as a chiral auxiliary is feasible. The extent of asymmetric induction is small and varies as a function of the steric bulk of the carbene/allene substituents with a diastereomeric excess of 3.5 ± 0.5% for R = CH_3 and 10.5 ± 0.5% for R = *t*-Bu. These values correspond to a difference in energy between diastereomeric transition states of only 22 cal/mol for the methyl-substituted system and 75 cal/mol for the *tert*-butyl system.

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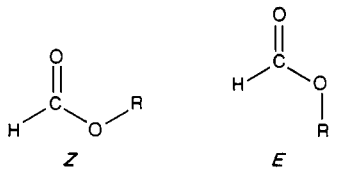
Dynamic Nuclear Magnetic Resonance Study of Vinyl Formate

Summary: Low-temperature carbon-13 NMR spectra of vinyl formate show that the populations of the *E* and *Z* conformations are 0.05 and 0.95 at −110 °C, with free energy barriers to interconversion at −87 °C of 8.3$_4$ and 9.2$_9$ kcal/mol.

Sir: Esters, amides and many related compounds have a strong preference for the *Z* conformation.[1] For methyl formate, the percentage of the *E* isomer in a favorable solvent (1:1 DMF/acetone-d_6) is only 0.3% at −83 °C,[2] and



Z *E*

1, R = CH_3; **2**, R = $(CH_3)_3C$; **3**, R = C_6H_5; **4**, R = $CH_2{=}CH$

several factors may be responsible for the large free energy difference of 2.2 kcal/mol between conformations: (1) Dipole–dipole interactions are more favorable for the *Z* conformation.[3] (2) The *Z* conformation may be stabilized by the interaction between a lone pair of electrons on the "ether" oxygen and σ^* of the carbonyl group.[4] (3) A cyclic "aromatic" system of six electrons is possible for the *Z* conformation, with two electrons each coming from the carbonyl π-bond, a lone pair of electrons on the "ether" oxygen, and a π-type orbital of the methyl group.[5]

"Aromaticity" also appears to be important for other alkyl groups; steric interactions in (*Z*)-**2** between oxygen and *tert*-butyl should be larger than the corresponding repulsion between the formyl hydrogen and *tert*-butyl in the *E* conformation, and the *E* − *Z* free energy difference in DMF/acetone-d_6 is smaller than for methyl formate, but the *Z* conformation is still favored by 0.48 kcal/mol.[2]

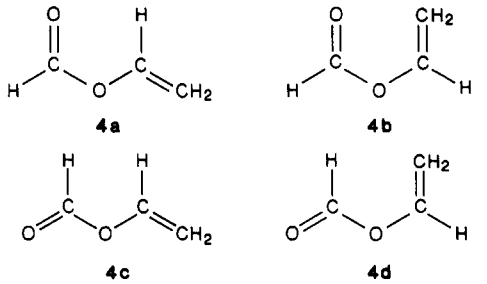
Aryl groups cannot complete an aromatic sextet in the *Z* conformation, and we have found a large population of the *E* conformation for phenyl thiolformate[6] and, more recently, for phenyl formate[7] (Table I). Vinyl esters should also be "nonaromatic", and we report here a dynamic NMR study of vinyl formate.

Table I. Populations of the *E* Isomers and *E* − *Z* Conformational Free Energy Differences for Esters of Formic Acid

ester	temp, °C	solvent	P_E	$\Delta G°$, kcal/mol	ref
1	−83	*a*	0.003	2.2	2
2	−105	*a*	0.19	0.48	2
2	−116	*b*	0.14	0.57	7
3	−117	*b*	0.20	0.43	7
4	−110	*b*	0.05	0.95	this work

[a] DMF/acetone-d_6 (1:1). [b] Acetone/acetaldehyde (1:3).

Four planar conformations are possible for vinyl formate, as shown in structures **4a–d**. Although several studies of this compound have been reported,[8–12] no experimental



4a **4b**

4c **4d**

evidence for the existence of the *E* conformations (**4c** or **4d**) has been described. The room-temperature 60-MHz proton NMR spectrum has been recorded[8] and shows long-range coupling to the formyl hydrogen. The microwave spectrum[9] of **4** was interpreted in terms of the planar conformation **4a**, and it was not possible to assign lines for any other conformation, although there were many lines that were not assigned. A later microwave study,[12] an electron-diffraction study,[12] and ab initio molecular orbital calculations[11,12] are in agreement with planar **4a** being the major conformation of vinyl formate, and the vibrational spectrum[10] and dipole moment[11] have also been interpreted in terms of this structure. The apparent planarity of this ester is in contrast to phenyl formate, which is reported[13,14] to have the phenyl group tilted by about 60°.

Because the *E* conformations are more polar than the *Z* isomers and are favored by polar solvents, we have taken

(1) For reviews, see: (a) Exner, O. In *The Chemistry of Double-Bonded Functional Groups*; Patai, S.; Ed.; Interscience; London, 1977; p 1. (b) Jones, G. I. L.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 1.
(2) Grindley, T. B. *Tetrahedron Lett.* **1982**, *23*, 1757.
(3) (a) For a listing of references discussing this effect, see ref 1a. (b) Recent calculations emphasize the importance of dipole–dipole interactions: Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.
(4) Larson, J. R.; Epiotis, N. D.; Bernardi, F. *J. Am. Chem. Soc.* **1978**, *100*, 5713.
(5) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1. See also ref 6 and references cited therein.
(6) Noe, E. A.; Sanders, T.; Garahi, M.; Hosseini, H.; Young, R. *J. Am. Chem. Soc.* **1985**, *107*, 4785.
(7) Mark, H. L.; Baker, T.; Noe, E. A. *J. Am. Chem. Soc.*, in press.
(8) Schaefer, T. *J. Chem. Phys.* **1962**, *36*, 2235.
(9) Rao, V. M.; Curl, R. F., Jr. *J. Chem. Phys.* **1964**, *40*, 3688.
(10) Gardenina, A. P.; Kotorlenko, L. A. *Opt. Spectrosc.* (*Engl. Transl.*) **1968**, *24*, 495.
(11) Aroney, M. J.; Bruce, E. A. W.; John, I. G.; Radon, L.; Ritchie, G. L. D. *Aust. J. Chem.* **1976**, *29*, 581.
(12) Pyckhout, W.; Van Alsenoy, C.; Geise, H. J.; Van Der Veken, B.; Coppens, P.; Traetteberg, M. *J. Mol. Struct.* **1986**, *147*, 85.
(13) Schaefer, T.; Penner, G. H. *Can. J. Chem.* **1987**, *65*, 2175.
(14) Schaefer, T.; Sebastian, R.; Penner, G. *Can. J. Chem.* **1988**, *66*, 1787.

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the low-temperature carbon-13 spectra of **4** in a 3:1 mixture of acetaldehyde and acetone.[15] At room temperature, chemical shifts relative to internal TMS of δ 159.06, 141.05, and 99.22 were found for the carbonyl carbon, the alkene carbon bonded to oxygen, and the CH_2 alkene carbon, respectively. Upon cooling, the first two carbons decoalesce, and chemical shifts at −110 °C of δ 159.51 and 163.58 were found for the carbonyl carbon and δ 140.23 and 145.07 for the alkene carbon attached to oxygen. The carbonyl carbons of the *E* conformations of alkyl[2,16] and aryl formates[7] have been found to absorb downfield of the *Z* conformations, and the minor (downfield) signals for both carbons of **4** were also assigned to the *E* isomer. From electronic integration, populations of 0.05 and 0.95 were found for the *E* and *Z* conformations, and populations at the coalescence temperature for the carbonyl group (−87 °C) were estimated with the assumption that $\Delta G°$ (0.95 kcal/mol) is independent of temperature. Rate constants of 620 and 47 s^{-1} were obtained[17] at −87 °C for the $E \rightarrow Z$ and $Z \rightarrow E$ conversions, and the corresponding barriers are $8.3_4 \pm 0.2$ and $9.2_9 \pm 0.2$ kcal/mol. These values are close to the barriers found for phenyl formate (8.1 and 8.5 kcal/mol).[7]

Molecular-orbital calculations for the *E* conformations indicate[11,12] that **4c** is more stable than **4d** and, as noted above, **4a** is lower in energy than **4b**. The conformational equilibrium can therefore be represented as **4a** ⇌ **4c**; any small amounts of **4b** or **4d** could not be detected separately in the slow-exchange carbon spectrum, as their signals would be averaged with **4a** or **4c**, respectively.

The estimate[12] that **4a** is at least 2.3 kcal/mol more stable than the next conformation is shown to be too high for solutions in a polar solvent. The finding of a larger population of (*E*)-vinyl formate (0.05) than for (*E*)-methyl formate (0.003)[2] provides evidence that aromaticity is an important effect in stabilizing the *Z* conformations of most esters.[18]

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Registry No. Vinyl formate, 692-45-5.

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(15) Spectra were recorded unlocked at 75.57 MHz, and the signal-to-noise ratio was improved by exponential multiplication of the FID, resulting in a line broadening of 3 Hz. A concentration of 20% by volume was used. Temperatures were measured by replacing the sample with an NMR tube containing solvent and a copper–constantan thermocouple. The accuracy of the thermocouple was checked by measuring the temperature of a pentane slush obtained by adding liquid nitrogen to pentane.

(16) Nakanishi, H.; Fujita, H.; Yamamoto, O. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 214.

(17) Calculated spectra were generated by a VAX computer connected by a modem to an IBM PC equipped with a Radio Shack TRS-80 plotter–printer, and using a dynamic NMR program written by Binsch and Kleier: Binsch, G.; Klier, D. A. *QCPE* **1969**, *11*, 140.

(18) The difference in populations of the *E* isomers for vinyl formate and methyl formate should be larger in the same solvent, as indicated by the two entries for *tert*-butyl formate in Table I.

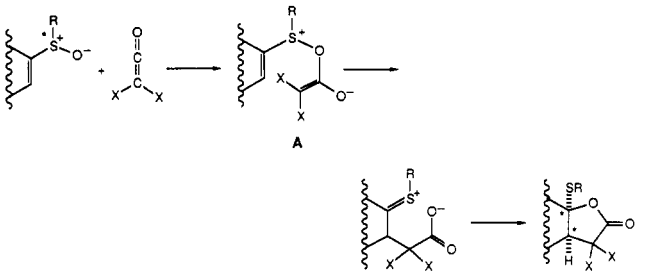
Reactions of Indole Sulfoxides with Dichloroketene: A New Approach to the Physostigmine Alkaloids

Summary: The reactions of 3-(phenylsulfinyl)- and 2-(methylsulfinyl)-*N*-(phenylsulfonyl)indoles with dichloroketene proceed at 0 °C to yield ring-fused butyrolactones **4** and **7**, respectively. Bicyclic indolines such as **7** can serve as intermediates in the synthesis of the physostigmine alkaloids.

Sir: Our recent reports[1] on the enantioselective lactonization of chiral vinyl sulfoxides with haloketenes have established this process as one of the most efficient protocols for chirality transfer from sulfur to carbon atoms. From a mechanistic standpoint this reaction proceeds via a 3,3-sigmatropic rearrangement of vinyloxysulfonium enolate system A as illustrated in Scheme I.

By analogy to other 3,3-sigmatropic rearrangements,[2] it was anticipated that the double bond of a vinyl sulfoxide could be part of a heteroaromatic ring. To this end, we investigated the reactions of indole derivatives having a

Scheme I



A

2- or 3-sulfinyl substituent.[3] At this time we report the successful lactonization of *N*-(arylsulfonyl)indole sulfoxides. Furthermore, the 2-substituted indoles serve as a unique precursors to be medicinally important physostigmine alkaloids **1**, which are anticholinesterases and miotics.[4] More recently, this alkaloid skeleton has been

(1) (a) Marino, J. P.; Perez, A. D. *J. Am. Chem. Soc.* **1984**, *106*, 7643. (b) Marino, J. P.; Fernandez de la Pradilla, R. *Tetrahedron Lett.* **1985**, *26*, 5382. (c) Marino, J. P.; Fernandez de Pradilla, R.; Laborde, E. *Synthesis* **1987**, 1088. (d) Marino, J. P.; Laborde, E.; Paley, R. *J. Am. Chem. Soc.* **1988**, *110*, 966.

(2) For a general review, see: Hill, R. K. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press, Inc.: New York, 1984; Chapter 8, p 503 in Vol. 3 (Part B).

(3) The analogous 2- and 3-(methylsulfinyl)benzofurans did not undergo the ketene–lactonization reaction at temperatures up to 110 °C. Only starting sulfoxides were recovered.

(4) For reviews, see: (a) Robinson, B. *The Alkaloids*; Manske, R. H. F., Ed.; Academic Press: New York, 1968; Vol. X, Chapter 5. (b) Robinson, B. *The Alkaloids*; Manske, R. H. F., Ed.; Academic Press: New York, 1971; Vol. XIII, Chapter 4.

0022-3263/89/1954-1782$01.50/0