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LIQUID ALKOXIDES OF A PERFLUOROTERTIARY ALCOHOL AND THEIR DERIVATIVES

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SUMMARY

Sodium and lithium alkoxides of $(CF_3)_2CFOCF_2CF_2C(CF_3)_2OH$ have been prepared in high yields by the addition of sodium hydride to the alcohol or in the case of the lithium salt through the addition of $(CF_3)_2C{=}O$ to the organolithium compound $(CF_3)_3CFOCF_2CF_2Li$. These salts react with active halides e.g. PCl_3 or cyanuric chloride to yield completely substituted products.

INTRODUCTION

Lithium [1,2,3], sodium [2,4-6] and potassium [2] salts of perfluoroalkyltertiary alcohols have been previously reported. These alkoxides react at a more favorable rate than the free alcohols, with a variety of active halogen compounds and provide a convenient method for the synthesis of many classes of compounds [6]. The volatile nature of these alkoxides, particularly of lithium and sodium derivatives, and their solubility in organic solvents has led to the inference that they are more covalent than ionic in nature [2].

We now report the preparation and reaction of lithium (II) and sodium alkoxides (III) of a perfluoroalkylethertertiary alcohol, 2,6-bis(trifluoromethyl)-5-oxa-heptan-2-ol (I). The preparation of this tertiary alcohol in 49.3% yield has been described earlier through a Grignard reaction [7]. These alkoxides provide perhaps the first examples of alkali metal alkoxides which are liquids at ambient temperature.

RESULTS

The lithium alkoxide (II) was prepared from an organolithium reagent and hexafluoroacetone in 94% yield. It was a colorless viscous

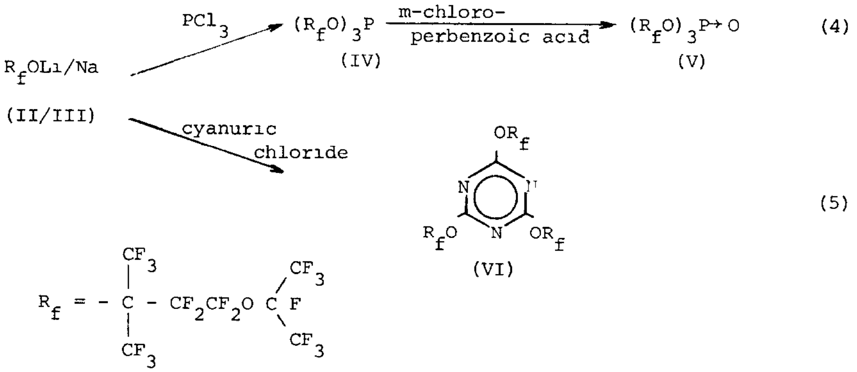
$$(CF_3)_2CFOCF_2CF_2I + n\text{-}C_4H_9Li \xrightarrow[-78°]{Et_2O} C_4H_9I + (CF_3)_2CFOCF_2CF_2Li \qquad (1)$$

$$(CF_3)_2CFOCF_2CF_2Li + (CF_3)_2C{=}O \longrightarrow \underset{(II)}{(CF_3)_2CFOCF_2CF_2C(CF_3)_2O\ Li} \qquad (2)$$

$$(CF_3)_2CFOCF_2CF_2C(CF_3)_2OLi + H^+ \longrightarrow \underset{(I)}{(CF_3)_2CFOCF_2CF_2C(CF_3)_2OH} \qquad (3)$$

liquid which could be distilled under reduced pressure without decomposition. The lithium alkoxide could be hydrolyzed with 3N HCl to yield the tertiary alcohol (I) in 72% overall yield based on the starting iodide. The sodium alkoxide (III) was prepared in 91.5% yield from the free tertiary alcohol by its reaction with sodium hydride in diethyl ether. It was also a colorless viscous liquid which could be distilled under reduced pressure without decomposition.

These alkoxides were reacted with phosphorus trichloride to obtain the corresponding phosphite (IV). Oxidation of the phosphite (IV) to phosphate (V) was accomplished by refluxing with m-chloroperbenzoic acid in $ClCF_2CFCl_2$. Both the phosphite and phosphate were resistant



to aqueous hydrolysis (two-phase) at room temperature over a period of one month. However, on refluxing with excess water for 24 h., about 45% of the phosphite had hydrolyzed to the alcohol while under identical conditions only 3% of the phosphate was affected.

Both alkoxides reacted readily with cyanuric chloride in refluxing 1:1 MeCN - $ClCF_2CFCl_2$ to yield sym.- 2,4,6-tris(perfluoroalkoxy)triazine (VI). The hydrolytic stability of the triazine was investigated by heating a solution in 1:2 THF-$ClCF_2CFCl_2$ at 90-100° in a pressure vial with H_2O, 12N HCl and KOH in amounts sufficient for complete hydrolysis: After heating for 20 h., the amounts of triazine hydrolyzed in neutral, acidic and basic media were 5.5%, 16.5% and 100% respectively.

EXPERIMENTAL

$(CF_3)_2CFOCF_2CF_2C(CF_3)_2OLi$ (II) (nc)

n-Butyllithium (0.148 mole, hexane soln.) was slowly added during 1 h. to a stirred diethyl ether solution (200 ml) of $(CF_3)_2CFOCF_2CF_2I$ (61.8 g; 0.15 mole) cooled to -78° and kept under an atmosphere of nitrogen. Hexafluoroacetone (35.0 g; 0.21 mole) was added to the organolithium compound, below the surface of the soln. during 3 h. The contents were then slowly allowed to warm up to room temperature overnight. The solvent and excess hexafluoroacetone were removed under reduced pressure. The flask had to be heated on a water bath while subjecting it to high vacuum to remove the last traces of n-BuI formed in the reaction. The colorless viscous liquid residue in the flask weighed 64.5 g (yield 94%). The crude lithium alkoxide was fractionated under reduced pressure to yield the pure product boiling at 155-157°/0.3 mm, as a colorless liquid, which was preserved in a nitrogen atmosphere. Analysis: Found: C,20.96;H,0.15;Li, 1.1% [AA Analysis];$C_8F_{17}O_2Li$ requires C,20.96;H,0.0%;Li,1.53%. Mass spectral analysis (chemical ionization) gave no parent ion peak at 458; however $(M\text{-}OLi)^+$ at 435 was found. IR spectrum did not show any absorption due to -OH group.

$(CF_3)_2CFOCF_2CF_2C(CF_3)_2OH$ (I)

To the lithium alkoxide (II) prepared as described above (225.0 g; 0.498 mole) was added slowly 6N HCl (90 ml) with stirring during 30 min. An exotherm was observed and stirring was continued for a period of 3 h. The lower layer of I formed was separated. The aqueous layer was extracted with $ClCF_2CFCl_2$, solvent evaporated and the small amount of the alcohol obtained combined with the lower layer. Conc. H_2SO_4(3.0 ml) was added to the alcohol and distilled to obtain 172.0 g (yield 76%) of pure I boiling at 123-124°. (lit B.P. 123-124°) [7]. It was identical in all respect to an authentic sample. Overall yield of the alcohol calculated from the starting iodide was 72%.

$(CF_3)_2CFOCF_2CF_2C(CF_3)_2ONa$ (III) (nc)

A 50% suspension of sodium hydride in mineral oil (4.32 g; 0.09 mole) was taken in a dry flask kept under a nitrogen atmosphere and washed 3 times with 50 ml each of anhydrous diethyl ether to remove the mineral oil. It was suspended in anhydrous diethyl ether (100 ml) and the alcohol I (45.2 g; 0.1 mole) in anhydrous diethyl ether (50 ml) added dropwise with stirring to maintain a gentle reflux. Addition took 2 h. The contents were stirred for another 30 min., filtered under nitrogen to remove suspended impurities and the solvent distilled to obtain the crude sodium alkoxide (III) as a turbid viscous liquid. It was distilled under reduced pressure at 155-156°/ 0.1 mm in a yield of 91.5%. Analysis: Found: C, 20.40; H, 0.0%; $C_8F_{17}O_2Na$ requires C, 20.27, H, 0.0%. Mass spectral analysis (chemical ionization) gave no parent ion peak at 474; but $(M\text{-}ONa)^+$ at 435 was found. IR spectrum showed no -OH group and ^{19}F NMR spectrum was consistent with structure.

$[(CF_3)_2CFOCF_2CF_2C(CF_3)_2O]_3P$ (IV) (nc)

$(CF_3)_2CFOCF_2CF_2C(CF_3)_2OLi$ (64.5 g; 0.141 mole) was dissolved in 1:6 dry MeCN-$ClCF_2CFCl_2$ (70 ml) in a nitrogen atmosphere. With stirring, PCl_3(6.46 g; 0.047 mole) in MeCN-$ClCF_2CFCl_2$ (20 ml) was slowly added during 90 min. A white ppt. of LiCl was formed. The contents were stirred for another 30 min. and filtered under nitrogen. The solvent was evaporated in a vacuum evaporator to yield the crude product which had essentially one product peak on GLC analysis. This was distilled under reduced pressure and the colorless liquid boiling at 65-67°/0.03 mm was collected. Yield of pure phosphite was 55.5%. Analysis: Found: C, 20.73; H, 0.09%; calculated for $C_{24}F_{51}O_6P$: C, 20.80; H, 0.0%. Mass spectral analysis showed molecular ion at 1384, and 1365 $(M\text{-}F)^+$. IR and ^{19}F NMR spectra were consistent with structure.

$[(CF_3)_2CFOCF_2CF_2C(CF_3)_2O\ ]_3P{\to}O$ (V) (nc)

$[(CF_3)_2CFOCF_2CF_2C\ (CF_3)_2O\ ]_3P$ (13.84 g; 0.01 mole) was dissolved in $ClCF_2CFCl_2$ (25 ml) and while stirring, a suspension of m-chloroperbenzoic acid (3.0 g; 0.0175 mole) in $ClCF_2CFCl_2$ (25ml) was added dropwise at room temperature. The temperature rose by ∿10°. Addition was complete in 1 h. The contents were stirred for another 4 h. and refluxed on a hot water bath for an additional 4 h. Analysis of the reaction mixture by GLC showed that the oxidation was complete by this time. The contents were filtered and the $ClCF_2CFCl_2$ solution was shaken repeatedly with 5% Na_2CO_3 solution to remove the acid. It was then washed with water and the solvent removed to yield the phosphate as a colorless liquid of over 99% purity as indicated by GLC analysis. B.P. (Siwoloboff) 243-244° (760 mm) yield, 80%. Analysis: Found: C, 20.32; H, 0.13%, calculated for $C_{24}F_{51}O_7P$: C, 20.50; H, 0.0%. Its mass spectrum showed the molecular ion peak at 1400 and the fragmentation was consistent with the phosphate structure. IR and ^{19}F NMR spectra were also consistent with the structure.

$[(CF_3)_2CFOCF_2CF_2C(CF_3)_2O\text{-}\overset{|}{C}{=}N\text{-}]_3$ (VI) (nc)

$(CF_3)_2CFOCF_2CF_2C(CF_3)_2OLi$ (16.1 g; 0.035 mole) was dissolved in 1:1 MeCN-$ClCF_2CFCl_2$ (50 ml) and while stirring under nitrogen, was heated to reflux. Freshly recrystallized cyanuric chloride (2.14 g 0.0116 mole) dissolved in 1:1 MeCN-$ClCF_2CFCl_2$ (50 ml) was added dropwise to the boiling solution during 1 h. Slow precipitation of LiCl was noticed. Refluxing was continued for a total period of 50 h. during which samples were withdrawn periodically and analyzed by GLC. At the end of this period, most of the lithium alkoxide (II) had been used up and there was noted a phase separation. The lower layer consisted essentially of the trisubstituted triazine containing about 2% of the disubstituted product as indicated by GLC/MS analysis.

The reaction mixture was diluted with $ClCF_2CFCl_2$ to solubilize the mixture, filtered to remove the LiCl and in order to destroy the small amount of lithium alkoxide (II) still present was agitated with 1N.HCl for 10 min. The organic layer was separated, and the solvents removed under reduced pressure to obtain the crude product (VI) as a pale yellow liquid. It was distilled under reduced pressure to yield the pure sym-2,4,6-tris(perfluoroalkoxy)triazine as a colorless liquid boiling at 130-131°/0.15 mm. On cooling, it solidified to a white solid melting at 29-30°C. Yield 77.5%. Analysis: Found: C, 22.72; H, 0.11; N, 2.95%. Calculated for $C_{27}F_{51}N_3O_6$, C, 22.64: H, 0.0; N, 2.935%. Mass spectral analysis gave the molecular ion peak at 1431. $(M\text{-}F)^+$ at 1412 and $(M\text{-}OR_f)^+$ at 980 were also observed. Its IR and ^{19}F NMR spectra were consistent with structure.

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