Silane Reductions in Acidic Media. 10. Ionic Hydrogenation of Cycloalkenes. Stereoselectivity and Mechanism[1a]

Michael P. Doyle*[1b] and Charles C. McOsker[1c]

Department of Chemistry, Hope College, Holland, Michigan 49423

Received June 27, 1977

Stereochemical results from reductions of $\Delta^{9(10)}$-octalin and 4-*tert*-butylmethylenecyclohexane in trifluoroacetic acid by sterically disparate organosilanes, ranging from *n*-butylsilane to tri-*tert*-butylsilane, are reported. Addition of trifluoroacetic acid to the carbon–carbon double bond of these alkenes results in the formation of an equilibrium mixture of isomeric tertiary trifluoroacetates and precedes organosilane reduction. Results are described which indicate that hydride transfer to a symmetrically solvated carbenium ion occurs in ionic hydrogenations of alkenes. Steric factors govern the stereochemical outcome of silane reductions of symmetrically solvated carbenium ions; both the number of substituents bonded to silicon and the steric bulk of these substituents are important determinants of stereoselectivity.

Ionic hydrogenation of alkenes by organosilanes in acidic media is reported to occur in two stages: proton addition followed by hydride transfer to the intermediate carbenium ion (eq 1).[2] Alcohols are likewise reduced by organosilanes

$$R_2C{=}CR_2 + H^+ \longrightarrow R_2\overset{+}{C}{-}\underset{H}{CR_2} \xrightarrow{R'_3SiH} \underset{H}{\overset{|}{R_2C}}{-}\underset{H}{\overset{|}{CR_2}} \quad (1)$$

through an ionic mechanism.[3] The effectiveness of hydride transfer from organosilanes is intimately associated with the electrophilic character of the cationic intermediate so that in protic acid media only carbenium ions generated from tri- or tetrasubstituted ethylenes and tertiary or certain benzylic alcohols abstract hydride from organosilanes.[2-5] Despite this limitation,[6] however, there continues to be considerable interest in the uses of organosilanes as selective reducing agents[2,4,7] and as efficient scavengers for carbenium ions.[8]

The stereoselectivity in organosilane reductions of alkenes and alcohols has been studied in limited detail.[2,3c,9] Carey and Tremper have reported that the ratio of isomeric hydrocarbons from the reduction of 4-*tert*-butyl-1-phenylcyclohexanols is independent of the geometry of the reactant alcohol and, because the trans-substituted cycloalkane is the dominant reduction product in reactions with organosilanes that possess different steric requirements, propose that the stereoselectivity of hydride transfer is determined by product development control.[3c] However, recent developments in the stereochemical understanding of carbocations under solvolytic conditions[8a,10] and of organosilane reductions in acidic media[1a,7d,11] suggest that the primary determinant of stereoselectivity in reductions of alkenes and alcohols by organosilanes may be more complex than previously imagined. Indeed, Fort and co-workers have found that the triethylsilane reduction of *cis*- or *trans*-9-decalol occurs with nearly complete retention of configuration in the formation of the isomeric decalins.[8a] The present study was undertaken to thoroughly examine the stepwise mechanism for ionic hydrogenation and to delineate those factors that influence stereoselectivity in organosilane reductions that occur in acidic media.

Results and Discussion

Representative model compounds for tri- and tetrasubstituted ethylenes, $\Delta^{9(10)}$-octalin and 4-*tert*-butylmethylenecyclohexane, were chosen for this investigation. Treatment of these alkenes in trifluoroacetic acid at 25 °C with a series of organosilanes that have widely different steric requirements produced the corresponding cycloalkanes in isolated yields of 80–95% (from $\Delta^{9(10)}$-octalin) and 60–85% (from 4-*tert*-butylmethylenecyclohexane). The relative yields of the less stable cycloalkane isomers and their corresponding isomeric ratios are presented in Table I. Clearly, steric factors are important determinants of the stereoselectivity in organosilane reductions.

The compound that is actually reduced in these reactions is unclear from previous studies of organosilane reductions. Kursanov and co-workers have reported, for example, that 1-methylcyclohexene is reduced in methylene chloride solutions of trifluoroacetic acid by triethylsilane at a rate that is from two to five times slower than is the addition product, 1-methylcyclohexyl trifluoroacetate.[7a] The implication from this and related experiments[12] is that simultaneous reduction of the alkene and trifluoroacetate occur, conceivably through the same or distinctly different[8a,10] carbenium ion intermediates. However, trifluoroacetic acid undergoes rapid addition to the carbon–carbon double bonds of both $\Delta^{9(10)}$-octalin and 4-*tert*-butylmethylenecyclohexane under the reaction conditions that we have employed; complete addition occurs within 5 min after mixing the olefin and trifluoroacetic acid. Reduction by triethylsilane, the most reactive organosilane employed in this study, is considerably slower: the time required for 50% conversion to cycloalkane is approximately 20 min with $\Delta^{9(10)}$-octalin and nearly 90 min with 4-*tert*-butylmethylenecyclohexane. With the exception of triethylsilane, reductions by the organosilanes that are listed in Table I are less than 10% complete within the first 5 min following mixing of trifluoroacetic acid with the alkene in the presence of the organosilane.[13] Thus trifluoroacetic acid addition to the reactant alkene is sufficiently more rapid than direct organosilane reduction of the alkene (eq 1) that the trifluoroacetate addition products must be considered to be the effective reactants in hydride transfer reactions with organosilanes (eq 2).[16]

$$R_2C{=}CR_2 \xrightarrow{CF_3COOH} \underset{H}{\overset{|}{R_2C}}{-}\underset{OOCCF_3}{\overset{|}{CR_2}} \xrightarrow{R'_3SiH} \underset{H}{\overset{|}{R_2C}}{-}\underset{H}{\overset{|}{CR_2}} \quad (2)$$

Addition of trifluoroacetic acid to $\Delta^{9(10)}$-octalin produced an isomeric mixture of 9-decalyl trifluoroacetates (67% trans, 33% cis). The isomeric trifluoroacetate ratio (67:33) remained constant during organosilane reduction. Similarly, 4-*tert*-butyl-1-methylcyclohexyl trifluoroacetate was formed from 4-*tert*-butylmethylenecyclohexane and trifluoroacetic acid in the isomeric proportion of 72% axial trifluoroacetate/28% equatorial trifluoroacetate. This trifluoroacetate ratio was also constant throughout the time required for organosilane reduction. Since the axial derivative has been demonstrated to be more reactive than the equatorial derivative in solvolysis reactions of similar cyclohexyl substrates,[8a,10,17] and since identical rates for reduction of the isomeric forms of the trifluoroacetates would be unlikely, the constancy in the isomeric

0022-3263/78/1943-0693$01.00/0

Table I. Stereoselectivities of Organosilane Reductions of Representative Cycloalkenes in Trifluoroacetic Acid[a]

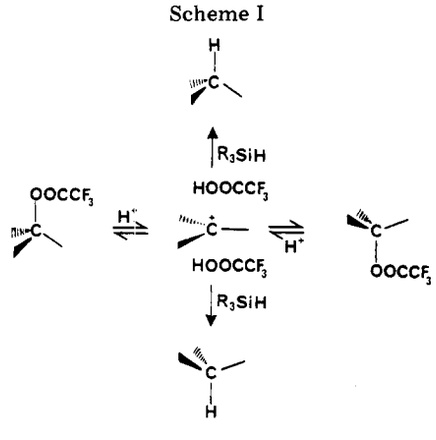
Silane	Registry no.	[Silane]/[Alkene]	Decahydronaphthalene		4-*tert*-Butyl-1-methylcyclohexane	
			% cis[b]	% cis/% trans	% cis[b]	% cis/% trans
n-$BuSiH_3$	1600-29-9	2.0	22	0.28		
		1.1	27	0.37	4	0.04
		0.36	37	0.59		
Et_2SiH_2	542-91-6	0.60	40	0.67	8	0.09
Et_3SiH	617-86-7	1.1	42	0.72	10	0.11
i-$Pent_3SiH$	17922-08-6	1.1	35	0.54	9	0.10
c-$Pent_3SiH$	33729-87-2	1.1	54	1.17		
Ph_3SiH	789-25-3	1.1	58[c]	1.38		
sec-Bu_3SiH	6531-11-9	1.1	72	2.57	16	0.19
t-Bu_2SiH_2	30736-07-3	0.55	77	3.35	16	0.19
t-Bu_2MeSiH	56310-20-4	1.1	83	4.88		
t-Bu_3SiH	13159-55-2	1.1	93	13.3		

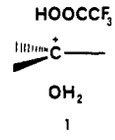
[a] Trifluoroacetic acid (5 molar equiv based on alkene) was added to the combined silane and alkene at 25 °C. [b] Relative product yield based on the average of at least two determinations. Precision of analyses is within ±1%. [c] Carey and Tremper report 61% of the cis isomer for reduction in methylene chloride solutions of trifluoroacetic acid.[3b]

ratio of trifluoroacetates during hydride transfer indicates that the trifluoroacetates are in isomeric equilibrium.

If the trifluoroacetate derivatives of alkenes are the effective reactants in organosilane reductions and if these derivatives are in isomeric equilibrium, the stereoselectivity for hydride transfer will be independent of the olefinic source of the isomeric trifluoroacetates. To test this hypothesis a mixture composed of 60% $\Delta^{9(10)}$-, 32% $\Delta^{1(9)}$-, and 8% $\Delta^{1(2)}$- plus $\Delta^{2(3)}$-octalin was reduced by triethylsilane in trifluoroacetic acid under the same conditions as those for the reactions in Table I. The relative yield of *cis*-decahydronaphthalene (42%) was identical with that reported in Table I.[18] In addition, reduction of *trans*-1-decalone by an equivalent molar amount of n-butylsilane in trifluoroacetic acid yielded the by-product decahydronaphthalene (3% yield) with essentially the same isomeric composition (29% *cis*-decahydronaphthalene) as that reported for ionic hydrogenation of $\Delta^{9(10)}$-octalin (27% *cis*-decahydronaphthalene). Similarly, triethylsilane reduction of 4-*tert*-butyl-1-methylcyclohexene in trifluoroacetic acid produced the same relative yield of *cis*-4-*tert*-butyl-1-methylcyclohexane (10%) as did 4-*tert*-butylmethylenecyclohexane. The combined results suggest that ionic hydrogenation of alkenes occurs by hydride transfer to a symmetrically solvated carbenium ion that is common to both isomeric trifluoroacetates and that stereoselectivity in this reduction process results from steric influences between the organosilane and the symmetrically solvated cation (Scheme I). This interpretation fully conforms with the observation by Fort and co-workers[8a] of predominant retention at carbon for reductions of *cis*- and *trans*-1-decalol by triethylsilane in methylene chloride solutions of trifluoroacetic acid. The cationic intermediate formed by trifluoroacetolysis of the isomeric 9-decalols is unsymmetrically solvated (1), and since the nucleophilicity of water is predictably greater than that of trifluoroacetic acid for replacement of hydride on silicon,[19] hydride transfer preferentially occurs from the water-solvated side of 1.[20,22] Organosilane reductions of *cis*- and *trans*-4-*tert*-butyl-1-phenylcyclohexanols[3c] apparently involve a symmetrically solvated cationic intermediate.

Scheme I





1

The dramatic increase in the yield of the less stable alkane isomer with the increasing size of the organosilane in reductions of $\Delta^{9(10)}$-decalin (Table I) and the absence of a correlation between the isomeric product ratio and the rate for hydride transfer indicate that stereoselectivity in reductions of symmetrically solvated carbenium ions are governed by steric factors. As was observed for reductions of cyclic ketones by organosilanes,[7d,11b] the number of substituents bonded to silicon and the steric bulk of these substituents are important determinants of stereoselectivity. The relative insensitivity of the percentage of the less stable cis isomer from ionic hydrogenation of 4-*tert*-butylmethylenecyclohexane to the steric bulk of the organosilane does, however, indicate that steric approach control[1a,23] may not be the sole factor responsible for the stereoselectivity that is observed in these reductions. The rate for reduction of 4-*tert*-butylmethylenecyclohexane is between 4 and 5 times slower than that for reduction of $\Delta^{9(10)}$-octalin by the organosilanes included in Table I. This same factor of between 4 and 5 also constitutes the ratio of percentage *cis*-decahydronaphthalene to *cis*-4-*tert*-butyl-1-methylcyclohexane.[24] Although steric factors are important in the ionic hydrogenation of alkenes, the data obtained in this study do not limit stereoselective control solely to the steric bulk of the organosilane. Additional stereochemical data are required to fully extract the intimate details of other factors that influence stereoselectivity in organosilane reductions of carbenium ions, particularly those that are related to the solvolytic behavior of tertiary alkyl substrates.

The stereoselectivities that are observed in organosilane reductions of carbenium ions provide a valuable reference for similar reductions by hydrocarbon reducing agents[25] and serve to characterize ionic hydrogenation processes. Comparison of the data in Table I with similar results for hydrogenation catalyzed by chloroplatinic acid–stannous chloride,[26] for example, indicates that this latter process operates as an ionic

hydrogenation; stereochemical results obtained for hydrogenations with platinum oxide[27] and soluble osmium, rhodium, iridium, or ruthenium catalysts[26] are distinctly different.

Experimental Section

General. Instrumentation has been previously described.[7d] Peak areas in GLC analyses were determined using the Varian Model 485 digital integrator and the Varian CDS 101 data system. Diethyl-, triethyl-, and triphenylsilane were commercially available and were used without further purification. *n*-Butylsilane was prepared from *n*-butyltrichlorosilane by reduction with lithium aluminum hydride.[7c] The syntheses of triisopentyl-, tri-*sec*-butyl-, and tricyclopentylsilane from trichlorosilane and the appropriate Grignard or organolithium reagent have been reported.[7d] Methods for the preparation of di-*tert*-butyl- and di-*tert*-butylmethylsilane have also been described.[28] Tri-*tert*-butylsilane was prepared from di-*tert*-butyldifluorosilane and *tert*-butyllithium in 81% yield.[29] The isomeric mixture of octalins (64% $\Delta^{9(10)}$-, 29% $\Delta^{1(9)}$-, and 7% $\Delta^{1(2)}$- and $\Delta^{2(3)}$-octalin) produced from commercial 2-decalol through dehydration with polyphosphoric acid[30] was isomerized over Amberlyst 15 (0.8 g/g of octalin) to an isomeric composition of 92% $\Delta^{9(10)}$, 4% $\Delta^{1(9)}$-, and 4% $\Delta^{1(2)}$-, $\Delta^{2(3)}$-octalin by refluxing the octalin mixture in a solution of 2:1 acetic acid–benzene (4 mL/mL of octalin) for 3 h under nitrogen.[31] 4-*tert*-Butylmethylenecyclohexane was synthesized from 4-*tert*-butylcyclohexanone and methylenetriphenylphosphine.[32] 4-*tert*-Butyl-1-methylcyclohexene was prepared by dehydration of 4-*tert*-butyl-1-methylcyclohexanol[33] using catalytic amounts of *p*-toluenesulfonic acid in refluxing benzene. Hydrogenation of 4-*tert*-butylmethylenecyclohexane in glacial acetic acid using a platinum oxide catalyst and 3 atm pressure gave 4-*tert*-butyl-1-methylcyclohexane (75% cis isomer) in 63% yield: lit.[34] 75% cis isomer.

General Procedure for Organosilane Reductions in Trifluoroacetic Acid. The olefin (generally 5.0 mmol) and a 10% molar excess of the organosilane were weighed into a round-bottom flask which was fitted with a condenser and placed in a water bath at 25 °C. Precautions were taken to avoid the introduction of water into the reaction system. Addition of trifluoroacetic acid (5.0 molar equiv) in one portion to the rapidly stirred solution effected an exothermic reaction that was independent of the organosilane. The extent of reaction was determined by ^{1}H NMR analyses through observation of the change in the characteristic absorption patterns for the organosilane (Si–*H*) and cycloalkene or trifluoroacetate addition product. Analysis of the reaction solution at 5 min after the addition of trifluoroacetic acid gave no evidence for the alkene reactant and showed only the trifluoroacetate derivative and, if reduction had occurred, the alkane product in addition to the organosilane reactant and product. 9-Decalyl trifluoroacetate: ^{1}H NMR (CF_3COOH): δ 2.85–2.40 (10 H, m, trans isomer) and 2.25–1.85 (10 H, m, cis isomer).[35] 4-*tert*-Butyl-1-methylcyclohexyl trifluoroacetate: ^{1}H NMR (CF_3COOH): δ 1.65 (s, axial-CH_3), and 1.58 (s, equatorial-CH_3). Organosilane reductions of $\Delta^{9(10)}$-octalin were complete within 5 d even when tri-*tert*-butylsilane was employed as the hydride donor; reductions of 4-*tert*-butylmethylenecyclohexane were between 4 and 5 times slower. After reduction was complete the reaction mixture was diluted with ether and the acidic ether solution was washed with saturated aqueous sodium bicarbonate until gas evolution ceased. The ether solution was then dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure to give the isomeric hydrocarbons and organosilane products which were analyzed by GLC. The composition of *cis*- and *trans*-decahydronaphthalenes was determined on a 6-ft column of 20% Carbowax 20M on Chromosorb P (120 °C) and on an 8-ft column of 20% SE-30 on Chromosorb W (95 °C); the 4-*tert*-butyl-1-methylcyclohexanes were analyzed on an 8-ft column of 20% SE-30 on Chromosorb W (75 °C). Silyl trifluoroacetates were identified as the sole silane product from these reductions by ^{1}H NMR and GLC analyses through comparison with authentic samples. The stereoselectivity observed for reductions of 4-*tert*-butylmethylenecyclohexane (Table 1) was independent of temperature over the range −15 to 50 °C with both triethylsilane and *n*-butylsilane.

Reductions by *n*-Butylsilane. The extent of reactions of $\Delta^{9(10)}$-octalin and 4-*tert*-butylmethylenecyclohexane with various molar equivalents of *n*-butylsilane (Table I) in trifluoroacetic acid was followed by ^{1}H NMR spectroscopic analysis. Only two of the three available silane hydrogens of *n*-butylsilane were reactive hydrides. Transfer of the first hydride was rapid and resulted in the formation of *n*-butylsilyl trifluoroacetate (δ 4.77, t, J = 2.7 Hz, Si–*H*). The rate of loss of the first hydride was more than 10 times faster than the rate for hydride transfer from *n*-butylsilyl trifluoroacetate. *n*-Butylsilyl ditrifluoroacetate was not detected in these reaction solutions. Similar stepwise reductions were observed in ionic hydrogenations that employed diethylsilane and di-*tert*-butylsilane; ^{1}H NMR (CF_3COOH): $Et_2SiHO_2CCF_3$ (δ 4.77, m, Si–*H*); *t*-$Bu_2SiHO_2CCF_3$ (δ 4.54, s, Si–*H*, δ 1.12, s, t-Bu).

Equilibration of Isomeric 4-*tert*-Butyl-1-methylcyclohexyl Trifluoroacetates in Trifluoroacetic Acid. 4-*tert*-Butyl-1-methylcyclohexanol was prepared from 4-*tert*-butylcyclohexanone and methylmagnesium bromide by the method of House and Respess.[33] The isomeric cis/trans alcohol ratio was determined by GLC analysis on a 10-ft column of 10% FFAP on Chromosorb P (190 °C) to be 1.48 (lit.[33] 1.50). The corresponding isomeric mixture of trifluoroacetate esters was prepared by the reaction of 4-*tert*-butyl-1-methylcyclohexanol with trifluoroacetic anhydride using a catalytic amount of trifluoroacetic acid; ^{1}H NMR (CCl_4): δ 0.88 (s, 9 H), 1.15–1.46 (m, 6 H), 1.56 (s, equatorial-CH_3), 1.60 (s, axial-CH_3), and 1.75–2.50 (m, 3 H). The isomeric cis/trans trifluoroacetate ratio (eq-CH_3/ax-CH_3) was 1.9. This mixture was dissolved in carbon tetrachloride and trifluoroacetic acid was added at regular intervals. The isomeric ratio changed from 1.9 to 2.57 within 15 min after 2 molar equiv of trifluoroacetic acid was added to the reaction solution. No further change in the isomeric trifluoroacetate ratio occurred upon subsequent additions of trifluoroacetic acid over a 21-h period or during organosilane reductions in separate experiments.

Acknowledgment. We are grateful to Charles T. West and Nancy Ball for their preliminary investigations.

Registry No.—Trifluoroacetic acid, 76-05-1; $\Delta^{9(10)}$-octalin, 493-03-8; 4-*tert*-butylmethylenecyclohexane, 13294-73-0; *trans*-9-decalyl trifluoroacetate, 64252-68-2; *cis*-9-decalyl trifluoroacetate, 64252-69-3; *cis*-4-*tert*-butyl-1-methylcyclohexyl trifluoroacetate, 64252-70-6; *trans*-4-*tert*-butyl-1-methylcyclohexyl trifluoroacetate, 64252-71-7; butylsilyl trifluoroacetate, 64252-72-8; $Et_2SiHO_2CCF_3$, 64252-73-9; *t*-$Bu_2SiHO_2CCF_3$, 64265-08-3; *cis*-4-*tert*-butyl-1-methylcyclohexanol, 10601-39-5; *trans*-4-*tert*-butyl-1-methylcyclohexanol, 13004-06-3.

References and Notes

(1) (a) Part 9: M. P. Doyle, C. C. McOsker, N. Ball, and C. T. West, *J. Org. Chem.*, **42**, 1922 (1977); (b) Camille and Henry Dreyfus Foundation Teacher Scholar Grant Awardee, 1973–1978; (c) National Science Foundation Undergraduate Research Participant, Summer, 1975.

(2) (a) D. N. Kursanov, Z. N. Parnes, and N. M. Loim, *Synthesis*, 633 (1974), and references therein; (b) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, **36**, 758 (1971), and previous articles in this series.

(3) (a) F. A. Carey, C.-L. Wang Hsu, *J. Organomet. Chem.*, **19**, 29 (1969); (b) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, **34**, 4 (1969); (c) F. A. Carey and H. S. Tremper, *J. Am. Chem. Soc.*, **90**, 2578 (1968).

(4) C. T. West, S. J. Donnelly, D. A. Kooistra, and M. P. Doyle, *J. Org. Chem.*, **38**, 2675 (1973).

(5) Secondary alcohols are reduced by organosilanes when boron trifluoride is employed as the acid catalyst: M. G. Adlington, M. Orfanopoulos, and J. L. Fry, *Tetrahedron Lett.*, 2955 (1976).

(6) Aluminum chloride catalyzed reductions of alkyl halides do not exhibit similar limitations: M. P. Doyle, C. C. McOsker, and C. T. West, *J. Org. Chem.*, **41**, 1393 (1976).

(7) (a) D. N. Kursanov, Z. N. Parnes, V. A. Tsyryapkin, R. V. Kudryavtsev, *Dokl. Akad. Nauk SSSR*, **202**, 874 (1972), and references therein; (b) J. L. Fry, *J. Chem. Soc., Chem. Commun.*, 45 (1974); (c) M. P. Doyle, D. J. DeBruyn, S. J. Donnelly, D. A. Kooistra, A. A. Odubela, C. T. West, and S. J. Zonnebelt, *J. Org. Chem.*, **39**, 2740 (1974); (d) M. P. Doyle and C. T. West, *ibid.*, **40**, 3821 (1975).

(8) (a) R. C. Fort, Jr., R. E. Hornish, and G. A. Liang, *J. Am. Chem. Soc.*, **92**, 7558 (1970); (b) M. P. Doyle, J. G. Kalmbacher, W. Wierenga, and J. E. DeBoer, *Tetrahedron Lett.*, 1455 (1974); (c) M. P. Doyle, M. A. Zaleta, J. E. DeBoer, and W. Wierenga, *J. Org. Chem.*, **38**, 1663 (1973).

(9) (a) T. A. Serebryakova, A. V. Zakhariychev, S. N. Ananchenko, and I. V. Torgov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1679 (1972); (b) T. A. Serebryakova, Z. N. Parnes, A. V. Zakharychev, S. N. Ananchenko, and I. V. Torgov, *Izv. Akad. Nauk SSSR, Ser Khim.*, 725 (1969).

(10) (a) R. C. Fort, Jr., and R. E. Hornish, *Chem. Commun.*, 11 (1969); (b) K. B. Becker, A. F. Boschung, M. Geisel, and C. A. Grob, *Helv. Chim. Acta*, **56**, 2747 (1973); G. E. Gream, *Aust. J. Chem.*, **25**, 1051 (1972).

(11) (a) M. P. Doyle, C. T. West, S. J. Donnelly, and C. C. McOsker, *J. Organomet. Chem.*, **117**, 129 (1976); (b) M. P. Doyle and C. T. West, *J. Org. Chem.*, **40**, 3835 (1975).

(12) (a) Z. N. Parnes, G. A. Khotimskaya, R. V. Kudryavtsev, and D. N. Kursanov, *Izv. Akad. Nauk SSSR*, 901 (1972); (b) Z. N. Parnes, G. I. Bolestova, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987 (1972).

(13) The order of reactivity of the organosilanes employed in this study, as determined by ^{1}H NMR analyses of reaction solutions at comparable time intervals, was: Et_3SiH > *i*-$Pent_3SiH$, Et_2SiH_2 > *n*-$BuSiH_3$, *c*-$Pent_3SiH$, *sec*-Bu_3SiH > *t*-Bu_2MeSiH > *t*-Bu_3SiH, *t*-Bu_2SiH_2. These qualitatively

determined hydrogen-donor abilities of organosilanes are substantially the same as those reported for organosilane reductions of 4-*tert*-butylcyclohexanone[14] and for olefin and alcohol reductions.[3c,15]
(14) M. P. Doyle and C. T. West, *J. Org. Chem.*, **40**, 3829 (1975).
(15) D. N. Kursanov, Z. N. Parnes, G. I. Bassova, N. M. Loim, and V. I. Zdanovich, *Tetrahedron*, **23**, 2235 (1967).
(16) The reduction of $\Delta^{9(10)}$-octalin by triethylsilane represents the only possible exception to this general consideration. Addition of triethylsilane to 9-decalyl trifluoroacetate in trifluoroacetic acid produced decahydronaphthalene in a 33:67 cis:trans product ratio. The difference between this result and that reported in Table I may be due to partial direct ionic hydrogenation of $\Delta^{9(10)}$-octalin and reflect a distinctly different stereochemical requirement for that process.
(17) (a) S. Winstein and W. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955); (b) C. A. Grob, W. Schwarz, and H. P. Fischer, *Helv. Chim. Acta*, **47**, 1385 (1964).
(18) $\Delta^{1(2)}$- and $\Delta^{2(3)}$-Octalin underwent slow addition of trifluoroacetic acid, but neither the olefin nor its addition product was reduced by triethylsilane.
(19) L. H. Sommer, "Stereochemistry, Mechanism, and Silicon", McGraw-Hill, New York, N.Y., 1965.
(20) This argument outlines the directional influence of the nucleophile (leaving group) on hydride transfer and does not assume that hydride transfer occurs with retention of configuration at silicon.[3a,21] A similar stereospecificity has been observed in reactions of *cis*- and *trans*-1-phenyl-4-*tert*-butylcyclohexanol with hydrogen chloride: K. D. Berlin, R. O. Lyerla, and D. E. Gibbs, *J. Org. Chem.*, **37**, 528 (1972).
(21) L. H. Sommer and D. L. Bauman, *J. Am. Chem. Soc.*, **91**, 7076 (1969).
(22) This interpretation suggests that water increases the rate of hydride transfer from silicon in reductions of trifluoroacetate derivatives in trifluoroacetic acid. Indeed, the addition of an equimolar amount of water (based on original alkene) to 1-methylcyclohexyl trifluoroacetate in 4 molar equiv of trifluoroacetic acid increased the rate for hydride transfer from *n*-butylsilane by a factor of 20.
(23) M. P. Doyle and C. T. West, "Stereoselective Reductions", Dowden, Hutchinson and Ross, Stroudsburg, Pa., 1976, Part III.
(24) The ratio of % *cis*-decahydronaphthalene to % *cis*-4-*tert*-butyl-1-phenylcyclohexane (from organosilane reductions of the more reactive 4-*tert*-butyl-1-phenylcyclohexanols[3c]) is between 1.2 and 1.4.
(25) R. M. Carlson and R. K. Hill, *J. Org. Chem.*, **34**, 4178 (1969).
(26) T. R. B. Mitchell, *J. Chem. Soc., B*, 823 (1970).
(27) S. Siegel and B. Dmuchovsky, *J. Am. Chem. Soc.*, **84**, 3132 (1962).
(28) M. P. Doyle and C. T. West, *J. Am. Chem. Soc.*, **97**, 3777 (1975).
(29) E. M. Dexheimer, L. Spialter, and L. D. Smithson, *J. Organomet. Chem.*, **102**, 21 (1975).
(30) W. G. Dauben, E. C. Martin, and G. J. Fonken, *J. Org. Chem.*, **23**, 1205 (1958).
(31) A. L. Tumolo, U.S. Patent 3 579 604 (1971); *Chem. Abstr.*, **75**, 48772 (1971). Analysis for $\Delta^{9(10)}$-octalin provides a minimum estimate of the contribution by this isomer.
(32) E. V. Couch, J. A. Landgrebe, and E. T. Casteneda, *J. Org. Chem.*, **40**, 1529 (1975).
(33) H. O. House and W. L. Respess, *J. Org. Chem.*, **30**, 301 (1965).
(34) S. Mitsui, K. Gohke, H. Saito, A. Nanbu, and Y. Senda, *Tetrahedron*, **29**, 1523 (1973).
(35) These assignments are in agreement with those for the 9-decalyl acetates and ethyl ethers.[10b]

Fluorination with Xenon Difluoride. Stereochemistry of Fluorine Addition to Phenyl-Substituted Cycloalkenes

Marko Zupan* and Boris Šket

Department of Chemistry and "J. Stefan" Institute, University of Ljubljana, Ljubljana Yugoslavia

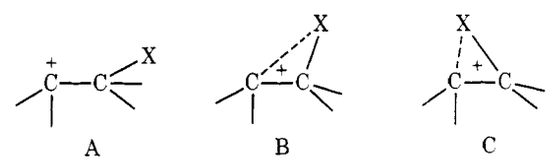
Received June 28, 1977

Acid-catalyzed liquid-phase fluorine addition with xenon difluoride to some phenyl-substituted cycloalkenes, i.e., 1-phenylcyclopentene, 1-phenylcyclohexene, and 1-phenylcycloheptene, results in the formation of vincinal difluorides in high yield. The ratio of syn and anti addition depends on ring magnitude. The stereochemistry of fluorine addition to aryl-substituted cyclohexenes also depends on the substituent in the phenyl ring.

The mechanisms of electrophilic addition of halogens have been widely investigated, both from the kinetic and stereochemical points of view.[1] Apart from the relative importance of the various kinetically significant processes, it is now known that the nature of the intermediates of the addition depends on the structure of the substrate, on the halogen, and on the reaction medium, ranging from strongly bridged ions (type C), to weakly bridged species (type B), or to open ions like A (Scheme I). If the cation is of the open structure A (X = F), a mixture of cis and trans adducts is generally expected. However, ion-pairing phenomena can cause preferential formation of the cis adduct and electronic, steric, or conformational effects can cause attack at one or the other side of the carbonium p orbital of A to be favored. On the other hand, the intermediate can have a bridged structure (C, X = Br), which will be presumably opened stereospecifically to form a trans adduct.

Recently we have observed that xenon difluoride readily adds fluorine to phenyl-substituted olefins to give the corresponding 1,2-difluorophenylalkanes in high yield and under mild conditions.[2] The ratios of *dl*-erythro and *dl*-threo difluorides formed by fluorination of alkyl- or phenyl-substituted olefins are nearly independent of the starting olefin, and in the trans series anti addition of fluorine predominates. We have suggested the formation of an open β-fluorocarbonium ion intermediate.[3] The intermediate from the trans olefin collapses preferentially to an anti adduct, while the cis olefin intermediate can freely rotate about the newly formed single bond, thus assuming a sterically more favorable conformation identical with that of the trans intermediate. As an extension

Scheme I



of our research, we therefore chose some phenyl-substituted cycloalkenes, i.e., 1-phenylcyclopentene, 1-phenylcyclohexene, and 1-phenylcycloheptene, as substrates in the acid-catalyzed liquid-phase fluorination reaction with xenon difluoride. We extended our studies to cycloolefins so as to eliminate a complexity which exists in an acyclic system, in which there is a possibility of rotation about the carbon–carbon single bond in the β-fluorocarbonium ion, depending on its lifetime and the energy barrier resisting free rotation about the newly formed single bond. From the data obtained it should be possible to get information about the influence of the ring magnitude on the stereochemistry of the fluorine addition. The variation of the substituent on the phenyl ring (X = H, *p*-OCH_3, *m*-Cl) in 1-phenylcyclohexene will give us further information about the effect of the stability of β-fluorocarbonium ions on the stereochemistry of fluorine addition.

Results and Discussion

The preparation of fluoroalkanes presents a different problem from that of other haloalkanes and necessitates a specific method of fluorination.[4] The acid-catalyzed liquid-phase fluorination of organic substrates with XeF_2 avoids some experimental difficulties, e.g., low temperature, high-

0022-3263/78/1943-0696$01.00/0