correlation between the length of the bridging linkage and the strength of the spin coupling in these binuclear oligomeric species, an interesting phenomenon for detailed theoretical study.

Being trans to the exceedingly short bridging Mn–O bonds, the rather long bonds (2.15 Å) to the pyridine ligands in $O(PyMnPc)_2$ may be subject to a structural trans effect. Indeed, the lengthening and weakening of these bonds by some sort of generalized synergistic mechanism[35] is rendered the more probable by the antiferromagnetic behavior of the molecule. Quite apart from such speculation, it is noteworthy that steric interactions of each phthalocyaninato core with the contiguous pair of pyridine–hydrogen atoms are not trivial, even though the observed orientations of both pyridine ligands[12] are nearly ideal for minimizing the steric repulsions.[36] Each of the specified hydrogen atoms lies above a six-membered chelate ring with three nitrogen and two carbon atoms of the aromatic core as near neighbors at calculated distances ranging from 2.68 to 2.80 Å. The van der Waals packing distance corresponding to direct superposition of a hydrogen above a core atom is 2.90 Å; a smaller value, perhaps as low as 2.80 Å, is more appropriate to the observed geometry of the five H···N and H···C contacts, and the energetic implications of the calculated separations are modest. A gross reduction of the axial Mn–N distance from the observed 2.15 Å to, let us say, the 1.96 Å that characterizes the equatorial Mn–N bonds is quite another matter, because it calls for a reduction in the critical H···N and H···C contacts (of which there are 20 in the molecule) to the range 2.51–2.64 Å.

The steric constraints imposed upon piperidine[23] and imidazole[28] molecules as axial ligands in low-spin iron porphyrins are detailed elsewhere.[23,28] Pyridine, in a similar role, is somewhat less constrained than is piperidine, but definitely more so than imidazole. (Differences in the geometries of five- and six-membered aromatic ring systems are surprisingly significant in this connection.)

The mean planes of the two porphinato cores in the $O(FeTPP)_2$ molecule are separated by ~5.20 Å, whereas the phthalocyaninato cores in the $O(PyMnPc)_2$ molecule approach ~3.40 Å, the characteristic spacing of fully aromatic molecules stacked in parallel array. Close approach of the porphinato cores in $O(FeTPP)_2$ to one another is debarred by the packing of the bulky phenyl substituents, a circumstance that may seriously affect the pattern of complexing bonds. Interactions between the porphinato cores in the $O(FeProto)_2$ molecule (*vide supra*) are sterically less constrained, and the role played by the vinyl substituents commands special interest. Structure and bonding in this oligomer may display features that are intermediate between those observed for the $O(FeTPP)_2$ and the $O(PyMnPc)_2$ molecules. Structure determination for a triclinic crystal of $O(FeProto)_2$ is currently in progress.[37]

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(35) *Cf.* (a) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966); (b) L. M. Venanzi, *Chem. Brit.*, **4**, 162 (1968), for a discussion of synergistic mechanisms.

(36) See ref 28, especially Figure 4 therein, for a detailed treatment of a closely related problem.

(37) L. J. Radonovich, W. S. Caughey, and J. L. Hoard.

Communications to the Editor

An Inversion Component in the Solvolytic Displacement Reactions of Alkyl-Substituted Vinyl Trifluoromethanesulfonates

Sir:

Solvolytic displacement at unsaturated (vinyl, sp^2) centers seems in nearly every case reported so far to have proceeded with complete randomization of stereochemistry, and this has formed one of the principal pieces of evidence for the existence of "free" vinyl cations.[1,2] Theoretical calculations support the inference that direct backside displacement should be more difficult at a vinyl than at a tetrahedral center.[3] As has been pointed out, however,[2] many of the substrates so far examined from which stereochemical information has been obtained are "activated"; *i.e.*, they generate rather highly stabilized vinyl cations. We now wish to report a study of simple, alkyl-substituted vinyl substrates which demonstrates that (in contrast to the behavior reported for activated systems[1]) their SN1 ionization reactions proceed with a significant amount of *inversion* of configuration at the vinyl center.

Solvolysis of 3-methyl-2-heptenyl trifluoromethanesulfonates (triflates) (*Z*)-**1** and (*E*)-**1**[4] took place readily at 60° in dry trifluoroethanol buffered with 2,6-lutidine and gave vinyl trifluoroethyl ethers (*Z*)-**2** and (*E*)-**2** as well as 1-methyl-1-*n*-butylallene (**3**) in the proportions

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(1) (a) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, **92**, 228 (1970); (b) D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1941 (1971); (c) Z. Rappoport and Y. Apeloig, *Proc. Israel J. Chem.*, **7**, 34 (1969); (d) Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, **91**, 6734 (1969).

(2) One apparent exception is noted: some excess *retention* of configuration has been observed in silver-catalyzed reactions in nonsolvolytic media; *cf.* G. F. P. Kernaghan and H. M. R. Hoffmann, *ibid.*, **92**, 6988 (1970).

(3) D. R. Kelsey and R. G. Bergman, *ibid.*, **93**, 1953 (1971).

(4) (a) Trifluoromethanesulfonates were prepared in all cases by reaction of the appropriate ketones with trifluoromethanesulfonic anhydride.[4b] Synthesis of the ketones will be described in a full paper; all new compounds exhibited analytical properties consistent with their assigned structures. Stereochemistries of vinyl triflates and trifluoroethyl ethers were assigned on the basis of chemical shifts[5a] and homoallylic coupling constants for the methyl groups ($J_{\text{trans}} = 1.4 \pm 0.1$ Hz, $J_{\text{cis}} = 0.9 \pm 0.1$ Hz).[4c] (b) T. E. Deuber, P. J. Stang, W. D. Pfeifer, R. H. Summerville, M. A. Imhoff, P. von R. Schleyer, K. Hummel, S. Blocker, C. E. Harding, and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **9**, 521 (1970); (c) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

(5) Vinyl triflates have been unequivocally shown to undergo SN1 solvolysis in protic media, even in alkyl-substituted cases. See, for example: (a) P. J. Stang and R. Summerville, *J. Amer. Chem. Soc.*, **91**, 4600 (1969); (b) W. M. Jones and D. D. Maness, *ibid.*, **91**, 4314 (1969). In addition, trifluoroethanol has been shown to efficiently promote SN1 ionization: *cf.* (c) W. S. Trahanovsky and M. P. Doyle, *ibid.*, **89**, 4867 (1967); (d) W. S. Trahanovsky and M. P. Doyle, *Tetrahedron Lett.*, 2155 (1968); (e) V. J. Shiner, W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Amer. Chem. Soc.*, **91**, 4838 (1969).

Table I. Products Formed in the Trifluoroethanolysis of (*Z*)- and (*E*)-3-Methyl-2-heptenyl 2-Trifluoromethanesulfonates ((*Z*)-**1** and (*E*)-**1**) at 60°

Substrate[d] (concn, *M*)	Buffer[a] concn, *M*	Products,[b] % (*Z*)-**2**	(*E*)-**2**	**3**	Ratio,[c] (*E*)-**2**/(*Z*)-**2**
(*Z*)-**1** (0.09)	0.18	15.2	70.6	14.2	4.6
(*Z*)-**1** (0.09)	0.36	15.6	69.1	15.3	4.4
(*Z*)-**1** (0.023)	0.045	15.8	71.2	12.9	4.5
(*E*)-**1** (0.09)[e]	0.18	23.9	58.6	17.5	2.4

[a] 2,6-Lutidine. [b] All products shown to be stable to the solvolysis conditions. Absolute yields were determined by vpc using an internal standard to be >95%. [c] Some irreproducibility in the percentage of **3** increases the error in the product percentages to about ±4%; however, the trifluoroethyl ether ratio is accurate to ±0.1. [d] No interconversion of (*Z*)-**1** and (*E*)-**1** is observed, indicating that ion-pair equilibration and internal return do not occur under these reaction conditions. [e] Product distribution listed for (*E*)-**1** is an average of two runs.

reported in Table I.[5] The data show unequivocally that, unlike systems in which the vinyl center is activated by cyclopropyl[1a,b] or aromatic[1c,d] substituents, triflates (*Z*)-**1** and (*E*)-**1** give rise to *different* ratios of products. Although the (*E*)/(*Z*) trifluoroethyl ether ratio is greater than 1 in both solvolyses, considerably more (*Z*)-(**2**) is produced from (*E*)-**1** than from (*Z*)-**1**. The mechanism of this reaction can therefore *exclusively* involve neither free vinyl cations nor direct, backside S_N2 displacement. Presently, we feel that the data are most economically rationalized by the intervention of ion pairs (*Z*)-**4** and (*E*)-**4**, where the side of the molecule from which the triflate group is departing (Scheme I) is shielded to some extent from attack by solvent. However, our data do not distinguish between this mechanism and an alternative scheme involving ionization directly to **5** and concurrent backside attack by solvent on (*Z*)-**1** and (*E*)-**1**.[6]

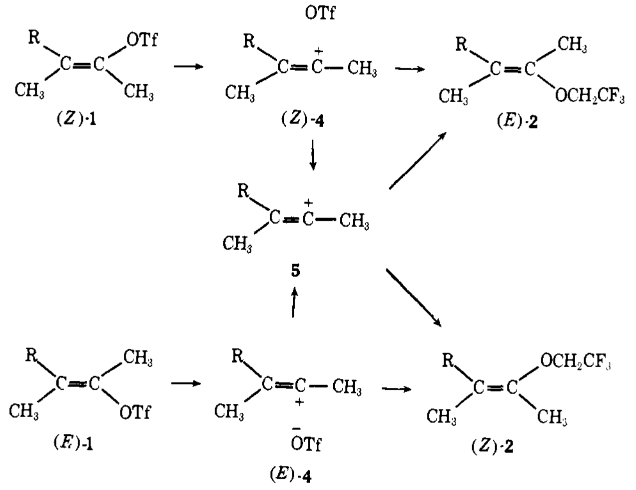
Table II. Ratios of (*E*)- and (*Z*)-Vinyl Acetate Products Formed on Ionization of Alkyl-Substituted Cyclopropylvinyl Iodides in AgOAc–HOAc at 25°

Substrate	Ratio,[a,b] *E*/*Z*
(*Z*)-**6**	1.21 ± 0.04
(*E*)-**6**	1.03 ± 0.02
(*Z*)-**8**	1.49 ± 0.02
(*E*)-**8**	1.38 ± 0.03

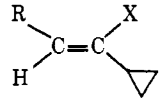
[a] Analyses performed on a 0.03 in. i.d. × 300 ft open tubular column coated with TCEP used in a Hewlett-Packard 5750 gas chromatograph equipped with an HP 3370 digital integrator. [b] Errors given as average deviation.

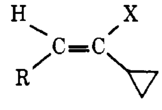
These results have prompted us to further investigate the stereochemistry of cyclopropyl-stabilized systems, in order to carefully determine whether some small inversion component occurs in those cases as well. The use of electronic digital vpc integration and open tubular columns for very precise measurement of product distributions has revealed a previously undetectable[1a,b] stereoselectivity in the silver-catalyzed ionization of iodides (*Z*)-**6** and (*E*)-**6** in acetic acid (Table II). Even in the case of dicyclopropyl-substituted iodides (*Z*)-**8** and (*E*)-**8**, repeated digital integration of a number of ionization runs reveals a small but identifiable inversion selectivity.

Scheme I



R = $CH_2CH_2CH_2CH_3$





(*Z*)-**6**, X = I; R = CH_3 (*E*)-**6**, X = I; R = CH_3
(*Z*)-**7**, X = OAc; R = CH_3 (*E*)-**7**, X = OAc; R = CH_3
(*Z*)-**8**, X = I; R = cyclopropyl (*E*)-**8**, X = I; R = cyclopropyl
(*Z*)-**9**, X = OAc; R = cyclopropyl (*E*)-**9**, X = OAc; R = cyclopropyl

In summary, inversion is a prominent part of the stereochemistry of S_N1 substitution of simple vinyl substrates, and even persists to some extent in cyclopropyl-activated systems. Our results suggest that careful investigation of other activated systems may also reveal small inversion components in those reactions. Finally, it seems clear that the overall net *retention* observed in the silver-catalyzed ionization of solvolytically *un*reactive vinyl halides in nonpolar, aprotic solvents[2] means that such ionizations are not in fact S_N1 reactions, as has been claimed,[2] but must be proceeding by more complex mechanisms, perhaps involving catalysis and nucleophilic trapping by aggregated silver salts.

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(6) For a discussion of attempts to settle this (still unsolved) problem in the solvolysis of aliphatic substrates, see (a) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, 91, 6031 (1969); (b) J. L. Kurz and J. C. Harris, *ibid.*, 92, 4117 (1970); (c) D. J. Raber, J. M. Harris, R. E. Hall, and P. von R. Schleyer, *ibid.*, 93, 4821 (1971).

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Observation of Olefinic Cyclization at a Vinyl Cation Center. An Inversion Preference for Intramolecular Nucleophilic Substitution by a Double Bond

Sir:

We wish to report the first observation of olefinic cyclization[1] at a vinyl cation center. We have also in-