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IMPROVED OXIDATION PROCEDURE WITH AROMATIC PEROXYACIDS[1]

F. Camps, J. Coll, A. Messeguer and M.A. Pericás

Instituto de Química Bio-Orgánica (C.S.I.C.)
Jorge Girona Salgado s/n . Barcelona-34. SPAIN.

Summary: *The application of the m-Chloroperbenzoic acid-potassium fluoride system in the Baeyer-Villiger oxidation of aromatic aldehydes and in the epoxidation of olefins has been studied.*

The use of fluoride ions as anionic activators by strong hydrogen bond formation with acid substrates is well documented in organic synthesis[2-6]. However, to our knowledge, this interaction with peroxycarboxylic acids has so far not been reported. In the present communication, we describe our preliminary results on the study of the m-chloroperbenzoic acid-potassium fluoride system in oxidation reactions.

We have observed that addition of activated potassium fluoride (1h, 100°/0.1 torr), in amounts ranging from 50-100% molar excess referred to initial m-CPBA, to the crude CH_2Cl_2 reaction mixtures resulting from conventional Baeyer-Villiger and epoxidation procedures, and stirring the mixture 1h at room temperature led to complete precipitation of m-CPBA and m-CBA. From the acid-free filtrates the corresponding reaction products can be isolated by standard methods.

This simplified work-up procedure avoids the usual acid removal by basic aqueous treatment which can decrease yields by promoting undesirable side reactions or by loss of water soluble products. Results of this application in the Baeyer-Villiger reaction on different substrates are summarized in Table 1.

Likewise, we have studied the performance of the preformed insoluble m-CPBA-KF complex in the above reactions. In the baeyer-Villiger oxidation, formation of formates was somewhat slower than that exhibited by the conventional procedure (*i.e.* 30% conversion of piperonal was observed after 24 h treatment with 100% molar excess of 1:1/m-CPBA-KF complex in CH_2Cl_2 at room temperature).

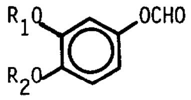
On the other hand, epoxidation rates of olefins with the preformed complex were satisfactory enough to warrant further study for preparation of acid labile epoxides. Reactions were carried out by addition of olefin (2 mmole) to a 1:1/m-CPBA-KF complex (6 mmole) in CH_2Cl_2. After stirring at room temperature overnight, the reaction mixture was filtered and fresh activated KF (6 mmole) was added to the filtrate to ensure complete elimination of the acids. Filtration and solvent evaporation at reduced pressure afforded crude epoxides (see Table 2).

The appearance of strong bands at 2100 and 1500 cm^{-1} in the IR spectra of m-CPBA and m-CBA-KF complexes (KBr), agree with the occurrence of strong hydrogen-fluoride bond interactions [2]. However, easy recovery of the aromatic acids from the complex suspended in water could be achieved by extraction with an organic solvent.

This "solid phase" epoxidation procedure can compete advantageously with the use of perbenzoic acids chemically bound to insoluble polystyrene polymers [7,8] and with the two phase epoxidation system in the presence of aqueous phosphate buffer [9]. Further work is in progress to study regioselective epoxidations and stabilization of other peroxyacids.

TABLE 1

Formates from substituted benzaldehydes



R_1	R_2	Yield*
CH_3	CH_3	90
—CH_2—		95
CH_3	H	77
H	CH_3	79

* based on pure (>99%) distilled product (GLC, NMR)

TABLE 2

Epoxidation of olefins

Substrate	Epoxide*
Cyclohexene	> 95%
Styrene	> 95%
α-Methylstyrene	> 95%
E-β-Methylstyrene	> 95%
Indene	70%**

* determined by GLC and NMR
** 25% of secondary products

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