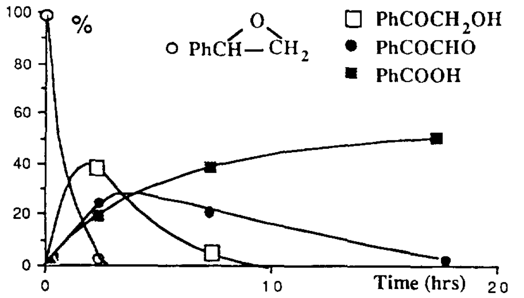


Fig 1. Kinetics of styrene epoxide transformation catalyzed by **1**, in DMSO at 80 °C.

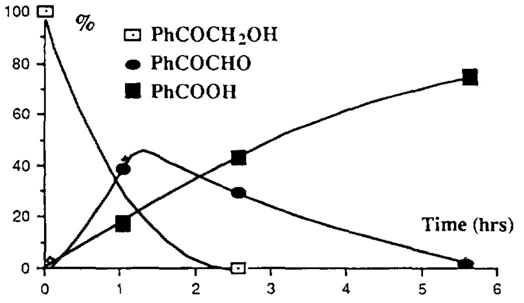


Fig 2. Kinetics of 2-hydroxyacetophenone transformation catalyzed by **1**, in DMF at 80 °C.

Figure 2 displays the ketol consumption with time, together with the formation and evolution of the reaction products during the course of 2-hydroxyacetophenone oxidation in DMSO at 80 °C in the presence of **1**. The data (table III, fig 2) were determined by monitoring the concentrations of the various compounds by NMR. This shows that, in our experimental conditions, the ketol is totally converted after 2.5 h and that the concentration in phenylglyoxal goes through a maximum (42%) after 1.5 h and then decreases at the benefit of benzoic acid.

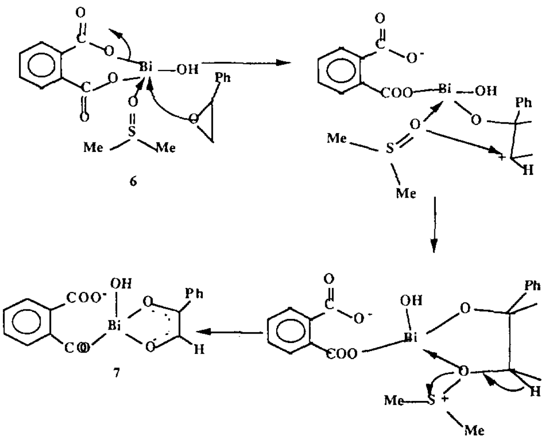
Discussion

We have prepared new series of bismuth(III) carboxylates derived from quinaldic acid and phthalic and diphenic dicarboxylic acids. The tris-carboxylato bismuth complex **2**, Bi[qui-(COO)]$_3$, obtained in the presence of quinaldic acid, with three five-membered chelate rings coordinated to the metal ion through the nitrogen atoms and the unidentate carboxylic group of the ligand, is analogous to the complexes that we had obtained in the presence of other pyridine- or pyrazine-2-monocarboxylic acids [12]. Our results indicated that the driving force in the formation of these adducts was the prior coordination of the nitrogen atom of the acid to bismuth. The presence of the nitrogen atom plays a key role in the formation of complexes **1–3**, which is consistent with the more drastic conditions required for the synthesis of Bi[phthal](OH) **4** containing only one phthalate ligand. In this case the driving force is probably stabilization by the seven-membered dicarboxylato chelate ring. Our results with diphenic acid indicate that the potential nine-membered chelate ring stabilization is no longer sufficient to force the acid–base reaction between diphenic acid and Bi_2O_3. We could only exploit the labile Bi-Ph bond in triphenylbismuth and prepare compound (C_6H_5)Bi[diphen] **5**.

These new complexes, together with the previously reported bismuth picolinate and dipicolinate, were found to catalyze the oxidative C-C bond cleavage of styrene epoxide and 2-hydroxyacetophenone into benzoic acid.

The activity of catalysts **1–5** depends on the nature of the ligand. The dicarboxylates **4** and **5** accelerate the oxidation process more efficiently than the bismuth pyridinecarboxylates **1–3**. These results are most likely to be related to the higher affinity of Bi(III) for amino ligands. On the other hand, the rather surprising difference in behavior between the triscarboxylates **1** and **2**, for which we expected close activities, can be tentatively attributed to differences in solubilities; the more soluble complex **2** would cause higher activity. The nature of the ligand also has an influence on the selectivity of the process. Thus, only traces of benzil were detected when the dicarboxylato complexes **4** or **5** were taken as catalysts, while its formation is obviously favored by the picolinato complex **1** with which a 25% yield of benzil was obtained in the oxidation of 2-hydroxyacetophenone.

When oxidation of epoxides is concerned, our results indicate that, in the first step, ie, the transformation of the epoxide into the corresponding α-ketol, the oxidant is DMSO. The role of the bismuth complex in that step is most likely to be the coactivation of both the epoxidic substrate and the oxidant in a solvate of type **6** as illustrated in scheme 2. After dimethyl sulfide evolution, **6** would be converted to the ketoalkoxide bismuth complex **7** in scheme 2. 2-Hydroxyacetophenone would result from this complex through treatment of the reaction mixture. Thus, the epoxide to α-ketol transformation is best described as a bismuth(III)-assisted Swern oxidation of an epoxide by DMSO.



Scheme 2

The second step in the epoxide oxidation process (first step in the ketol oxidation) is the formation of phenylglyoxal which could result from an intramolecular redox process in the intermediate complex **7**. More work is currently in progress to fully understand the various reaction steps, the role of bismuth and oxygen and the precise nature of the intermediates.

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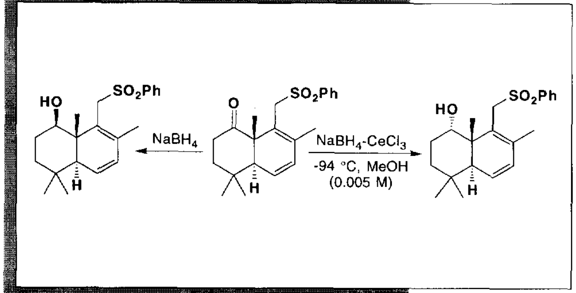

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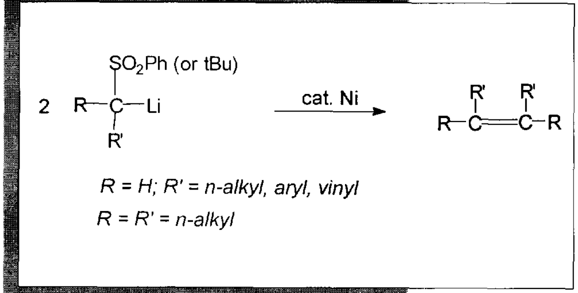
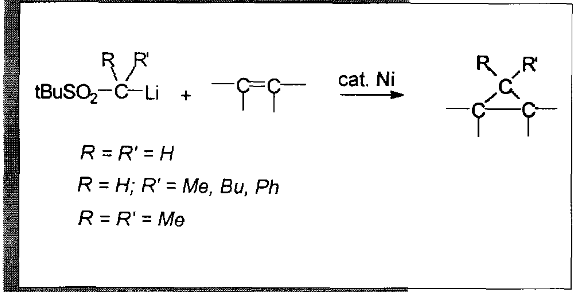
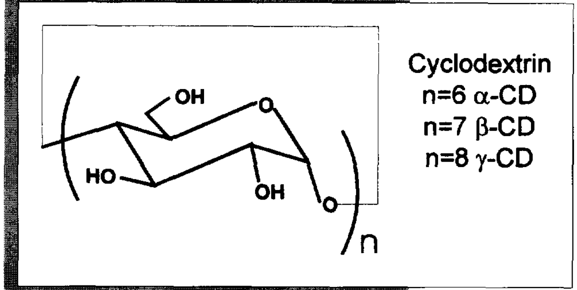
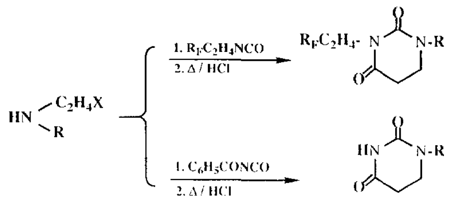
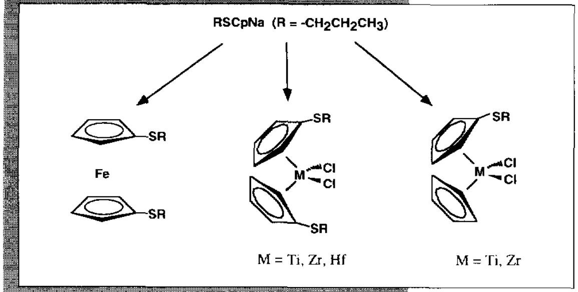


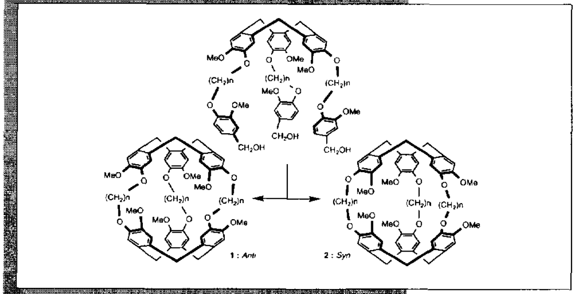


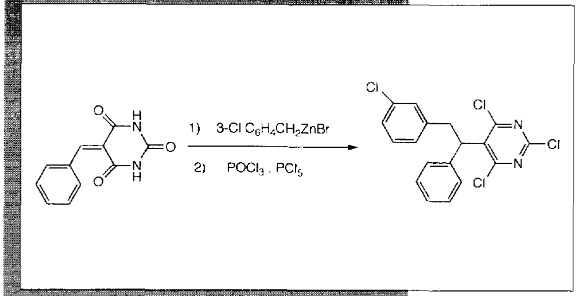


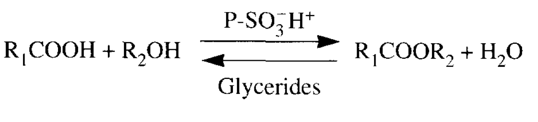


R = CH_3,C_2H_5,nC_3H_7,nC_4H_9, $R_FC_2H_4$- avec R_F = C_4H_9,C_6F_{13},C_8F_{17};
X = CN ou $CONH_2$.

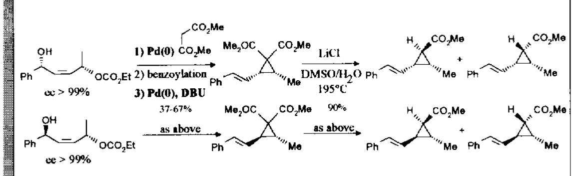


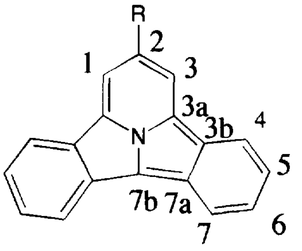




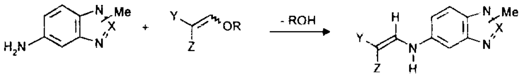


$$R_1COOH + R_2OH \underset{\text{Glycerides}}{\overset{\text{P-SO}_3^-\text{H}^+}{\rightleftharpoons}} R_1COOR_2 + H_2O$$

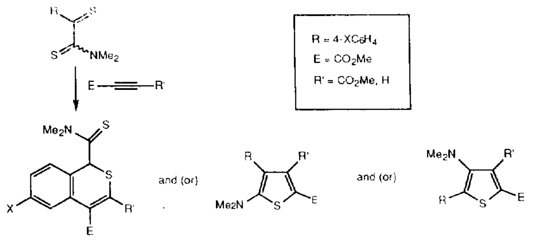


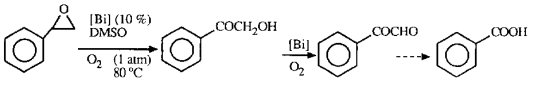


2a: R=H
2b: R=CH_3
2c: R=PhCO
2d: R=Ph



X = CH, N R = Et: Y, Z = COMe, COMe; CN, COMe; COMe, COOEt
R = Me: Y, Z = COMe, COOMe





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