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FACILE OXY-VINYL [1,3]SHIFT PROMOTED BY TETRABUTYLAMMONIUM FLUORIDE: A HYDROINDOLE SYNTHESIS[1)]

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The oxy-vinyl alkoxides generated from trimethylsilyloxy-vinyl (or methoxyvinyl)-cyclobutanes by tetra-n-butylammonium fluoride undergo a facile [1,3]shift to produce a two-carbon unit ring expansion compound under extremely mild conditions. Thus, 7-trimethylsilyloxy-7-vinyl(or methoxyvinyl)-2-azabicyclo[3.2.0]heptane-3,4-diones readily gave hydroindole derivatives in good yields.

KEYWORDS——— [1,3]shift; oxy-vinyl [1,3]shift ; tetra-n-butylammonium fluoride; TBAF-induced shift; trimethylsilyloxy-vinyl-cyclobutane; trimethylsilyloxy-methoxyvinyl-cyclobutane; hydroindole

Oxy-vinyl [1,3]shift is a useful synthetic tool to effect two-carbon unit ring enlargement. The reaction is achieved by heating a trialkylsilyloxy-vinyl derivative at high temperature.[2)] An alkoxide in an oxy-vinyl system is known to accelerate the reaction enormously, thus making it possible to reduce the reaction temperature. The accelerative effect has been observed in potassium,[3),4),5)] sodium[4)] and lithium alkoxides,[5)] which are usually generated in situ by action of metal hydride or alkyl lithium on trialkylsilyloxy-vinyl compounds. However, the method when applied to the compounds sensitive to strong alkali is not expected to avoid undesirable side reactions. we now report that quarternary ammonium alkoxides generated from the Si-O bond fission of trimethylsilyloxy-vinyl compounds by tetra-n-butylammonium fluoride (TBAF) causes a facile [1,3]shift to produce a two-carbon unit ring expansion compound under extremely mild conditions.

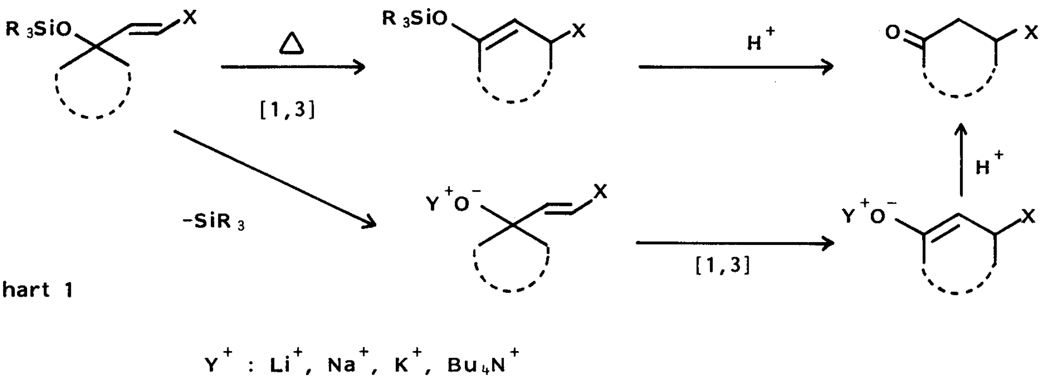
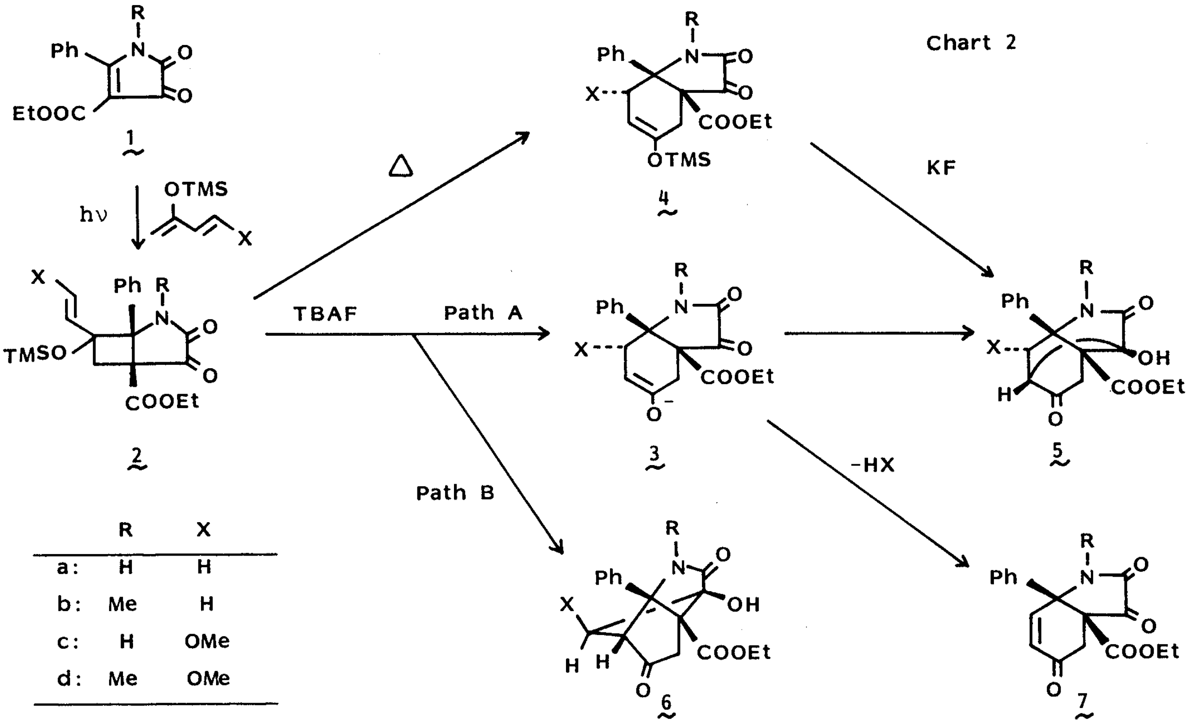


Chart 1

Y^+ : Li^+, Na^+, K^+, Bu_4N^+

In a previous work we have shown[6)] that the trimethylsilyloxy-vinyl-cyclobutanes 2a-2b, photoadducts of the dioxopyrroline 1 to 2-trimethylsilyloxybutadiene, rearranged in refluxing toluene for several hours giving rise to the enol ether 4a-b, the [1,3]shift products. When the same substrate 2 was treated with TBAF in tetrahydrofuran at -30°C for several minutes, a similar [1,3]shift (Path A) occurred predominantly, though a [1,2]shift ring expansion reaction (Path B) was observed as a side reaction. Thus, 2a and 2b yielded the ketol 5a and 5b[6)] as the major and the isomeric ketol 6a and 6b as the minor products, respectively (see Table 1). 5 is an intramolecular aldol condensation product of the enolate 3 resulting from the expected [1,3]shift, and 6 is a product of an intramolecular Prins type cyclization with concomitant [1,2]shift. (Details of the latter reaction will be discussed in a separate paper.)[7)] In contrast to TBAF, potassium hydride gave a poor result; 2a gave only a complex mixture when treated in THF at 0°C.



	R	X
a:	H	H
b:	Me	H
c:	H	OMe
d:	Me	OMe

Chart 2

Table 1. TBAF Induced and Thermal Rearrangement of 2a-d

	TBAF induced shift				Thermal shift		
	Conditions		Yield(%)		Conditions[a)]		Yield(%)[b)]
	Temp.(°C)	Time	5([1,3]shift)	6([1,2]shift)	Temp.(°C)	Time	5([1,3]shift)
2a	-30°	10 min	57	28	120°	3 h	50 (58)[d)]
2b	-30°	2 min	63	32	140°	4 h	52 (51)[d)]
2c	-30°	3 min	88	-	120°	3 h	57
2d	-30°	2 min	83[c)]	-	150°	3 h	44

a) Heating in toluene in a sealed tube.

b) Yields were obtained by the weight of the ketols 5 isolated after treatment of the resulting enol silylether 4 with KF.

c) The enone (7b) was isolated.

d) Reported yield in ref.6.

In the case of the trimethylsilyloxy-methoxyvinyl cyclobutane 2c (mp 168-170°C) and its N-methyl derivative 2d (mp 150-152°C), photoadducts of 1-methoxy-3-trimethylsilyloxy-butadiene to 1a and 1b, respectively, the [1,3]shift (path A) occurred exclusively, followed by two competitive reactions: the intramolecular aldol condensation or β-elimination of the methoxy group. Occurrence of either path seems to depend on the nature of substrates. Thus, 2c gave the ketol 5c$^{8)}$ and 2d formed the enone 7$^{8)}$ in excellent yield. For comparison, we carried out the thermal reaction of 2c and 2d. Heating of 2c and 2d in toluene afforded [1,3]shift products 4c-d (characterized as 5c and 5d respectively after treatment with potassium fluoride), however in lower yields (Table 1).

As shown in the Table 1, the TBAF method is apparently superior to the thermal method for the oxy-vinyl compounds, though the path B rearrangement occurred as a side reaction in some instances. In thermolysis, the fragmentation reaction of the cyclobutanes to the dioxopyrroline 1 was always observed as a side reaction, thus decreasing the yield of [1,3]shift product. In conclusion, the TBAF-induced alkoxy-accelerated [1,3]shift of oxy-vinyl compounds proceeds under extremely mild conditions and is applicable for an alkali sensitive polyfunctional compound, promising that this methodology, when coupled with photocycloaddition, will provide a novel annulation approach to six-membered carbocyclic compounds from cyclic enones and trimethylsilyloxy-butadienes.

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8) All new compounds gave correct molecular formula.
5c: mp 201-203°C. IR(Nujol) cm^{-1}: 3200, 1760, 1740, 1715. ^{1}H-NMR(CDCl$_3$) δ: 0.99 (3H, t, J=7 Hz), 2.61(2H, ABq, Δδ=0.24 ppm, J=20 Hz), 2.91(1H, br s), 3.28(3H, s), 4.01(2H, q, J=7 Hz), 4.18(1H, s), 7.44(5H, s).
5d: mp 164-166°C. IR(Nujol) cm^{-1}: 3375, 1765, 1730, 1710. ^{1}H-NMR(CDCl$_3$) δ: 1.15 (3H, t, J=7 Hz), 2.34(1H, d, J=19 Hz), 2.60(1H, dd, J=1 and 19 Hz), 2.77(3H, s), 2.88(1H, d, J=1 Hz), 3.39(3H, s), 4.35(1H, s), 7.2-7.5(5H, m).
7b: mp 170-171°C. IR(Nujol) cm^{-1}: 1775, 1745, 1720, 1680. ^{1}H-NMR(CDCl$_3$) δ: 1.06 (3H, t, J=7 Hz), 3.14(2H, s), 3.16(3H, s), 3.7-4.0(2H, m), 6.31(1H, d, J=10 Hz), 6.84(1H, d, J=10 Hz), 7.2-7.6(5H, m).

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