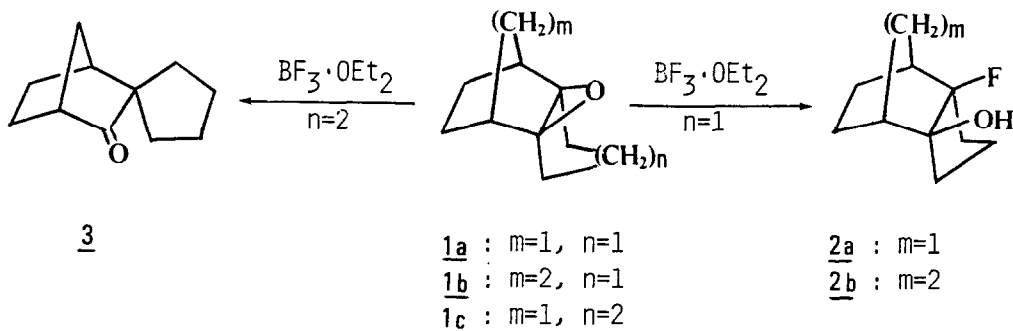


NOVEL FLUORIDE TRANSFER IN THE REACTION OF
 TRICYCLIC EPOXIDES WITH BORON TRIFLUORIDE

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Summary: Reaction of the tricyclic epoxides (1a) and (1b) with boron trifluoride etherate leads to fluorohydrins (2a) and (2b) derived in the novel fluoride transfer, whereas (1c) undergoes isomerization to spiro ketone (3).

The isomerization of epoxides to carbonyl compounds or allylic alcohols has been studied extensively in recent years.¹ Spiro ketones are obtained from acid-catalyzed rearrangement of tetrasubstituted epoxides.² We report here the novel fluoride transfer in the reaction of tricyclic tetrasubstituted epoxides, exo-2,6-epoxytricyclo[5.2.1.0^{2,6}]decane (1a) and 2,6-epoxytricyclo[5.2.2.0^{2,6}]undecane (1b) with boron trifluoride etherate, affording fluorohydrins (2a) and (2b).

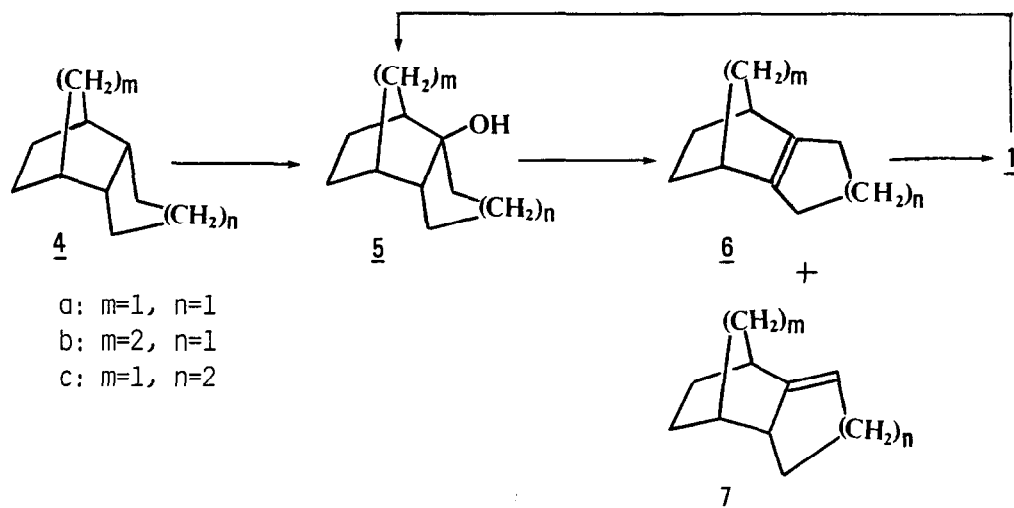


As part of a continuing study of the synthesis and chemistry of tricyclic olefins,³ we synthesized unique tetrasubstituted olefins, tricyclo[5.2.1.0^{2,6}]dec-2(6)-ene (6a),⁴ tricyclo[5.2.2.0^{2,6}]undec-2(6)-ene (6b), and tricyclo[6.2.1.0^{2,7}]undec-2(7)-ene (6c),⁵ and examined the reaction of their epoxides (1) with boron trifluoride etherate.

Dehydration of tertiary alcohols (5), obtained by bridgehead hydroxidation of the corresponding hydrocarbons (4) with *m*-chloroperbenzoic acid,⁶ with *p*-toluenesulfonyl chloride and pyridine at 5 °C gave 6 as the major products

in yields of 61%, 54%, and 56%, respectively, along with the minor positional isomers (7). Without separation, the mixture of olefins was treated with *m*-chloroperbenzoic acid to yield two epoxides from which the major isomers, 1 were isolated by column chromatography. The structures of 1 were determined by the reduction with lithium in ethylenediamine⁷ to the starting alcohols 5 (Scheme 1).

Scheme 1

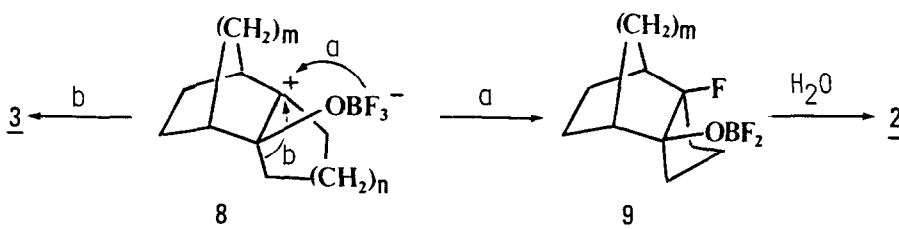


Reaction of 1a (10 mmol) with boron trifluoride etherate (10.6 mmol) in 50 ml of diethyl ether was completed within 5 min at 5 °C to afford fluorohydrin 2a (m.p. 81.5–83.5 °C) as a sole product in 44% yield, and no trace of the rearranged product could be detected. The structure of 2a was assigned on the basis of spectral data [IR (neat) 3580, 3450, 1100, 1055, 960, 940, 900, and 880 cm^{-1} ; ^{13}C NMR (CDCl_3 - SiMe_4 , in p.p.m.), 23.14 (t, $^3J_{\text{F}}=9.4$ Hz), 23.14 (t), 23.69 (t, $^3J_{\text{F}}=7.7$ Hz), 32.48 (t, $^2J_{\text{F}}=25.9$ Hz), 35.30 (t), 38.92 (t), 46.21 (d, $^2J_{\text{F}}=26.4$ Hz), 48.47 (d), 86.94 (s, $^2J_{\text{F}}=12.7$ Hz), 109.67 (s, $^1J_{\text{F}}=197.4$ Hz)⁸; MS (m/z) 170 (1%) (M^+), 102 (100%) ($\text{M}^+-\text{C}_5\text{H}_8$)].

Treatment of 1b under the same reaction conditions gave similarly a single major product, fluorohydrin 2b (m.p. 65–66 °C) in 51% yield. On the contrary, only the rearranged spiro ketone (3)⁹ was obtained from 1c in 48% yield.

A possible mechanism for the formation of 2 and 3 may be as follows (see Scheme 2). Rupture of the epoxide ring with boron trifluoride etherate would give the zwitterionic intermediate (8). The boron trifluoride catalyzed rearrangement of epoxides has been most satisfactorily interpreted in terms of the intermediacy of a discrete carbonium ion.¹⁰ Subsequent transfer of fluoride anion to the cationic center C-2 would lead to fluoroborate (9) (path a), which is hydrolyzed to yield 2. Spiro ketone 3 would be obtained by 1,2-alkyl shift in 8 (path b).

Scheme 2



Such fluoride transfer within zwitterionic fluoroborate has not been previously observed, although intermolecular fluoride transfers have been recently reported in the boron trifluoride promoted reactions of diazoketones¹¹ and of alkyl hypohalites with alkenes.¹² The behavior of 1a and 1b is in strong contrast to the observed isomerisation of 1c and other tricyclic epoxides giving spiro ketones.^{2b, 3f} In 1a and 1b, the carbon migrations to afford spiro ketones or the loss of proton to give allylic alcohol¹³ appears to be unfavorable due to the instability of the products.¹⁴ Further efforts are in progress to determine the effects of the ring strain and the steric hindrance on the reactivity of tetrasubstituted epoxides.

References and Notes

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4. All new compounds gave satisfactory elemental analyses and spectral data. Selected physical and spectral data are as follows.
1a: IR (neat) 1295, 1128, 950, 905, 815 cm^{-1} ; ^{13}C NMR (CDCl_3) δ 23.04 (t, 2C), 24.92 (t, 2C), 27.92 (t), 34.90 (t), 38.53 (d, 2C), 69.16 (s, 2C).

- 1b: IR (neat) 1305, 1160, 920, 880, 810 cm^{-1} ; ^{13}C NMR (CDCl_3) δ 21.36 (t) 23.09 (t, 2C), 24.19 (t, 2C), 27.60 (t, 2C), 29.48 (d, 2C), 67.18 (s, 2C).
- 1c: IR (neat) 1300, 1195, 1165, 965, 870, 795 cm^{-1} ; ^{13}C NMR (CDCl_3) δ 21.17 (t, 2C), 22.17 (t, 2C), 24.43 (t, 2C), 29.24 (t), 40.58 (d, 2C), 60.06 (s, 2C). 2b: ^{13}C NMR (CDCl_3) δ 19.78 (t, $^3J_{\text{F}}=5.9$ Hz), 20.33 (t), 21.69 (t), 22.20 (t), 22.38 (t, $^3J_{\text{F}}=8.8$ Hz), 34.04 (d, $^2J_{\text{F}}=22.5$ Hz), 35.15 (d), 35.84 (t, $^2J_{\text{F}}=28.3$ Hz), 38.12 (t), 79.52 (s, $^2J_{\text{F}}=13.7$ Hz), 104.33 (s, $^1J_{\text{F}}=189.5$ Hz). 3: IR (neat) 1735 cm^{-1} ; ^{13}C NMR (CDCl_3) δ 23.90 (t), 25.46 (t), 26.38 (t), 26.77 (t), 32.72 (t), 36.04 (t), 36.43 (t), 46.53 (d), 49.79 (d), 58.96 (s), 168.99 (s). 5c: m.p. 52–53 °C; IR (KBr) 3350, 975 cm^{-1} ; ^{13}C NMR (CDCl_3) δ 16.05 (t), 19.51 (t), 21.00 (t), 21.21 (t), 24.19 (t), 26.90 (t), 36.48 (t), 40.38 (d), 49.21 (d), 51.55 (d), 78.45 (s).
- 6a: ^{13}C NMR (CDCl_3) δ 25.71 (t, 2C), 27.55 (t), 28.01 (t, 2C), 41.90 (d, 2C), 49.55 (t), 149.82 (s, 2C). 6b: ^{13}C NMR (CDCl_3) δ 23.56 (t), 26.68 (t, 4C), 31.21 (d, 2C), 32.87 (t, 2C), 142.27 (s, 2C). 6c: ^{13}C NMR (CDCl_3) δ 23.51 (t, 4C), 26.38 (t, 2C), 45.40 (d, 2C), 46.53 (t), 139.19 (s, 2C).
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