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LIQUID PHASE OXIDATION CATALYZED BY BISMUTH SULFATE.
A NEW SYNTHESIS OF 1-CYCLOPENTENE-1-CARBOXALDEHYDE

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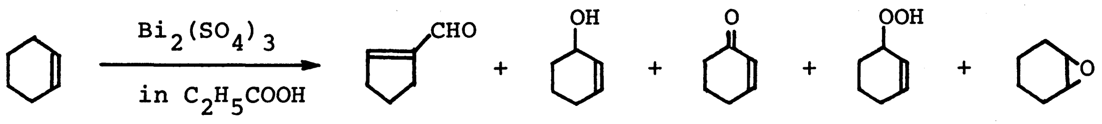
Autoxidation of cyclohexene catalyzed by insoluble bismuth sulfate in acidic solvents gave 1-cyclopentene-1-carboxaldehyde selectively. A new mechanism for the autoxidation involving isomerization of peroxyradical catalyzed by acidic site was presented.

The liquid phase autoxidation catalyzed by soluble transition metal salts has long been investigated and several typical mechanisms such as Haber-Weiss mechanism have been well established. However, little attention has been paid to the reaction catalyzed by insoluble metal salts. In the present paper, oxidation of cyclohexene catalyzed by bismuth sulfate was investigated and we found that the reaction gave 1-cyclopentene-1-carboxaldehyde (**1**) selectively in the acidic solvents.



1 90% **2** 6.5% **3** 3.2% **4** **5**

A typical reaction procedure is shown in the following. Bismuth sulfate catalyst was prepared by calcination of the commercial reagent at 200°C for 3 hr and was allowed to stand for a long time in contact with air to absorb 0.8-1.0% water. 0.5 g of the catalyst was suspended in 5 ml of solvent and 5 ml of olefin and the mixture was stirred under one atmospheric oxygen pressure at 65°C. After

Table 1. The autoxidation of cyclohexene catalyzed by bismuth sulfate[a]

Solvent	$-\frac{dO_2}{dt} \times 10^5$ (mole/l.sec)	Selectivity (%)[b] 1	2	3	4	5
benzene	0.23	5.3	50.5	30.0	9.0	tr.
acetic acid	6.05	92.0	—	3.0	tr.	tr.
propionic acid (PA)	6.25	90.0	6.5	3.2	tr.	tr.
PA + pyridine[c]	1.08	1.1	52.5	44.3	2.0	tr.
PA[d]	12.9	0	53.8	34.2	10.8	0.5

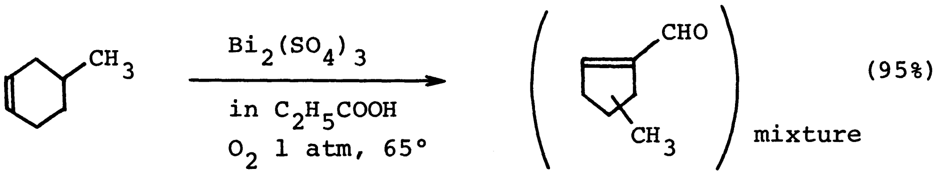
a) No oxygen was absorbed in acetonitrile and in n-hexane.

b) Based on cyclohexene reacted. c) 2.90×10^{-2} mole/l.

d) $Co(OCOCH_3)_2$ catalyst was used.

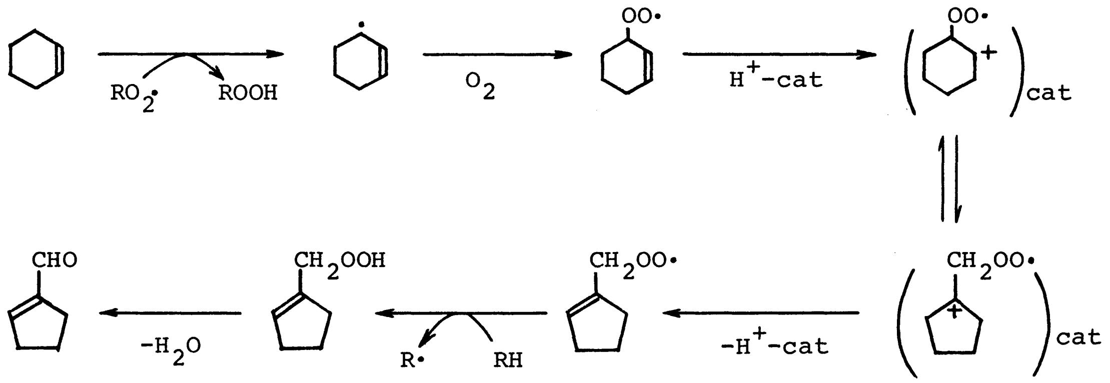
the prescribed amount of oxygen (100 ml) was absorbed, the reaction mixture was analyzed by glc. The results are shown in Table 1.

It is noted that the rate of oxidation was greatly enhanced in the acidic solvents. In addition, the product distribution was quite different depending upon the solvent used. The main products obtained in benzene were cyclohexenol (**2**) and cyclohexenon (**3**) which were identical with those obtained in the ordinary autoxidation catalyzed by soluble transition metal salt, $Co(OCOCH_3)_2$. 1-Cyclopentene-1-carboxaldehyde (**1**)[1] was mainly obtained in acetic acid and in propionic acid. Although there have been reported several methods for preparation of **1**,[2] direct oxidation of cyclohexene to form **1** has not been reported yet.



In a similar manner, oxidations of several cycloolefins were examined. 4-Methyl-cyclohexene was oxidized to corresponding aldehydes in high selectivity. The reaction was retarded when 1, 2 or 3 position of cycloolefin was substituted by alkyl group. The rate of oxygen absorption was quite slow in 1-methyl-cyclohexene, 3-methyl-cyclohexene or 1-methyl-cyclopentene oxidation.

The rate of oxygen absorption in cyclohexene oxidation was directly proportional to the amount of catalyst used. Because of low solubility of bismuth sulfate,[3)] this fact suggests that the reaction proceeds heterogeneously. In order to confirm heterogeneous catalysis, further reaction was carried out without adding any solid catalyst in the acetic acid solvent which was prerefluxed on the bismuth sulfate catalyst for 2 hr at reaction temperature. It was found that the rate of oxygen absorption was slower than 1/10 of the rate of normal catalytic reaction. Thus, it is clear that small amount of bismuth compound dissolved in the acidic solvent has virtually no effect on the oxidation and the reaction proceeds on the surface of insoluble bismuth sulfate catalyst. The fact that bismuth acetate was almost inactive for the reaction is also favorable for above conclution.



The reaction may be explained by considering an isomerization of peroxy-radical on acidic site of bismuth sulfate. The result that addition of small amount of pyridine inhibited the reaction and changed the product distribution supports the important role of acidic catalysis. A possibility of isomerization of reactant olefin is ruled out by the fact that 1-methyl-cyclopentene was oxidized very slowly at the experimental conditions adopted. Isomerization of **3** to **1** was also checked and ruled out. Further investigations are now in progress.

References and notes

1) The product was extracted by ether from basic aquaous solution of the reaction mixture, isolated by glc and identified by the following analysis.
m/e = 96 (M^+), nmr; $\delta(CCl_4)$ 9.70(s, -CHO), 6.75(m, 1H), 2.60(m, 4H), 2.00(m, 2H). ir; ν_{CHO} = 1680, $\nu_{\text{cyclopentene ring}}$ = 790, 815 cm^{-1}. Anal. Calcd. for

C_6H_8O; C, 74.97; H, 8.38. Found; C, 74.36; H, 8.71%.

2) J. English and G. M. Barber, J. Amer. Chem. Soc., 71, 3310 (1944): M. S. Kharasch and G. James, J. Org. Chem., 16, 150 (1951): A. Misono, T. Osa and T. Yamagishi, J. Chem. Soc. Japan, 87, 980 (1966): H. Farve and J. P. Lapointe, Can. J. Chem., 49, 3851 (1971): G. Magnusson and S. Thoren, J. Org. Chem., 38, 1380 (1973).

3) Solubility of bismuth sulfate in acetic acid determined by the colorimetric analysis was 2.82 x 10^{-5} mole/l (0.0002 g/5 ml) at 65°C.

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