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SHORT COMMUNICATION

Simultaneous Fluorination and Functionalization of Neopentane and 1,4-Dioxane

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The reaction of fluorine/oxygen mixtures on hydrocarbon polymers has been shown to convert pendant methyl groups to acid fluoride groups [1]. The degree of functionalization was shown to vary directly with the fluorine/oxygen ratio [1].

In subsequent work on small molecules under lower temperature conditions in the low-temperature-gradient (LTG) reactor developed by Adcock, Marachin and Lagow [2], it was found that functionalization occurred with more difficulty because of presumably the approximately 100°C lower operating temperatures. Yields were also lower because crosslinking which occurs in both cases tends to reduce the volatility of products resulting in low volatility residues in the reactor. Single product yields of approximately ten percent were typical of hydrocarbon molecules possessing many equivalent sites. In all cases tried it was necessary that 'oxy-fluorination' result in convergence of substitution isomers to as few final products as possible. Such behavior is a feature of the two cases presented, neopentane and 1,4-dioxane. Difunctionalization of neopentane was induced by continuous oxygen introduction until the final stages of the process. When oxygen was present only in the first half of the reaction sequence and then shut off, monofunctionalization and crosslinking occurred along with moderate yields of F-neopentane. When oxygen was present only in the last half of the reaction reduced functionalization occurred, fluorination proceeded in high yields and crosslinking was almost eliminated. The use of a 17KV silent discharge (Figure 1) in the fluorine/oxygen inlet stream resulted in an increase of functionalized materials but absolute yields remained about constant since crosslinking also increased. Those reactions in which increased functionalization occurred also exhibited increased amounts of hydrogen containing materials. It was always necessary to stop the flow of oxygen and expose the volatile materials to pure elemental fluorine as they were volatilized out of the reactor. Failure to do so produced even greater quantities of hydrogen containing materials and concomitant reduction in the perfluorinated materials. The general course of the neopentane





runs can be summarized in Scheme A[3]. The numbers in parenthesis are glc assays and indicate molar amounts relative to F-neopentane. The yields of F-neopentane rarely exceeded 15% of theoretical assuming only fluorination. The total mass of products collected rarely exceeded 50% of the mass expected assuming only F-pivaloy1 fluoride was formed; this was undoubtedly due to crosslinking of molecules resulting in involatile 'wax like' films observed to form on the copper packing in the reactor. In general four major glc peaks were isolated in the ratios given except that compounds II and V were coincident on both 15% QF-1 and 15% SE-52 (Analabs) columns and were not separated but analysed by  $^{19}\mathrm{F}$  NMR (South Carolina NMR Facility, Columbia, S.C. under NSF-CHE78-18723).

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SCHEME A

In addition small quantities of compounds which oxidize ferrocene (orange) to ferricenium (blue) were ubiquitous impurities always present in small amounts. On the basis of the ESR studies of R. E. Florin[4] it seems reasonable to assume, at least in the unactivated cases, that these impurities are fluoroperoxy derivatives although fluoroxy species cannot be ruled out. Florin noted that ESR spectra characteristic of peroxy radicals appeared rapidly in hydrogen containing polymers when treated with dilute fluorine. He attributed these peroxy radicals to the reaction of molecular oxygen impurity with undetectibly low, steady state concentrations of hydrocarbon and fluorocarbon radicals [4].

The reaction of oxygen/fluorine mixtures with 1,4-dioxane leads to diglycolyl difluoride as principal functionalized product. Other principal products included F-1,4-dioxane, and 2-Hydry1-F-1,4-dioxane [5]. Assayed yields of diglycolyl difluoride approached twenty percent but isolated yields were much lower (3-4%) due to the more difficult work up. Diglycolyl difluoride is the only functionalized product isolated since induction of a carbonyl at position two and at positions two and six yield that product while induction at positions two and five or two

and three result in destructive hydrolysis of the ring system forming carbonate: and oxalates or their fluorinated precursors. The higher raw yields were not surprising because dioxane is a very easy molecule to fluorinate by the LTG met The dioxane ring is much more accessible to fluorine presumably because of the oxygens." In contrast cyclohexane proved very difficult just as its fluorination is much more difficult vis a vis 1,4-dioxane. The dioxane runs may be summariz in Scheme B.



In each of the above reaction runs (summarized by schemes A+B) products we identified by comparison with authentic samples prepared by LTC fluorination of the parent hydrocarbons. Detailed LTG fluorination procedures are cited in the literature.<sup>3,5</sup> Oxyfluorination consisted of admitting 0.5 cc/m molecular oxyge concurrent with fluorine until the next to last fluorination zone began to warm from  $-78^{\circ}$ C. The oxygen was then shut off and only pure fluorine admitted. The discharge experiments passed pure oxygen through a specially made ozonizer tube before mixing with fluorine although  $F_2/0_2$  mixtures were used in two cases whic caused extensive erosion of the TFE dielectrics in the tube.

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m F}$  and  $^1{
m H}$  mmr spectra of the various compounds is gratefully acknowledged.

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  Characterization of Compounds: (a) VI and VII see references 3c and 3d; (b)
- for compound VIII see J. R. Trockmorton, J. Org. Chem., 34, 3438 (1969) and R. E. Banks, E. D. Burling, B. A. Dodd and K. Mullen, J. Chem Soc., C, 1969 1706; (c) the <sup>19</sup>F NMR of diglycolyl fluoride in CCl<sub>4</sub> versus ext. CFCl<sub>3</sub> was a triplet at  $\phi$  = +80.01 ppm (relative intensity 2) and a pentet at  $\phi$  = -10.( ppm intensity 1); J = 2.1 hz.

By contrast LTG direct fluorination of cyclohexane produces a large excess of hydrogen containing fluorocyclohexanes (containing up to four hydrogens) relative to the perfluorinated cyclohexane.