References and Notes

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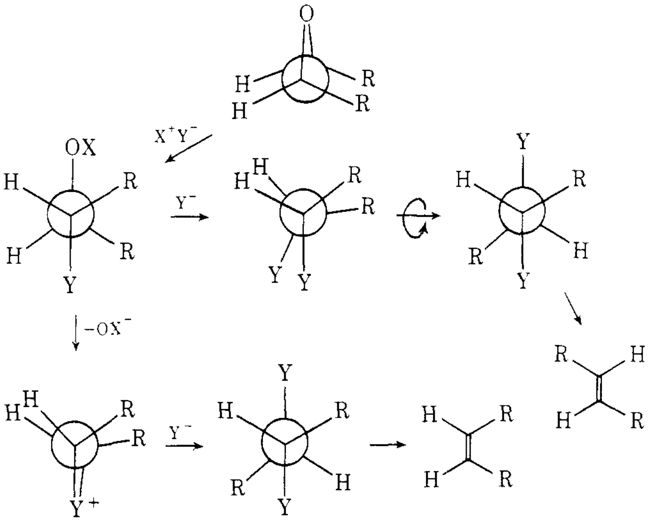
Communications

Conversion of Epoxides to Olefins with Trifluoroacetyl Iodide and Sodium Iodide[1]

Summary: Trifluoroacetyl iodide has been found to react with epoxides in the presence of excess sodium iodide to produce the related olefins in high yield; the reaction stereospecifically generates olefins of the same geometry as the epoxides.

Sir: Several methods of deoxygenating epoxides to produce olefins have been reported. Nonstereospecific procedures include treatment of epoxides with chromous salts[2] or with zinc-copper couple.[3] Stereospecificity is obtained using reagents such as triphenylphosphine selenide,[4] potassium selenocyanate–methanol,[5] hexamethyldisilane–KOMe,[6] and lithium diphenylphosphide.[7] We recently described the conversions of epoxides to *vic*-dihalides with triphenylphosphine dihalides;[8] the dihalides were then reduced to olefins with, for example, zinc. The diastereomer content of the *vic*-dihalide was found to be quite solvent dependent; deviation from the predominant backside displacement of C–O by bromide with increasing solvent polarity was ascribed to internal participation by the bromine which had performed the initial displacement (Scheme I). To the extent that such bridging occurred, the diastereomer of opposite configuration was formed, and the olefin ultimately generated was of the same geometry as that of the initial epoxide.

Scheme I



X^+Y^-
Ph_3PBr, Br
CF_3CO, I

Table I. Reactions of Epoxides with Trifluoroacetyl Iodide

Reactant	Geometry	Product	Geometry	% yield
1,2-Epoxycyclohexane		Cyclohexene		77[a]
1,2-Epoxydecane		1-Decene		91[b]
5,6-Epoxydecane	93% *Z*	5-Decene	93% *Z*	95[b]
5,6-Epoxydecane	94% *E*	5-Decene	95.5% *E*	95[b]
7,9-Epoxy-2-methyloctadecane	97.5% *Z*	2-Methyl-7-octadecene	97.7% *Z*	90[a]
7,8-Epoxy-2-methyloctadecane	97.5% *E*	2-Methyl-7-octadecene	>97% *E*	90[a]

[a] Estimated by GLC. [b] Distilled yield; checked by GLC.

We wished to construct a product from an epoxide that might react exclusively via an onium ion to convert that epoxide to the olefin of the same geometry. Neighboring iodine is, of course, more proficient in interacting with an adjacent carbonium ion than is bromine. However, triphenylphosphine diiodide could not be made to react with aliphatic epoxides.

It was found that trifluoroacetic anhydride (1 equiv) and sodium iodide (1 equiv) reacted exothermically with (*Z*)-7,8-epoxy-2-methyloctadecane[9] (in 1:1 CH_3CN–THF) to produce a β-iodotrifluoroacetate [NMR (CCl_4) δ 4.06 (m, CHI), 4.72 (m, CHO_2CCF_3)] which on exposure to sodium iodide (3 equiv) in the same solvent system for 24 h spontaneously generated iodine, sodium trifluoroacetate, and the corresponding *Z* olefin in 90% yield. Similarly, the corresponding *E* epoxide upon treatment with trifluoroacetyl iodide (generated in situ) and excess sodium iodide produced the *E* olefin, again in 90% yield. In the absence of more definitive data, it is presumed that the yellow–orange solution of anhydride and sodium iodide contains trifluoroacetyl iodide; the epoxides are stable in solutions containing trifluoroacetic anhydride alone. Identification of the gross structure of the olefins was made by comparison with authentic samples;[8] analysis of geometry was accomplished by epoxidation with *m*-chloroperbenzoic acid, and examination of the resulting epoxides by capillary gas chromatography (DEGS, 4 mm × 46 m, 170 °C, helium carrier at 4 mL/min). Retention times were 10.2 (*trans*-epoxide) and 10.8 min (*cis*-epoxide); the initially employed *cis*-epoxide (97.5% cis) provided 97.7% *cis*-olefin, and the *trans*-epoxide (97.5% trans) provided >98% *trans*-olefin. The conversions of several epoxides to olefins with trifluoroacetyl iodide generated in situ from trifluoroacetic anhydride and NaI are given in Table I. It is apparent that the reaction proceeds in high yield and is stereospecific for the epoxides of 1,2-dialkylethenes.

The transformations involved bear comparison with the familiar Prevost reaction in which olefins react with silver acetate and iodine to produce *vic*-acetates by trans addition. The intermediate iodoacetates solvolyze in acetic acid with carbonyl oxygen participation and replacement of iodide by acetate. The carbonyl oxygen of the trifluoroacetyl group, however, is much less nucleophilic, and excess iodide ion is present. Hence, the trifluoroacetate group is replaced either with the intermediacy of an iodonium ion, as indicated in Scheme I, or directly as part of a concerted elimination process initiated by attack of iodide ion upon bound iodine. Both processes lead to the same stereochemical result.

In a typical experiment, sodium iodide, which has been oven dried at 110 °C overnight (4 equiv), is placed in a reaction vessel fitted with a drying tube. Dry acetonitrile and dry tetrahydrofuran (1 mL/mmol of epoxide) are injected into the reaction vessel. Stirring is initiated and trifluoroacetic anhydride (1 equiv) is injected. After 5 min, the deep yellow solution is cooled in an ice bath, and the epoxide (1 equiv) is injected neat. When the reaction is conducted in this manner, no noticeable evolution of heat occurs. After 5 min, the bath is removed and the mixture is allowed to stir for 24 h. The reaction mixtures were worked up by dilution with aqueous $NaHSO_3$ and extraction into petroleum ether, followed by distillation of the olefins. Current work is directed to examining the scope of the reactions of trifluoroacetyl halides and related compounds with epoxides.

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