CHEMISTRY LETTERS, pp. 465-466, 1978. Published by the Chemical Society of Japan

PREPARATION OF VINYL CHLORIDES FROM ENOLIZABLE ALDEHYDES

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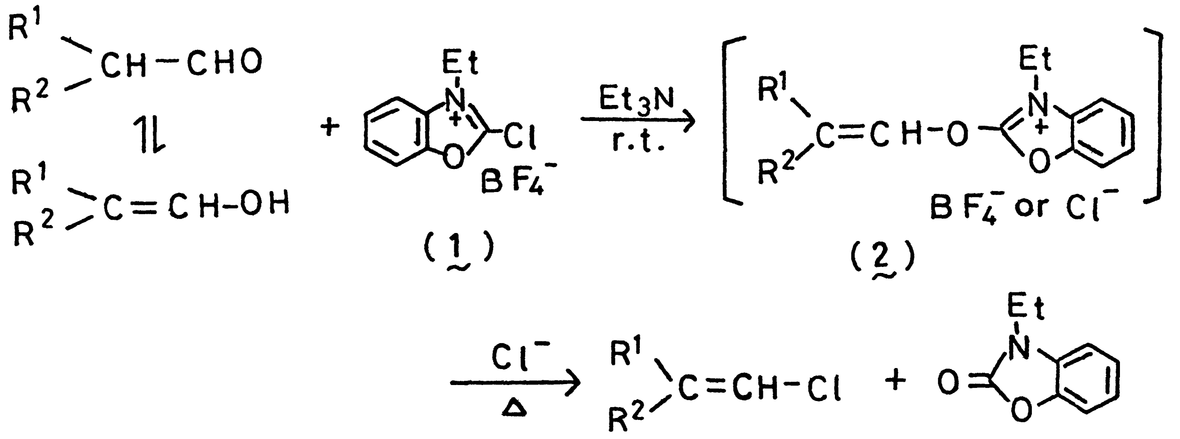
Treatment of enolizable aldehydes with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate, triethylamine and tetraethylammonium chloride affords vinyl chlorides in good yields under mild conditions.

In the course of our synthetic investigation utilizing the onium salts of azaaromatics, 2-chloro-3-ethylbenzoxazolium tetrafluoroborate (1) has been shown to be a useful and specific reagent for the replacement by chlorine or the elimination of certain oxygenated functions.[1), 2), 3), 4)]

We have now found that enolizable aldehydes are easily converted to vinyl chlorides in good yields on treatment with 1 in the presence of tetraethylammonium chloride and triethylamine as shown in the following scheme.



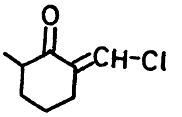
A typical procedure is described for the preparation of 3-chloro-2-phenylacrylonitrile: A solution of triethylamine (1.2 mmol) in 1,2-dichloroethane (5 ml) was slowly added at 0°C under an argon atmosphere to a mixture of α-formylphenylacetonitrile (3, 1 mmol), 1 (1.2 mmol) and tetraethylammonium chloride (1.5 mmol), and the reaction mixture was stirred at room temperature for 1 hr. Then it was refluxed for 2 hrs. and cooled. After evaporation of the solvent, the residue was chromatographed on silica gel to give 3-chloro-2-phenylacrylonitrile (81% yield).

In a similar manner, various vinyl chlorides were prepared in good yields as shown in the Table. The vinyl chlorides gave satisfactory elemental and spectral (ir and nmr) analyses.

Further, it was shown that 3-(s-butylthio)-2-phenylacrylonitrile (86% yield) or β-cyanostyryl propionate (79% yield) was obtained when a dichloromethane solution of 1 (1.2 mmol), 3 (1 mmol) and triethylamine (3.2 mmol) was treated with

2-butanethiol (2 mmol) or propionic acid (2 mmol) at room temperature for 24 hr. The results indicate that active intermediate (2), formed from enolizable aldehyde and 1 at room temperature, in turn is attacked by nucleophiles to afford the corresponding vinyl derivatives.

Table. Synthesis of Vinyl Chlorides from Enolizable Aldehydes

Vinyl Chloride			NMR spectrum[a]	
R^1	R^2	Yield (%)	δH(vinyl)[b] E , Z	integral ratio E:Z
C_6H_5-	-CN	81	7.12(s), 7.21(s)	2:1
p-Cl-C_6H_4-	-CN	80	7.08(s), 7.33(s)	2:1
C_6H_5-	-$CO_2C_2H_5$	77	6.52(s), 7.50(s)	1:1
C_2H_5-	-COC_6H_5	88	6.75(s)	E only
$CH_3(CH_2)_3$-	-COC_6H_5	82	6.77(s)	E only
C_6H_5-	-COC_6H_5	88	6.62(s), 6.85(s)	1:10
		81	6.99(t, J=2Hz)	E only

a) $CDCl_3$ solutions using TMS as internal reference.

b) Stereostructural assignment was made by estimating the substituent shielding coefficients of olefines[6].

There appeared no reports concerning the general method for the direct preparation of vinyl chlorides from enolizable aldehydes. For example, it was reported[5] that attempts to convert 3-oxoaldehydes to the corresponding β-chlorovinyl ketones by the use of efficient chlorinating reagent, triphenylphosphine in carbon tetrachloride, were unsuccessful.

The present method opened a new and general route to the synthesis of vinyl chloride from enolizable aldehyde by using 2-chlorobenzoxazolium salt.

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(Received February 28, 1978)