

## Novel molecules and industrial processes inspired by G.H. Cady's research on hypofluorites

Darryl D. DesMarteau<sup>a,\*</sup>, Walter Navarrini<sup>b</sup>, Alessandro Zedda<sup>b</sup>, Antonio Russo<sup>b</sup>,  
Vittorio Montanari<sup>b</sup>

<sup>a</sup> Department of Chemistry, Clemson University, Clemson, SC 29634-1905, USA

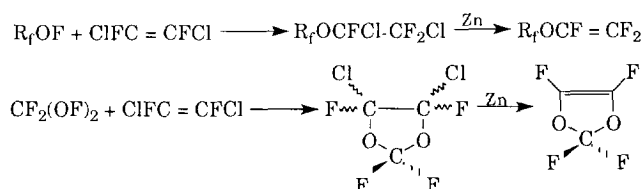
<sup>b</sup> CRS, Ausimont, Via S. Pietro 50, 20021 Bollate (Milano), Italy

*Keywords:* Hypofluorites; Novel reactions; Industrial processes

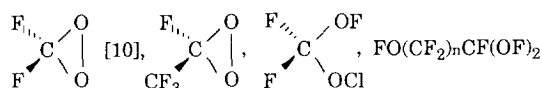
The first reported compound containing an oxygen–fluorine bond was OF<sub>2</sub> reported by Lebeau and Damiens in 1927 [1]. The second unequivocal example was FONO<sub>2</sub> reported by Cady in 1934 [2]. Perhaps due to the explosive nature of FONO<sub>2</sub>, few investigators have carried out research in this field and, by 1959, Cady listed only 11 examples of known or claimed compounds containing oxygen–fluorine bonds [1]; eight of these examples were prepared by Cady and his coworkers. Of these compounds, trifluoromethyl hypofluorite, CF<sub>3</sub>OF, first reported by Kellogg and Cady in 1948 [3], was a seminal discovery.

The high stability of CF<sub>3</sub>OF and its energetic nature led to extensive research in the synthesis of fluorocarbon hypofluorites beginning in the late 1950s, as potential high-energy oxidants for rocket propulsion. This work, particularly that by scientists at 3 M Co. and at Rohm and Haas Co., was reported beginning in 1965 [4]. The latter work reinforced the fact that hypofluorites of carbon were possible in a wide variety of structures. It also demonstrated the catalytic fluorination of carbonyl fluoride with AgF<sub>2</sub>, first observed by Cady, could be very effectively extended to a wide variety of carbonyl compounds using alkali metal fluorides in place of AgF<sub>2</sub> [5].

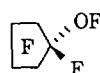
Cady recognized that CF<sub>3</sub>OF was a potentially important compound and he obtained a US patent [6]. However the first commercial use of CF<sub>3</sub>OF and other hypofluorites has only occurred recently, long after the lifetime of the patent. Based in part on research that showed that CF<sub>3</sub>OF could be added to a variety of alkenes [7], Ausimont have developed commercial processes based on R<sub>f</sub>OF for the preparation of fluorinated vinyl ethers [8] and extended this to novel dioxoles using CF<sub>2</sub>(OF)<sub>2</sub> and other bis(hypofluorites) [9].



On the basis of the above commercial developments and on a continuing interest in the synthesis and chemistry of hypofluorites, recent research has led to a number of novel results. In a fitting tribute to Professor G.H. Cady, the synthesis of several novel compounds will be presented. In several cases these compounds owe their origin to earlier work by Cady. Novel compounds will include



and



along with interesting reactions of CF<sub>3</sub>OOCF<sub>2</sub>OF, FOCF<sub>2</sub>OOCF<sub>2</sub>OF, (CF<sub>3</sub>)<sub>2</sub>C(OF)<sub>2</sub> and FC(O)OF with alkenes.

### References

- [1] G.H. Cady, in *XVIIIth Int. Congr. Pure Appl. Chem.*, Butterworths, London, 1969, Vol. 1, pp. 205–213.
- [2] G.H. Cady, *J. Am. Chem. Soc.*, 56 (1934) 2635.

- [3] K.B. Kellogg and G.H. Cady, *J. Am. Chem. Soc.*, **70** (1948) 3986.
- [4] M. Lustig and J.M. Shreeve, *Adv. Fluorine Chem.*, **7** (1973) 175.
- [5] M. Lustig, A.R. Pitochelli and J.K. Ruff, *J. Am. Chem. Soc.*, **89** (1967) 2841.
- [6] G.H. Cady and K.B. Kellogg, US Patent 2689254, 1954; [*Chem. Abs.*, **49** (1954) 11681].
- [7] K.K. Johri and D.D. DesMarteau, *J. Org. Chem.*, **46** (1981) 5081.
- [8] G. Guglielmo and G.P. Gambaretto, US Patent 4400872, 1990; [*Chem. Abs.*, **109** (1988) 112428].
- [9] W. Navarrini and B. Letanzio, US Patent 5245054, 1993; [*Chem. Abs.*, **117** (1992) 234003].
- [10] A. Russo and D.D. DesMarteau, *Angew. Chem., Int. Ed. Engl.*, **32** (1993) 905.