An Unusual Rearrangement of a Diepoxide

Richard D. Chambers, Julian F. S. Vaughan and Steven J. Mullins

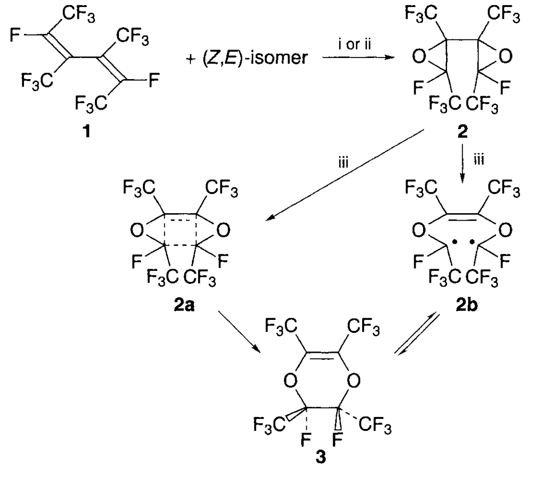
Department of Chemistry, University Science Laboratories, South Road, Durham, UK DH1 3LE

The diepoxide derived from perfluoro-3,4-dimethyl-2,4-diene undergoes quantitative rearrangement, at 200 °C, to the corresponding 1,4-dioxine derivative.

Recently, we described an effective synthesis of the fluorinated diene **1**.[1,2] Subsequently, we explored the synthesis and chemistry of the derived diepoxide, initially as a potential source of new perfluoropolyethers, but a novel rearrangement intervened.

We have investigated two methods for epoxidation of **1**; first the more conventional use of calcium hypochlorite,[3] which indeed gave the diepoxide **2**. Also, we have applied the method described by Meth–Cohn and coworkers,[4] who have developed the procedure using *tert*-butylhydroperoxide/*tert*-butyl-lithium for use with electron deficient systems, not involving fluorine. Indeed this procedure also worked well for synthesis of **2** and, subsequently, we have successfully used the procedure for systems on which calcium hypochlorite was ineffective. One of the surprising features of formation of **2** is that ^{19}F nmr data indicates that it was produced as a single diastereoisomer! Only three sharp resonances were observed for **2**, at δ_F −66.1, CF_3CF, −76.3, CF_3C and −154.7, CF_3CF produced by either method, even though a *mixture* containing mainly the (*Z,Z*) isomer of **1** was used. This indicated that the epoxidation processes are subject to thermodynamic control. Furthermore, the sharpness of the spectra for **2** makes it very unlikely that two diastereoisomers are present, but leaves open the interesting question of why there should be such stereospecificity for the formation of **2** which, at this stage, we are unable to answer.

Remarkably, when we attempted to ring open the diepoxide by heating with alkali-metal fluorides, a smooth rearrangement occurred and subsequently we discovered that the reaction occurs simply by heating at 200 °C. The product, see Scheme 1, showed that **2** had been almost quantitatively converted to perfluoro-2,3,5,6-tetramethyl-5,6-dihydro-1,4-dioxine **3**. This rearrangement is, to our knowledge, unprecedented and could be described either as a concerted process **2a** or possibly proceeding *via* radical intermediates **2b**. The latter mechanism would be reminiscent of the ring opening processes for cyclopropane systems, described by Viehe and coworkers,[5] which occur readily when 'capto-dative' radicals can be formed as intermediates. This would lead to the consideration of trifluoromethyl and oxygen being favourable substituents at a radical centre, as a capto-dative pair.



Scheme 1 *Reagents and conditions*: i, $Ca(OCl)_2$, CH_3CN, room temp., 1 d (64%); ii, $\mathrm{Bu^tOOH}$, BuLi, THF, −78 °C room temp. (70%); iii, sealed tube, 200 °C, 1 d (96%)

So far, we have been unable to establish unambiguously the stereochemistry of **3**; however, the ^{19}F NMR spectrum showed only two signals for CF_3 (δ_F −66.8, $CF_3C{=}C$, −77.3, CF_3CF) and one signal for C–F (δ_F −151.2). This implies high symmetry and further support for a symmetrical system stems from a six bond coupling between trifluoromethyl groups $CF_3C{=}C$ and $CF_3C{-}F$, J = 5.0 Hz, as compared with a value of J = 2.4 Hz for a five bond coupling between $CF_3C{=}C$ and the tertiary fluorine at CF_3CF. This suggests that the trifluoromethyl groups in **3** have a *trans* configuration at the saturated sites and that they have an equatorial conformation, to account for the $^6J > {}^5J$ values. The starting diene **1** has a predominant configuration in which the trifluoromethyl groups are all *trans* and the resultant diepoxide is a single isomer, to which we also attribute the all *trans* configuration. Therefore, the stereochemistry appears to be retained during the rearrangement process but it should be noted that the *trans*-arrangement of trifluoromethyl groups could arise from either concerted or diradical routes, **2a** and **2b**, respectively, because the latter would simply be the product of thermodynamic control. At this stage we have not distinguished between these possibilities.

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