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A NEW METHOD FOR THE TRANSFORMATION OF 1,2-EPOXIDES TO 1,2-DICHLOROALKANES

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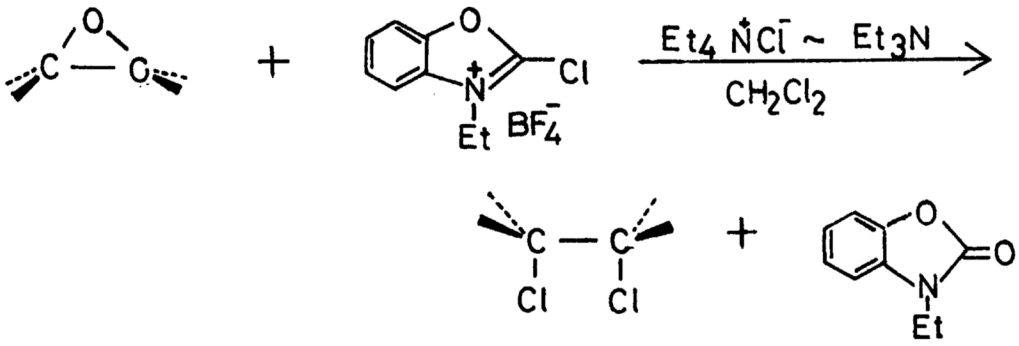
Treatment of 1,2-epoxides with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate and tetraethylammonium chloride affords 1,2-dichloroalkanes in good yields under mild conditions with good stereospecificity.

In the course of our synthetic investigation utilizing the onium salts of azaaromatics, 2-chloro-3-ethylbenzoxazolium tetrafluoroborate has been shown to be a useful and specific reagent for the replacement by chlorine or the elimination of certain oxygenated functions. For example, alcohols are converted to alkyl chlorides[1] and formamides are dehydrated to isocyanides in good yields.[2]

We have now found that 1,2-epoxides were easily converted to 1,2-dichloroalkanes in good yields on treatment with 2-chloro-3-ethylbenzoxazolium tetrafluoroborate in the presence of tetraethylammonium chloride and triethylamine[3] as shown in the following equation.

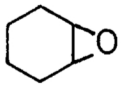
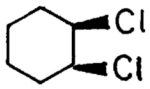


The methods for the preparation of 1,2-dichloroalkanes from 1,2-epoxides in the literature[4] [5] [6] require prolonged heating in a solvent such as pyridine or chloroform for the completion of the reaction. However, according to the present procedure using the 2-chlorobenzoxazolium salt, epoxides are easily converted to the corresponding dichloroalkanes in good yields at room temperature in a stereospecific manner.

The following is a typical procedure for the preparation of 1,2-dichloroalkanes by the present method. To a stirred suspension of 2-chloro-3-ethylbenzoxazolium tetrafluoroborate [1.2 mmol], tetraethylammonium chloride [1.0 mmol], and trans-1,2-diphenyl-1,2-epoxyethane [1.0 mmol] in dichloromethane [4 ml] was added dropwise triethylamine [1.2 mmol] in dichloromethane [2 ml] at 0°C under an

argon atmosphere. The resulting mixture was stirred at room temperature for 48 hr. After evaporation of the solvent under reduced pressure, the residue was directly chromatographed on silica gel eluting with hexane to give 1,2-dichloro-1,2-diphenylethane in 77% yield (dl : meso = 77 : 23).

Table Synthesis of 1,2-Dichloroalkanes from 1,2-Epoxides

1,2-Epoxide	1,2-Dichloroalkane	Reaction Time	Yield (%)
C_6H_5-CH-CH_2 (O)	C_6H_5-CH(Cl)-CH_2(Cl)	2 days	81
trans C_6H_5-CH-CH-C_6H_5 (O)	C_6H_5-CH(Cl)-CH(Cl)-C_6H_5	2 days	77 (dl:meso 77:23)[a]
CH_3-(-CH_2-)$_6$-CH-CH_2 (O)	CH_3-(-CH_2-)$_6$-CH(Cl)-CH_2(Cl)	2 days	75[b]
p-CH_3-C_6H_4-O-CH_2-CH-CH_2 (O)	p-CH_3-C_6H_4-O-CH_2-CH(Cl)-CH_2(Cl)	overnight	95
CH_3-(-CH_2-)$_7$-O-CH_2-CH-CH_2 (O)	CH_3-(-CH_2-)$_7$-O-CH_2-CH(Cl)-CH_2(Cl)	overnight	84
 c)		2 days	58[d] (cis:trans 98:2)[e]

a) The ratio was determined by the integral ratio of nmr spectrum; dl-1,2-dichloro-1,2-diphenylethane, ($CDCl_3$) δ =5.27(s, 2H) and 7.20(s, 10H); meso-1,2-dichloro-1,2-diphenylethane, ($CDCl_3$) δ =5.27(s, 2H) and 7.54(s, 10H).
b) The product obtained by short path distillation (150°C/31~32 mmHg) was concomitant with a trace of 3-ethyl-2-benzoxazolinone.
c) Two molar amounts of tetraethylammonium chloride were used.
d) The products obtained by short path distillation (130°C/30~31 mmHg) consisted of 1,2-dichlorocyclohexane and a small amount of 3-chlorocyclohexene which were detected by nmr, and the yield of 1,2-dichlorocyclohexane was determined by the integral ratio of nmr spectrum.
e) The ratio was determined by g.l.c. technique on a 2m column packed with O.V.17 at 150°C and 40 ml/min of N_2. The retention times were: trans, 54 sec; cis, 72 sec.

It should be noted that the present method is of quite utility; various 1,2-epoxides are easily converted to 1,2-dichloroalkanes in good yields under mild conditions with good stereospecificity by simple procedure using readily available 2-chloro-3-ethylbenzoxazolium tetrafluoroborate.

REFERENCES AND NOTE

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3) The reaction also proceeded in the absence of either triethylamine or tetraethylammonium chloride to give the dichloroalkane in moderate yield.
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