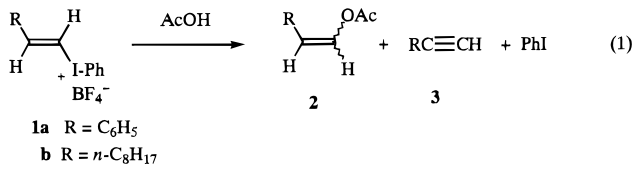
Acetolysis of Styryl and 1-Decenyl Iodonium Salts. Occurrence of Two-Step Mechanism via Vinylenephenonium Ion and One-Step Inversion Mechanism

Tadashi Okuyama* and Masahito Ochiai

Faculty of Engineering Science, Osaka University
Toyonaka, Osaka 560, Japan
Faculty of Pharmaceutical Sciences
University of Tokushima
Shomachi, Tokushima 770, Japan

Received February 21, 1997

Vinyl iodonium salts are good precursors of vinyl cations because of a very high leaving ability of the iodonio group, evaluated to be some 10^6 times as high as that of triflate.[1] However, a primary vinyl cation still seemed difficult to generate from a 1-alkenyl iodonium salt. The latter salt readily undergoes nucleophilic substitution with halide ions leading to a completely inverted product in aprotic solvents.[2] Reaction of the styryl iodonium salt (**1**, R = phenyl) is much slower than that of the 1-alkenyl salt (**1**, R = alkyl) and results in more of the elimination product. However, prolonged reaction of (*E*)-styryl(phenyl)iodonium tetrafluoroborate (**1a**)[3] in acetic acid was found to lead to mainly the retained substitution product ((*E*)-**2a**), while that of (*E*)-1-decenyl(phenyl)iodonium tetrafluoroborate (**1b**)[3] led to exclusively the inverted product ((*Z*)-**2b**). The retained product (*E*)-**2a** was assumed from labeling experiments to be formed from the intermediate vinylenephenonium ion, while the inversion product (*Z*)-**2** is considered to result from a one-step in-plane (S_N2) route.



(1)

1a R = C_6H_5
b R = *n*-C_8H_{17}

Reaction of **1b** in (unbuffered) acetic acid was carried out at 50 °C, and only the single isomer of **2b** and accompanying iodobenzene were obtained in ca. 50% yield[4] after 28 h. Any sign of the other isomer of **2b** or other products was not found by VPC or ^{1}H NMR. The stereochemistry of the **2b** obtained is assumed to be a *Z* configuration from the ^{1}H NMR spectrum;[5] the coupling constant between the olefinic protons (J = 6.4 Hz) and chemical shifts are compared with relevant data. Thus, the substitution of **1b** at the vinylic carbon occurs exclusively with inversion of configuration.

Reaction of **1a** is much slower; only 2.2% yield of **2a** was obtained after 76 h at 50 °C. The reaction at 70 °C for 7 days gave 37% of **2a** and 4.5% of **3a** as well as accompanying iodobenzene (55%). The substitution product **2a** comprises two isomers at a ratio of 85:15; the main isomer is assigned to an *E* configuration and the minor one to *Z* by ^{1}H NMR (Figure 1a).[6]

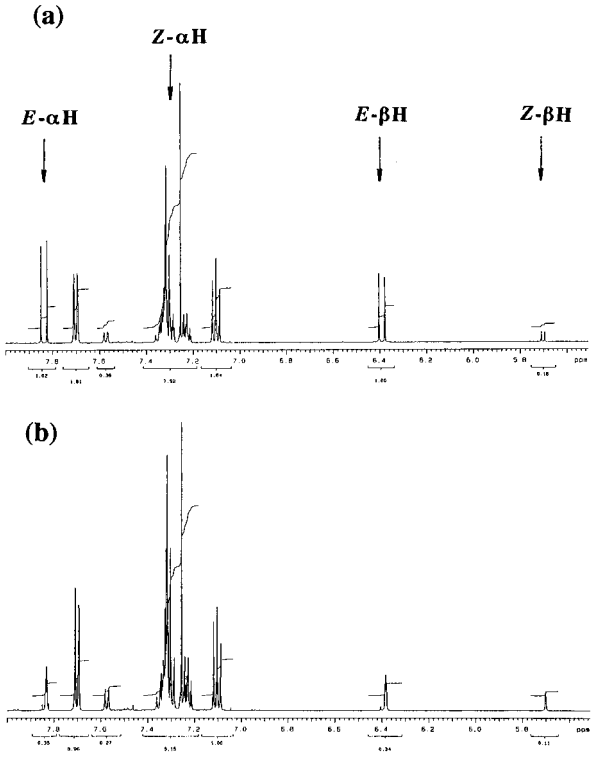


Figure 1. ^{1}H NMR spectra of the product mixtures obtained from the reactions of **1a** (a) and the α-deuterated **1a** (b) in acetic acid at 70 °C for 7 days. The spectra were recorded at 500 MHz on a Varian INOVA 500 spectrometer.

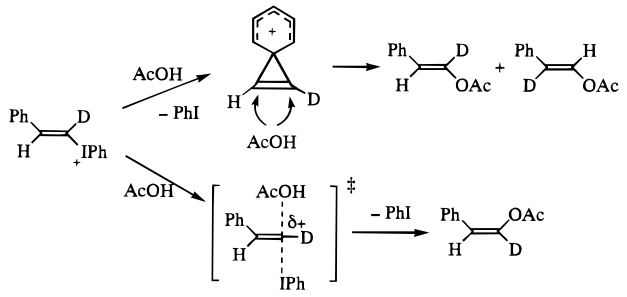
The α-deuterated **1a**[7] undergoes similar reaction in acetic acid at 70 °C, resulting in the same isomeric mixture (by VPC) of the monodeuterated **2a** (GC MS). The ^{1}H NMR spectrum of the product mixture (Figure 1b) shows that a deuterium is distributed equally both at the α and *β* positions of (*E*)-**2a** while it is essentially located only at the original α position of the *Z* isomer of **2a**. The former conclusion may be obvious from the signals for the olefinic protons (6.39 and 7.84 ppm). Both doublet signals coalesce essentially into slightly separated triplets coupled with the other olefinic deuterium and the integral intensities are both about one-half that expected from the intensity of the signal for the acetyl group. The latter conclusion regarding (*Z*)-**2a** is less obvious. The signal for the α proton even of the protium product (7.29 ppm) is not clearly seen (Figure 1a), but it overlaps with the phenyl signals as the 2D NMR clearly indicates (not shown). The spectrum of this region of the deuterium products (Figure 1b) is simpler than that of the protium counterpart (Figure 1a), suggesting the disappearance of the α proton, if we examine the spectra closely. The signal for the *β* proton (5.70 ppm) is a broad singlet due to the deuterium coupling, and the intensity is about one-third that of the acetyl signal. When the NMR data is examined in another way, the relative integral intensity of the acetyl signals for (*E*)-**2a** and (*Z*)-**2a** obtained from the deuterated substrate conforms to the relative VPC peak area (85:15), but that of the *β* protons is low, 0.34:0.11 = 46:15. The signal intensity of the α proton (0.35) of (*E*)-**2a** is about one-half that calculated and nearly equal to that of the *β* proton (0.34).

Scrambling of the D/H isotope in (*E*)-**2a** is most reasonably interpreted by the formation of the symmetric vinylene-

(1) Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. *J. Am. Chem. Soc.* **1995**, *117*, 3360.
(2) Ochiai, M.; Oshima, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7059.
(3) The iodonium salts were obtained as described previously. Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095.
(4) Yields of the products were determined by VPC using tetradecane as an internal standard.
(5) ^{1}H NMR ($CDCl_3$) of (*Z*)-**2b**: *δ* 2.14 (s, CH_3CO), 4.86 (dt, *β*-H, J = 6.4, 12.7 Hz), 6.98 (dt, α-H, J = 6.4, 1.6 Hz), 0.9, 1.3, 1.5 (octyl).
(6) ^{1}H NMR ($CDCl_3$), (*E*)-**2a**: *δ* 2.19 (s, CH_3CO), 6.39 (d, *β*-H, J = 12.7 Hz), 7.84 (d, α-H, J = 12.7 Hz). (*Z*)-**2a**: *δ* 2.27 (s, CH_3CO), 5.70 (d, *β*-H, J = 7.1 Hz), 7.29 (d, α-H, J = 7.1 Hz).
(7) The α-deuterated **1a** (the isotopic purity = 98.8%) was prepared by Lewis acid-catalyzed boron−iodine(III) exchange reaction of (*E*)-styrylboronic acid-α-*d* with (diacetoxyiodo)benzene. This reaction will be reported elsewhere.

S0002-7863(97)00560-X CCC: $14.00

Scheme 1



phenonium ion which undergoes nucleophilic attack at the α and β carbons with an equal probability (Scheme 1).

Although formation of α,β-dimethylvinylenephenonium intermediate has been inferred from kinetic and stereochemical results on solvolysis of 1-methyl-2-phenyl-1-propenyl triflate,[8] the present results clearly show formation of a primary vinylenephenonium ion.

The lack of the isotopic scrambling in (*Z*)-**2a** implies that this inverted product arises from direct reaction of acetic acid with **1a** but not from the intervention of the ionic intermediate. The external participation of a weakly nucleophilic acetic acid must occur competitively with participation of the internal phenyl group. The direct pathway may be classified as the in-plane vinylic S_N2 mechanism. A possibility of this pathway has recently been suggested from theoretical calculations.[9,10] The present observations provide some experimental evidence in addition to the observed inversion of nucleophilic substitution.[2,11,12] Reaction of **1b** with acetic acid resulting in a complete inversion may also be accommodated with the vinylic S_N2 mechanism. This process may involve ionization followed by immediate nucleophilic trapping of the ion before the departure of the leaving iodobenzene. However, this possibility is unlikely from the results of reaction rates; acetolysis of **1b** is 2 orders of magnitude faster than that of **1a**. 1-Decenyl cation should be less stable, if it were formed, than the phenonium ion, and the ionization mechanism should have resulted in the reverse relative rates. Nucleophilic substitution of **1b** with halide ions leading to complete inversion[2] seems also to be accommodated with the in-plane S_N2 mechanism, as will be published elsewhere.

Acknowledgment. We thank Takema Nagaoka and Hiroshi Okuda for their technical assistances. This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (07240103) from the Ministry of Education, Science, and Culture, Japan.

JA9705607

(8) Stang, P. J.; Dueber, T. E. *J. Am. Chem. Soc.* **1977**, *99*, 2602. Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107.

(9) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 5961.

(10) Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1995**, *117*, 2297.

(11) Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1993**, *115*, 4527.

(12) Shainyan, B. A.; Rappoport, Z. *J. Org. Chem.* **1993**, *58*, 3421.