alkenes which would react readily with TCNE.

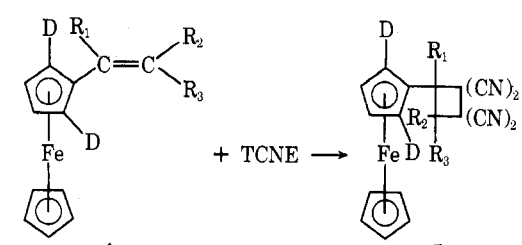
Results and Discussion

A series of substituted vinylferrocenes was prepared and allowed to react with TCNE in tetrahydrofuran solution. The parent system (**2a**) reacted quite readily (room temperature, 2 hr) to produce a yellow crystalline 1:1 adduct in 71% yield. The other alkenes reacted similarly (Table I). The nmr spectra (Table II) were consistent with a formulation such as **3**. The nmr spectra of **3b** and **3c** exhibited a one-proton multiplet absorption downfield from the singlet absorption of the unsubstituted cyclopentadienyl ring of the ferrocene system. In order to assign this absorption, the ring-deuterated alkenes **4a** and **4b** were prepared and treated with TCNE. The adducts and their nondeuterated counterparts had identical decomposition points. In each case, deuteration caused disappearance of the one-proton absorption as well as a decrease in the τ 5.59 multiplet. This indicated that the structure of the adducts was such that the α ring protons of the ferrocene system were in different magnetic environments. A molecular model of the compounds confirmed this postulate. These findings suggested that the absorption of R_1 was obscured by the ferrocene system when R_1 = H and therefore only approximate values for this proton could be assigned.



2 **3**

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = CH_3$; $R_2 = R_3 = H$
c, $R_1 = H$; $R_2 = R_3 = CH_3$
d, $R_1 = R_3 = H$; $R_2 = CH_3$
e, $R_1 = R_2 = H$; $R_3 = CH_3$



4 **5**

a, $R_1 = CH_3$; $R_2 = R_3 = H$
b, $R_1 = H$; $R_2 = R_3 = CH_3$

In order to examine the mechanism by which these reactions occurred, the reactions of the cis and trans isomers of 1-ferrocenylpropene (**2d** and **2e**) with TCNE were studied; however, the pure isomers had not been described previously. Their syntheses were accomplished by modifications of the Wittig reaction. Reaction of ethyltriphenylphosphonium bromide, methyllithium, and formylferrocene according to the Schlosser–Christmann procedure[6] produced the trans isomer (J = 15 Hz). The "salt-free" Wittig reaction[7] of ethyltriphenylphosphorane and formylferrocene yielded the cis isomer (J = 11.5 Hz). Nmr