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EXPLOSION OF THE LITHIUM SALT OF A PROPARGYL ETHER CONTAINING FLUORINE

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SUMMARY

In the course of a work-up procedure a substantial quantity of Li $C\equiv C-CH_2-OCF_2CF_2H$ exploded. We advise that lithiated fluorochemicals should be prepared and handled with great precautions.

Little is known on the stability of acetylenic lithium compounds bearing fully or partially fluorinated substituents. 3,3,3-Trifluoropropynyllithium has been shown to be stable up to 0°C in ether solution [1], and small quantities of $C_5F_{11}C\equiv CLi$ could even be isolated in solid form and dried at room temperature [2] .

It has been reported [3] that the reaction of propargyl alcohol in the presence of its sodium salt with tetrafluoroethylene in dimethoxyethane leads to $HC\equiv CCH_2OCF_2CF_2H$ (I). However, when we reacted propargyl alcohol with TFE in dimethylformamide using potassium hydroxide as the catalyst a mixture of (I) and of the novel allenyl ether $H_2C=C=CHOCF_2CF_2H$ (II) was obtained in a molar ratio of 4:6 and a total yield of 75 %. This mixture could be distilled at atmospheric pressure without noticeable decomposition but no complete separation of the two isomers could be achieved. Since all attempts at a base-catalyzed rearrangement of (I) into (II) failed, compound (II) was separated by the following procedure using metal-hydrogen exchange:

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To a stirred mixture of (I) (0,14 mole) and of (II) (0,18 mole) in 50 ml of diethylether a solution of CH_3Li (0,14 mole) in 90 ml of ether was added dropwise at 0°C under argon. After the evolution of methane had ceased, a pale yellow solution was obtained. (II) together with the solvent were then removed at 0°C under reduced pressure and were condensed in receivers cooled with dry ice. Redistillation of the volatiles gave pure (II) boiling at 76°C which was identified by ^1H and ^{19}F-NMR-spectra. The $LiC{\equiv}CCH_2OCF_2CF_2H$ remaining as a wet slurry in the reaction flask was hydrolysed to regenerate (I) after having been stored for 2 days at room temperature.

When the preparation described above was repeated on a threefold scale, a violent explosion occured at the moment when most of the volatiles had been removed and a white precipitate of the lithium salt had formed. A co-worker suffered severe injuries from glass splinters and the pressure wave, and had to be medically treated in hospital for 10 days. It is unclear whether this explosion of $LiC{=}CCH_2\ OCF_2\ CF_2\ H$ was triggered by an air leakage or by other causes. It is clear however that lithium salt is obviously a very hazardous compound.

Warning:

Lithium acetylides containing fluorinated groups should only be prepared at low temperatures (at least below -20°C) and handled in form of dilute solutions and in small quantities. Protective measures such as thick-meshed wire gauze and safety screens are strongly recommended.

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