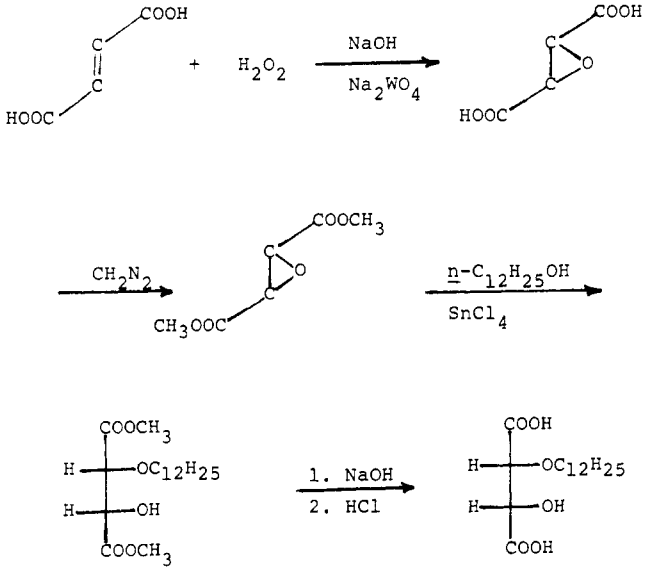
Scheme I. Synthesis of *O*-*n*-Dodecyl-*erythro*-Tartaric Acid[a]



[a] The threo diastereomer was prepared in a similar fashion by starting with maleic acid.

The above analysis implies that conformations *erythro*-**2** and *threo*-**2** predominate for the two diastereomers and that, consequently, the erythro form should possess a larger J_{AB} than the threo form. This is exactly what is observed (4.2 vs. 2.1 Hz). The generally low values for the vicinal coupling constants are undoubtedly related to the well-known effect of electronegative substituents.[4] We see an example of this effect in the compound shown in Figure 3[5] for which J_{AB} = 5.5 Hz and J_{BC} = 2 Hz. Our data and interpretation are reasonable with respect to these numbers.

The conformational stability of the tartrates upon micellization differs from the cases mentioned above [1,2] where perturbations are clearly observed. Even with these, however, the changes are small from an energy standpoint. We conclude that the head-group units within the Stern layer of micelles must be loosely packed and well separated by water. This is completely consistent with our "porous cluster" model[6-8] in which the micelle is viewed as a disorganized assemblage with rough surfaces, water-filled pockets, and no intimate contact among head groups.

Experimental Section

Coupling constants were obtained by averaging ten tracings from a Varian EM-390 spectrometer set at a sweep width of 2 ppm. Surface tension data were secured with the aid of a Fisher Tensiomat.

***O*-*n*-Dodecyl-*erythro*-tartaric Acid and *O*-*n*-Dodecyl-*threo*-tartaric Acid.** Since direct *O*-alkylations of tartaric acid failed (NaH or BuLi, RBr or ROTs, DMF), we utilized the pathway shown in Scheme I. Epoxidation of furmaric acid (to give ultimately erythro compound) and maleic acid (to give ultimately threo compound) was carried out by using the procedure of Payne and Williams.[9] The diacids suspended in ether were then esterified with diazomethane at 0 °C to give dimethyl *trans*-epoxysuccinate [mp 70–72 °C (lit.[10] mp 73 °C)] and dimethyl *cis*-epoxysuccinate [bp 110 °C (0.75 mm)]. Ring opening of the epoxides to form the dodecyl ethers failed in our hands using: (1) dodecanol plus H_2SO_4 catalyst;[11] (2) dodecanol plus boron trifluoride etherate catalyst;[12] (3) sodium dodecoxide in DMF or THF. However, the desired products were obtained as colorless oils (which were not further purified) with $SnCl_4$ as the catalyst (0.04 mol of dimethyl epoxysuccinate, 0.08 mol of *n*-dodecanol, and 0.64 g of $SnCl_4$ heated with stirring at 85 °C for 1 h and at 115 °C for 3 h). Hydrolysis of the methyl esters was accomplished with 3.5 M NaOH in refluxing methanol for 2.5 h. The erythro diacid melted at 147–148 °C (white crystals from water), gave a neutralization equivalent of 158.5 (calcd 159.2), and had an elemental analysis as follows: C, 59.86; H, 9.58 (calcd for $C_{16}H_{30}O_6$: C, 60.35; H, 9.50). The threo product melted at 125–127 °C (white crystals from water), gave a neutralization equivalent of 159.1, and had an elemental analysis as follows: C, 60.00; H, 9.32. NMR spectra confirmed the structure of the products.[13,14]

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Registry No. *O*-Ethyl *erythro*-tartrate dianion, 83693-40-7; *O*-ethyl *threo*-tartrate dianion, 83693-41-8; *O*-dodecyl *erythro*-tartrate dianion, 83693-42-9; *O*-dodecyl *threo*-tartrate dianion, 83693-43-0; dimethyl *cis*-epoxysuccinate, 56958-97-5.

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(14) Attempts to place a dodecanoyl group on the OH of the dodecyltartrates failed. These double-chained compounds would have permitted a conformational study of molecules in vesicle bilayers.

m-Chloroperoxybenzoic Acid–Potassium Fluoride System: Study of Its Stability and Reaction with α-Methylstyrene

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The strong interaction between fluoride ions and compounds with acidic hydrogens is well documented in the literature.[1] In this context, we have recently reported a preliminary account of the extension of this interaction to peroxy carboxylic acids, by the use of the MCPBA–KF system in the Baeyer–Villiger oxidation of aromatic aldehydes and in the epoxidation of olefins.[2] As we had stated, one of the practical advantageous effects of adding KF to solutions containing *m*-chloroperbenzoic acid (MCPBA) and *m*-chlorobenzoic acid (MCBA) was the complete removal of these acids by precipitation. However, we anticipated that this addition could result in the concomitant labilization of the hydroperoxide bond, which is considered to be critical for the stability of the organic peroxy acid.[3] Accordingly, we deemed that an evaluation of the stability of the above system was required to es-

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Table I. Stability of 1:2 MCPBA-KF Complex as a Solid

temp,[b] °C	time	% active oxygen content[a]
rt	0	32.6
rt	20 min	28.2
rt	40 min	23.8
rt	65 min	21.0
rt	15 h	<3.0
0	15 h	11.4
0	35 h	5.7
−20	12 h	30.0
−20	35 h	29.3
−20	1 week	24.0

[a] The percent active oxygen content of starting MCPBA was 90.2. [b] The designation rt = room temperature.

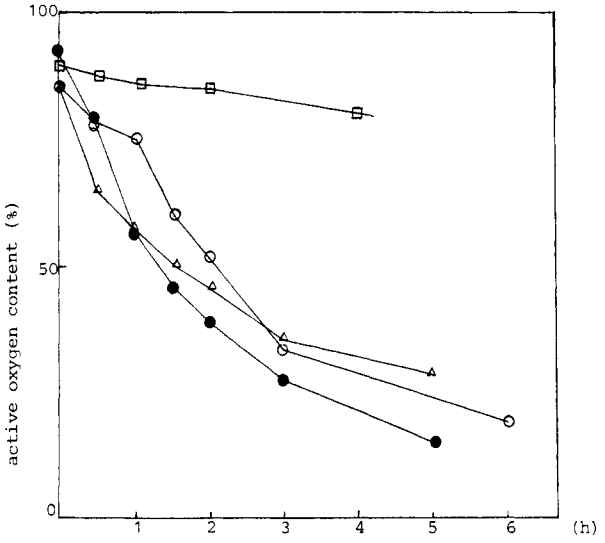

Figure 1. Plots of active oxygen content of 1:2 MCPBA–KF complex with time in different solvents at room temperature: ●, methylene chloride; △, hexane; ○, 2-propanol; □, methanol.

tablish the scope of its applications.

In the present paper we report the results of the study of the stability of the MCPBA–KF system as dry solid and in the presence of different solvents, as well as the application of this reagent in the preparation of α-methylstyrene oxide, a very reactive model.

Results and Discussion

Stability of the 1:2 MCPBA–KF Complex. First we were interested in ascertaining the stability of the complex as a dry solid. The complex could be quantitatively obtained by addition of a CH_2Cl_2 solution of MCPBA to a well stirred suspension of a 100% molar excess of activated KF in the same solvent at room temperature, followed by filtration. The nonhygroscopic amorphous 1:2 complex appeared to be stable at room temperature, but iodometric titration showed a rapid decrease of its active oxygen content which dropped to ca. 20% of the starting peroxy acid value after 40 min (Table I), being converted into the stable MCBA–KF complex, as it was confirmed by IR comparison with an authentic sample independently prepared. However, storage of the MCPBA–KF complex at 0 °C somewhat lessened the loss of activity, and at −20 °C the initial value was appreciably preserved after 1 week.

On the other hand, the stability of the complex in different solvents at room temperature seemed to be related to the degree of its insolubility (Figure 1). In solvents such as hexane, CH_2Cl_2, and 2-propanol in which the insolubility is highest, the active oxygen content is rapidly lost, although the values observed are somewhat higher than those found in dry solid. According to our expectations, also in this case storage of the heterogeneous system at low temperatures resulted in a notable persistence of activity, when compared to that found in the above conditions (18 h at 0 °C, 56.0%; 18 h at −20 °C, 82.0%). Finally, erratic results were found in methanol under heterogeneous conditions, whereas the stability of the complex in solution[4] was remarkably high.

Table II. Epoxidation of α-Methylstyrene (1) with MCPBA–KF Complex at Room Temperature

KF/MCPBA/1 molar ratio	solvent	reaction time, h	% yield of 2[a]
1/1/0.8	methylene chloride	20	14[b]
2/1/0.6	methylene chloride	20	81
2/1/0.5	methylene chloride	20	90
2/1/0.4	methylene chloride	20	90[c]
4/1/0.8	methylene chloride	20	17[b]
0/1/0.8	methylene chloride[d]	6.5	0
2/1/0.4	methanol	20	10
0/1/0.8	methanol	20	0
2/1/0.4	2-propanol	24	0
2/1/0.4	2-propanol/ methylene chloride (10%)	24	10
2/1/0.4	2-propanol/ methylene chloride (20%)	24	42
2/1/0.4	hexane	24	7

[a] Calculated from NMR spectra of the reaction mixture except as indicated. [b] Calculated from NMR spectra of the distilled mixture. [c] Of distilled 2 (>95% purity, estimated by NMR). [d] Following the procedure reported by Imuta and Ziffer[5] (at 0 °C, in the presence of phosphate buffer).

Epoxidation of α-Methylstyrene (1) with MCPBA–KF Complex. In spite of the progress achieved in recent years to develop improved procedures for preparation of labile epoxides by reaction of olefins with peroxy acids,[5] α-methylstyrene oxide (2) still remains an elusive target. A literature search revealed that satisfactory yields of 2 could only be obtained by two-step procedures via halohydrins,[6] whereas direct epoxidation of 1 with MCPBA led to poor yields of 2 (27%) due to the concomitant formation of significant amounts of acetophenone, hydratropic aldehyde, and other byproducts.[7] In the light of these results, the 95% yield of 2 claimed by Russian authors in the epoxidation of 1 with peroxybenzoic acid[8] should be questioned.

Similarly, we failed to obtain good yields of 2 when we tested the epoxidation of 1 by the two-phase buffered procedure described by Imuta and Ziffer,[5] which has been succesfully applied in the preparation of other styrenic epoxides. Although we detected the formation of 2 by GLC monitoring, isolation from the crude reaction mixture could not be achieved, due to simultaneous decomposition during the reaction course and workup procedure.

Our observation that epoxide 2 prepared by an indirect route[6a] remained stable in the presence of a 1:2 MCBA–KF suspension in CH_2Cl_2 for 24 h at room temperature opened the possibility for a more detailed investigation of the MCPBA–KF complex as a reagent to perform the direct

(4) Under conditions below the solubility of KF in methanol (~13 g/L), addition of MCPBA afforded a homogeneous solution.

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epoxidation of 1. Accordingly, a study of the reaction was carried out under different conditions, and the corresponding results are depicted in Table II.

Best results were achieved when a 2:1:0.4 molar ratio of KF–MCPBA–1 in CH_2Cl_2 was used. After 20 h at room temperature the starting material was completely transformed and a 90% yield of epoxide **2** could be isolated from the reaction mixture. The use of higher or lower KF molar proportions reduced drastically the yield of **2**, whereas clean but incomplete epoxidation was observed when the above 2:1 KF–MCPBA complex ratio proportion vs. olefin amount was diminished.

The use of other solvents afforded poorer yields: in hexane **1** was recovered almost unreacted, whereas in 2-propanol and methanol, besides incomplete epoxidation, decomposition was also observed.

From these results we conclude that MCPBA–KF complex suspended in CH_2Cl_2 affords a system active and persistent enough to promote complete epoxidation of α-methylstyrene and to allow the isolation of the resulting epoxide **2** in almost quantitative yield, plausibly due to the inactivation of any acid-catalyzed side reaction.

Experimental Section

Proton nuclear magnetic spectra (^1H NMR) were recorded on a Perkin-Elmer R12B spectrometer with Me_4Si as an internal standard. Gas–liquid chromatography was performed with a Perkin-Elmer Model 990 using a glass column packed with 3% OV-101 on silanized Chromosorb W. Commercially available *m*-chloroperoxybenzoic acid (Fluka) and α-methylstyrene (Fluka) were used without further purification. Solvents were dried and purified by standard procedures.

Preparation and Activity Evaluation of MCBPA–KF Complex. General Procedure. (a) To a suspension of 70–120 mg of freshly activated KF [1 h at 120 °C (0.1 torr)] in 25 mL of CH_2Cl_2 was added the appropriate amount of MCPBA, and the mixture was virgorously stirred for 30 min at room temperature. Then the complex was filtered off, washed thoroughly with CH_2Cl_2, dried under vacuum for 45 min, and stored at the temperature indicated in Table I. After the given time the complex was decomposed by addition of H_2O, the aqueous solution was extracted with CH_2Cl_2, and the active oxygen content was determined iodometrically in the organic layer.[9] Titration of the aqueous layer showed a residual oxygen content of less that 1%.

(b) Activity evaluation in the presence of a solvent was carried out by preparing the complex directly in the desired solvent, stirring the mixture for the given period of time (Figure 1), decomposing the complex, and titrating for the active oxygen content. For hexane and CH_2Cl_2, water was added and the organic layer worked up as in part a; for 2-propanol and methanol, AcOH was added, and titration was carried out directly in the alcohol–acetic acid mixture.

Epoxidation of α-Methylstyrene with MCPBA–KF Complex. General Procedure. The complex prepared as in b was stirred for 30 min at room temperature, the appropriate ratio of olefin was added, and the reaction mixture was stirred at room temperature for the given period of time. When reaction was completed (GLC monitoring), MCPBA–KF and/or MCBA complexes were removed by filtration and washed thoroughly with the same solvent, and the joint filtrates were dried over Na_2SO_4. When hexane or CH_2Cl_2 was used, complex elimination was complete, whereas significant amounts of acidic products were present in the filtrate when working with hydroxylic solvents.

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New Synthetic Route to an α-Alkoxy-α-arylacetic Ester Using Formaldehyde Dimethyl Dithioacetal *S,S*-Dioxide

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Formaldehyde dimethyl dithioacetal S,S-dioxide (**1**) is a useful organic reagent. For example, β,γ-unsaturated carboxylic esters could be synthesized by allylation of **1** followed by oxidation and acid-catalyzed decompposition in methanol.[1] Recently, a new method for making acyclic and cyclic ketones was effected by dialkylation of **1** and subsequent acid hydrolysis.[2] We have further investigated the synthetic utility of **1**, and find that **1** provides a new route from an aromatic aldehyde (**2**) to an α-alkoxy-α-arylacetic ester (**5**).

As outlined in Scheme I, the present route comprises three steps: (i) a Knoevenagel-type condensation of **1** with **2** to give 2-aryl-1-(methylsulfonyl)-1-(methylthio)ethene (**3**); (ii) oxidation of **3** to the corresponding *S,S,S'*-trioxide (**4**); (iii) treatment of **4** with an acid (HCl or H_2SO_4) in an appropriate alcohol (ROH), leading to **5**.

For the first step with benzaldehyde as **2**, several conditions (NaH in DMF;[3] *t*-BuOK in *t*-BuOH;[3] EtONa in EtOH; K_2CO_3 in THF,[4] MeOH, EtOH, or *i*-PrOH; piperidine in MeOH[4]) were examined and the use of K_2CO_3 (2 mol equiv) in refluxing *i*-PrOH gave the best result. In this reaction, only one geometric isomer was produced, and its geometry was deduced to be *E* by analogy of the present reaction to the condensation of benzaldehyde with formaldehyde dimethyl dithioacetal *S*-oxide.[5] Under similar conditions, other aromatic aldehydes (**2b–2e**) could be converted to the corresponding **3** in good to high yields. Oxidation of **3** into **4** was easily accomplished with H_2O_2 (1.1 mol equiv) in AcOH at room temperature for 2 days. When the thus obtained **4** was subjected to the reaction of HCl in refluxing MeOH, acid-catalyzed addition of MeOH, a Pummerer-type reaction, and hydrolysis successively occurred and methyl α-methoxy-α-arylacetate (**5**, R = CH_3) was produced (Scheme II). Table I summarizes these results.

When *i*-PrOH was employed as an alcohol in the final transformation, a more complicated result was observed. Refluxing a solution of **4a** in the presence of HCl in *i*-PrOH gave 1-chloro-2-isopropoxy-1-(methylsulfonyl)-1-(methylthio)-2-phenylethane (Ph(*i*-PrO)CHCCl(SCH_3)(SO_2CH_3), **10**) as a major product which might be formed by trapping the intermediary cation (**8**, R = *i*-Pr) of Scheme II with chloride anion. However, treatment of **4a** with H_2SO_4 in refluxing *i*-PrOH resulted in production of **5a** (R = *i*-Pr) and the methanethiol ester (**11**) of α-isopropoxy-α-

$$\mathbf{4a} \xrightarrow[i\text{-PrOH}]{H_2SO_4} \underset{R = i\text{-Pr}}{\mathbf{5a}} + \underset{\mathbf{11}}{Ph(i\text{-PrO})CHCOSCH_3} \rightarrow \underset{\mathbf{12}}{Ph(i\text{-PrO})CHCOOH}$$

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(6) When **4a** was treated with H_2SO_4 in *t*-BuOH, the corresponding **5a** (R = *t*-Bu) was not produced.

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