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Best oxygen transfer agent organic chemistry has to offer - HOF/CH₃CN

Most oxidants are metal oxides such as CrO₃, KMnO₄ and alike. Compounds containing the peroxide moiety (-O-O-) serve occasionally either as oxidants or oxygen transfer agents, mainly as reagent for epoxidation of certain olefins. The problem with most orthodox oxygen transfer agents is that they are relatively weak (a weak electrophilic oxygen) and need a strong nucleophilic center in order to react successfully. The only imaginable compound with strong electrophilic oxygen is one where the oxygen is bound to an element which is more electronegative than itself and this is possible only when it is bonded with fluorine. HOF is known for more than 50 years and made by passing F₂ through ice. It is very unstable and decomposes in 10 minutes even at -100°C making it unsuitable for any synthetic purposes. When however, we passed dilute fluorine in nitrogen (about 10%) through aqueous acetonitrile an oxidative solution was obtained which proved to be the complex of HOF with CH₃CN (HOF•CH₃CN). This complex is stable at 0°C for more than an hour allowing a wide array of chemical syntheses to be executed. This complex is able to transfer its oxygen to many substrates and produce many unknown oxides which could not be made before despite continues efforts for many years. Among these reactions we will mention phenanthroline-N,N-dioxide, perfluorinated sulfones, All-S,S-dioxothiophenes including their oligomers (important ingredients in electronics), epoxidation of electron poor olefins, oxidation of vicinal amines to vic-dinitro derivatives, success in making the elusive N,N-dioxopyridazine and many more. In addition, since the reacting oxygen originates from the water molecule, it is relatively simple and cheap to constructing alcohols with the isotope.

References

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Webinar

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Biography

Shlomo Rozen was born in Bulgaria and immigrated to Israel as a small child. He received his Ph.D. from the Hebrew University of Jerusalem and then spent 3 years in the Research Institute for Medicine and Chemistry, Cambridge, MA, under Nobel laureate D. H. R. Barton, where he began work with elemental fluorine. In 1976, he joined the School of Chemistry at the Tel Aviv University where he assumed the position of Professor of Chemistry in 1989. On multiple occasions he had held a position of visiting scientist at the Central Research Department of the DuPont Company. His main goal in chemistry is to demonstrate that elemental fluorine and reagents derived from it are very useful in general organic chemistry, as well as in fluorine chemistry and chemists should discard their unjustified fears and prejudice against this long known but somewhat neglected element.