Synthesis of Perfluoro-oxydiacetic Acid

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Summary A convenient synthesis of the suggested polymer intermediate perfluoro-oxydiacetic acid is described.

THE synthesis of polymers containing perfluoroether linkages has received considerable attention in recent years.[1,2] Perfluoro-oxydialkanoic acids, $O[(CF_2)_nCO_2H]_2$, may be used as the starting materials in some approaches to the synthesis of such polymers. In particular a recent publication cites the use of perfluoro-oxydiacetic acid as an intermediate in exploratory polymer synthesis.[3] These workers made perfluoro-oxydiacetic acid by oxidizing 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran, obtained from the reaction of sulphur tetrafluoride with dichloromaleic anhydride.[4] The alternative published syntheses start from perfluoro-*N*-fluoromorpholine, which was prepared in 8% yield by electrochemical fluorination of morpholine.[5] We have recently used a synthesis of perfluoro-oxydiacetic acid which is more convenient than those reported.

The synthesis consists essentially of exchange fluorination of perchloro-2,5-dihydrofuran and subsequent oxidation of the products 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran and perfluoro-2,5-dihydrofuran.† Perchloro-2,5-dihydrofuran may be prepared by chlorination of furan,[6] or from hexachlorobuta-1,3-diene *via* ethoxylation, chlorination, and $FeCl_3$-catalysed cyclization.[7] The exchange fluorination can be accomplished by several reagents.[8] With anhydrous hydrogen fluoride (nickel-lined autoclave,

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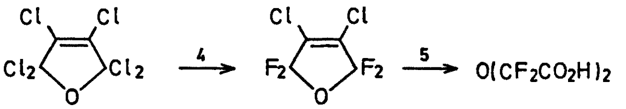
† Elemental analyses, n.m.r., i.r., and mass spectra of new compounds were consistent with the assigned structures.

90°, 15 hr.) 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (23%) was obtained. With potassium fluoride in *N*-methyl-2-pyrrolidone at 195°, perfluoro-2,5-dihydrofuran (49%) and 2,2,4-trichloro-3,5,5-trifluoro-2,5-dihydrofuran (5%) were obtained. Fluorination with antimony trifluoride–antimony pentachloride (molar ratios $SbF_3 : SbCl_5 : C_4Cl_6O$, 4 : 1 : 2) gave 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (77%); the yield was lower in the absence of antimony pentachloride and 2,3,4-trichloro-2,5,5-trifluoro-, *cis*- and *trans*-2,3,4,5-tetrachloro-2,5-difluoro-, and 2,3,4,5,5-pentachloro-2-fluoro-2,5-dihydrofurans were also obtained. A common product of the work-up of these fluorination reactions was 4-hydroxy-2,3-dichloro-4,4-difluorobut-2-enoic acid γ-lactone. Oxidation of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran with potassium permanganate in acetone[9] gave perfluoro-oxydiacetic acid (82%); the same product was obtained from the oxidation of perfluoro-2,5-dihydrofuran (b.p. < 0°) in a rocking autoclave (25°, 41 hr.) with aqueous alkaline permanganate, albeit in lower yield (66%).

We have found the following route the most convenient:

$$CCl_2{=}CCl{-}CCl{=}CCl_2 \xrightarrow{1} CCl_2{=}CCl{-}CCl{=}CClOC_2H_5 \xrightarrow{2}$$

$$(CCl_3{-}CCl{=}CCl{-}CClO \rightleftharpoons CCl_2{=}CCl{-}CCl_2{-}CClO) \xrightarrow{3}$$



1. NaOEt in EtOH; 2. Cl_2; 3. $FeCl_3$; 4. SbF_3–$SbCl_5$; 5. $KMnO_4$ in acetone.

Using this route, perfluoro-oxydiacetic acid has regularly been prepared in yields greater than 60% from perchloro-2,5-dihydrofuran. The previous authors report the synthesis of hexachloro-2,5-dihydrofuran from hexachlorobuta-1,3-diene in yields of 62%, but we have obtained only 48%.

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