

The reaction of difluorodioxirane with caesium trifluoromethoxide

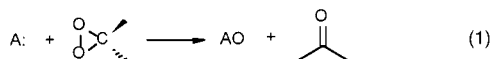
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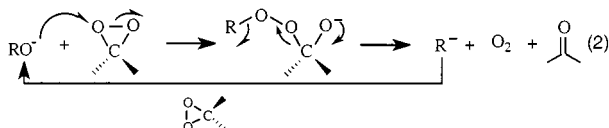
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The reaction of difluorodioxirane with caesium trifluoromethoxide in the presence of CsF forms $\text{CF}_3\text{OOC}(\text{O})\text{F}$ and the new compounds $\text{CF}_3\text{O}(\text{OCF}_2\text{O})_n\text{OC}(\text{O})\text{F}$ ($n = 1-3$); ^{13}C labeling shows that the dioxirane undergoes ring opening at the O–O bond.

Dioxiranes are powerful oxygen transfer reagents which have been studied extensively over the last twenty years.^{1–3} Epoxidations, heteroatom oxidations and C–H insertion reactions are the most investigated reactions of dioxiranes. The heteroatom oxidations are generally explained by an $\text{S}_{\text{N}}2$ type attack of the heteroatom lone pair (A:) on the dioxirane peroxide bond [eqn. (1)].⁴



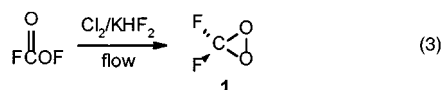
The mechanism is based on the fact that oxygen-type nucleophiles catalytically decompose dioxiranes with evolution of molecular oxygen [eqn. (2)].⁵



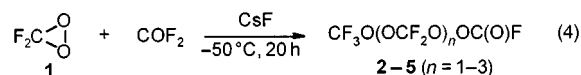
Until now, no peroxide related product has been detected in these reactions. Our recent investigation of difluorodioxirane **1** chemistry provides direct evidence of this mechanism.

Difluorodioxirane is one of the most stable dioxiranes known. The first successful synthesis of **1** was based on the reaction of its isomer fluorocarbonyl hypofluorite $[\text{FC}(\text{O})\text{OF}]$ with ClF in the presence of CsF .^{6†} As expected, **1** is a powerful oxidant and can undergo reactions that are typical of dioxiranes. It readily transfers oxygen to alkenes, forming epoxides and COF_2 in high yield.⁶ Beside this, little is known about the reactivity of **1**. Here we report a very unusual result from the reaction of **1** with COF_2 in the presence of CsF .

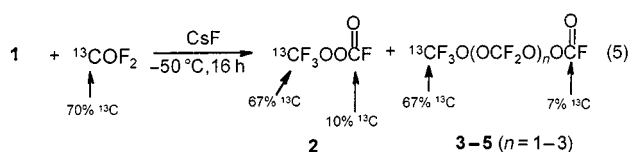
Difluorodioxirane was originally prepared by passing a 1:1 (v/v) mixture of $\text{FC}(\text{O})\text{OF}$ and ClF over a CsF catalyst.⁶ We have improved this method by using Cl_2 and the new catalyst KHF_2 .[‡] A 1:1 (v/v) mixture of $\text{FC}(\text{O})\text{OF}$ and Cl_2 passed through a Teflon tube containing the new catalyst KHF_2 provided **1** in moderate but higher yields (30–50%) [eqn. (3)]. Also the dioxirane **1** prepared by this procedure is easily purified by vacuum fractional condensation as a mixture of **1** (70–90%) and COF_2 (10–30%). The mechanism of this reaction is assumed to be the same as previously proposed.⁶



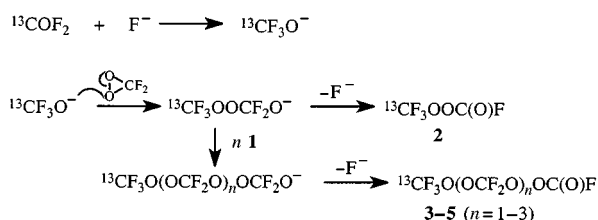
The O–O bond length in **1** is 157.6 pm, and is the longest O–O bond ever calculated and measured.⁷ The relatively weak O–O bond should be easily broken but to date no direct evidence was available for this. Recent studies on the reaction of **1** with COF_2 in the presence of CsF show that dioxirane reacts by ring opening at the O–O bond [eqn. (4)].



We were able to show that the reaction occurred at the oxygen atom of the difluorodioxirane by using ^{13}C labeled COF_2 [eqn. (5)].^{§¶}



A reasonable mechanistic proposal is given in Scheme 1. The well-known trifluoromethoxy anion is first formed by the reaction of carbonyl fluoride with caesium fluoride.⁸ Then an $\text{S}_{\text{N}}2$ -type attack of this anion on the dioxirane peroxide bond occurs to give $\text{CF}_3\text{OOCF}_2\text{O}^-$, which loses fluoride to form **2**,⁹ or reacts further with the dioxirane to form the new oligomeric peroxides **3–5**. The ^{13}C distribution in the products makes it clear that the predominate reaction is the attack of CF_3O^- on the dioxirane at oxygen and not at the more electropositive carbon. Previously we had suggested¹⁰ that reaction of **1** with CsF might form CF_3OO^- and **2** could then be formed by reaction with COF_2 . However this path would lead to the ^{13}C label in the carbonyl group, contrary to what is observed. The small amount of ^{13}C present in the carbonyl carbon arises from secondary reactions of the products, which have been confirmed by additional ^{13}C labeling experiments. These results will be described in a future publication.



Scheme 1

Remarkably the ^{19}F chemical shifts for **2–5** can be assigned from a mixture of the compounds. The NMR data is presented in Fig. 1 for pure **2** and **3** and for **4** and **5** taken from a mixture of **3–5**. Compound **2** is unequivocally identified by comparison with known samples prepared by other routes. For **3–5** the chemical shifts for the CF_3OO and the OOCF_2OO groups are characteristic and show a large shift relative to CF_3O and OCF_2O functions in fluorocarbon ethers. While the chemical shift differences between **2–5** are small, at 188 MHz all the signals except the $\text{C}(\text{O})\text{F}$ are separated and the expected peak integration for each compound is observed. Finally ^{19}F bound to ^{13}C and ^{12}C exhibits substantial isotopic shifts in the ^{19}F NMR in addition to the large $^1J_{\text{F}-^{13}\text{C}}$ coupling, making it trivial to discern the presence of ^{13}C .

A variety of other novel fluorocarbon peroxides can be formed by related reactions with other nucleophiles and the

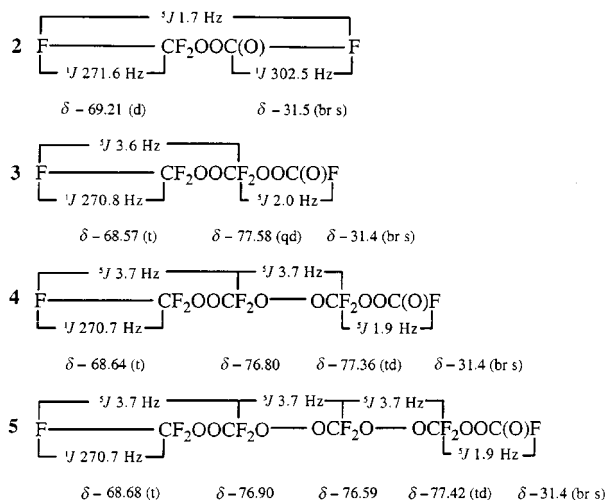


Fig. 1 ^{19}F NMR data for **2–5** (CCl_4 solvent, CFCl_3 reference, external D_2O lock, 188 MHz). Data for **4** and **5** come from a mixture of **3–5**.

chemistry of difluorodioxirane is proving to be quite extraordinary.

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Notes and references

† **CAUTION!** The chemicals employed in this work are hazardous and should only be used by experienced personnel familiar with the safe handling of toxic strong oxidizers.

‡ In a typical reaction a mixture of equimolar amounts (0.5–3.0 mmol) of $\text{FC}(\text{O})\text{OF}$ and Cl_2 at 23°C were passed at reduced pressure through a Teflon FEP tube (35×1 cm outer diameter) containing 20 g of pelletized KHF_2 catalyst. The calculated flow rate of the mixture through the tube was $0.37 \text{ cm}^3 \text{ s}^{-1}$. The effluent exited into a trap cooled to -196°C and under dynamic vacuum. The gases condensed at -196°C were vacuum distilled several times through traps at -145 and -196°C . This procedure gave **1** in

the -196°C trap, contaminated with a small amount of COF_2 . *Selected data* for **1**: $\delta_{\text{C}} -92.4$ (s), $\delta_{\text{F}} -20.7$ (d, $^1J_{\text{C-F}} = 283.3$) $\delta_{\text{C}} 119.5$ (t). The original report of the ^{19}F NMR data in ref. 6 is in error.

§ Two 500 ml ss cylinders fitted with ss valves were connected to the vacuum line through a PFA tee closed by an ss valve. The cylinders were evacuated and one was filled with 7 mmol of fluorine gas and the other with 7 mmol of ^{13}CO (99% ^{13}C). At 22°C , the cylinders valves were then opened to the closed and evacuated tee in the order fluorine/ ^{13}CO . After 4 h, the contents of the two cylinders were passed through the tee into a trap cooled to -196°C under dynamic vacuum. Unreacted F_2 and ^{13}CO passed through the -196°C trap and through a soda lime scrubber. The contents of the -196°C trap were then passed through -140 and -196°C traps under dynamic vacuum to give pure $^{13}\text{COF}_2$ (3.5 mmol, 50%) in the -196°C trap. *Selected data* for $^{13}\text{COF}_2$: $\delta_{\text{C}} 133.8$ (t); $\delta_{\text{F}} -20.7$ (d, $^1J_{\text{C-F}} 311.3$); $\nu_{\text{max}}/\text{cm}^{-1}$ 1882.1, 1208.2, 957.9, 749.5, 648.6.

¶ The reactions of **1** with COF_2 and $^{13}\text{COF}_2$ were carried out in a 150 ml ss cylinder which contained 2 g of dry powdered CsF. Compound **1** (0.3 mmol) and carbonyl fluoride (0.3 mmol) were then vacuum transferred into the cylinder cooled to -196°C . The mixture was then allowed to warm to -50°C over 1 h and remained at -50°C for 16–20 h. The products were separated by vacuum fractional condensation through traps at -90 , -110 , -130 and -196°C . The -90°C fraction consisted of **3**, **4** and **5** (0.03 mmol), the -110°C fraction consisted of **3** (0.03 mmol), the -130°C fraction consisted of **2** (0.07 mmol) and the -196°C fraction consisted of COF_2 (0.3 mmol). Compounds **2–5** were identified by NMR (see Fig. 1) and IR. *Selected data* for **2**: $\delta_{\text{C}} 122.6$ (q, CF_3 , $^1J_{\text{C-F}} 271.6$); 141.2 [d, $\text{C}(\text{O})\text{F}$, $^1J_{\text{C-F}} 302.9$]; $\nu_{\text{max}}/\text{cm}^{-1}$ 1874, 1254, 1209, 1153, 1005, 930, 750, 614.

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