

Effect of Polyether Linkages on the Carboxylation of Sodium Phenoxide

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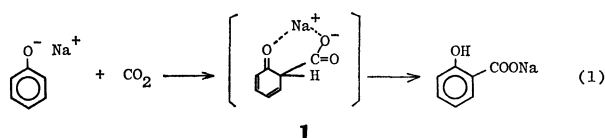
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Synopsis. In the carboxylation of sodium phenoxide under mild conditions, the crown compound or polyethers with three to five ether linkages caused carboxylation to give *o*- and *p*-hydroxybenzoic acids, but not ethers with one or two linkages. The chelation of sodium phenoxide with polyethers changed the formation ratio of isomers.

It is well known that various polyethers have properties in which a neutral molecule encircles metal ions or related cation, and changes the chemical or physical character of metal ion or the paired anion, such as reactivity, solubility, or catalytic activity.¹⁾ With potassium phenoxides, chelation with crown ethers achieves conversion of phenols into their chalcones,²⁾ the chelation increasing the reactivity of potassium phenoxide.

In the Kolbe-Schmitt reactions, sodium phenoxide exclusively gives *o*-hydroxybenzoic acid (salicylic acid).³⁾ Preferential formation of *o*-isomer is explained in terms of intramolecular chelation in the intermediate (1) (Eq. 1).



So far, only a few reports have appeared on the effect of polyethers on the carboxylation of sodium phenoxide. In this report, we will show how the chelation with polyethers influences the reaction of sodium phenoxide with carbon dioxide under mild conditions.

In a typical experiment, 0.03 mol of sodium phenoxide in dry diglyme (1.0 mol) was stirred under carbon dioxide atmosphere at 80 °C for 10 h. After work-up of the reaction mixture, pure *o*-hydroxybenzoic acid was isolated in 5% yield as the sole product. Similar reactions were carried out in some polyether solvents. The results are summarized in Table 1.

The conversion of the reactant was low due to the mild reaction conditions. However, the results indicate that the number of ether linkages in solvent molecule influences the carboxylation of sodium phenoxide. A solvent with three to five ether linkages in a molecule gave rise to carboxylation of aromatic ring, but not a solvent with one or two. Use of tetraglyme in the reaction resulted in the formation of *p*-hydroxybenzoic acid, in spite of the preferential formation of *o*-isomer under the usual Kolbe-Schmitt conditions, *i.e.*, under high temperature and high pressure of carbon dioxide.³⁾

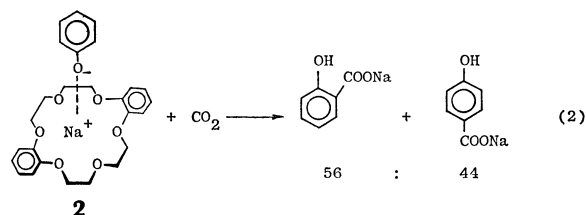
Sodium phenoxide in monoglyme solvent gives no aromatic acids (Table 1). However, in the presence of a small amount of dibenzo-18-crown-6, carboxylation

TABLE 1. EFFECT OF POLYETHERS ON THE CARBOXYLATION OF SODIUM PHENOXIDE

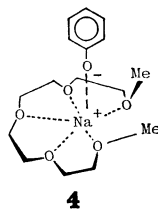
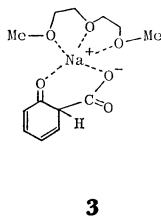
Polyethers	Yield/%		
	Yield of hydroxybenzoic acid ^{a)}	Composition <i>o</i> -isomer, <i>p</i> -isomer	
Tetrahydrofuran	0	0	0
2,2'-Bi(tetrahydrofuranyl)	0	0	0
H ₃ CO(CH ₂ CH ₂ O) _n CH ₃			
<i>n</i> = 1	0	0	0
2	5	100	0
2	7	97	3
3	5	80	20
4	4	20	80
4	3	25	75

a) Based on the amount of sodium phenoxide.

slowly proceeds in monoglyme to give a mixture of *o*-hydroxybenzoic acid and the *p*-isomer. Thus, a mixture of sodium phenoxide (0.03 mol) and dibenzo-18-crown-6 (0.005 mol) was stirred in monoglyme (1.0 mol) at 80 °C for 10 h under carbon dioxide atmosphere. After neutralization of the reaction products, a mixture of aromatic acids was isolated in a 3.5% yield, which contained *o*- (56%) and *p*-acid (44%). The 1:1 formation of *o*- and *p*-isomers is in line with the expected reactivity at *o*- and *p*-positions of free phenoxide ion.⁴⁾ This shows that the carboxylation may proceed *via* a phenoxide ion separated from the paired sodium ion by chelation with crown ether (Eq. 2).



The results of reactions in noncyclic polyethers are also explained in terms of the chelation of sodium phenoxide with polyethers. Diglyme and triglyme may activate sodium phenoxide to react with carbon dioxide, but cannot form free phenoxide ion because of their weak chelation ability. The formation of probable intermediate (3) may lead to *o*-isomer. On the other hand, tetraglyme completely binds sodium ion to form an analogous intermediate (4) to 2. The complex (4) might have a less coplanar chelating ring as compared with that in 2 due to the terminal methyl groups. The preferential formation of *p*-isomer might show the steric effect at *o*-position by methyl groups.



Experimental

Materials. Sodium phenoxide and dibenzo-18-crown-6 were prepared according to the methods described by Mori *et al.*,⁵ and Pedersen,⁶ respectively. 2,2'-Bi(tetrahydrofuran) was prepared in a 24% yield by the photoreduction of acetone in tetrahydrofuran (molar ratio of acetone/THF; 1/10): n_D^{25} 1.4572 (lit.,⁷ n_D^{20} 1.4512), Mass (m/e); 142 (M^+), 71 ($M^+/2$). The IR and NMR were identical with those of authentic material. Commercially available monoglyme, diglyme, triglyme, and tetraglyme were distilled on sodium under reduced pressure before use.

Carboxylation of Sodium Phenoxide in Diglyme. A mixture of 3.48 g of sodium phenoxide (0.03 mol) and 134 g of diglyme (1.0 mol) was stirred at 80 °C for 10 h bubbling with dried carbon dioxide in a dried four necked flask, equipped with a stirrer sealed by liquid paraffin, a Dimroht condenser with calcium chloride tube, a thermometer, and an introducing tube of carbon dioxide. After the reaction, 40 ml of 15% aqueous sodium hydroxide was added to the reaction mixture and the organic solvent was separated in a separating funnel. The aqueous layer was washed with a small amount of diethyl ether and afterwards was acidified with concd HCl, followed by extraction with diethyl ether. After the ether solution had been dried on anhydrous sodium sulfate, evap-

oration of ether gave 207 mg of pure salicylic acid, which was identified with the authentic material by mp measurement, IR, and NMR.

Similar reactions using tri- or tetraglyme, or dibenzo-18-crown-6 gave a mixture of organic acids, in which the formation ratio of *o*- and *p*-isomers was determined by GLC using OV-101 column (182 °C, carrier gas; H_2).

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- 4) When benzyl anion is considered as a model of phenoxide ion, the total π -electron density at *p*-position is somewhat larger than that at *o*-position ($o/p=1.142/1.144$), the Frontier electron densities being almost equal at both positions. Thus, the reaction of phenoxide ion with carbon dioxide, known as a hard acid, should give a considerable large *o*/*p* ratio when the steric effect is neglected. In the present reaction, the *o*/*p* ratio was 0.63; see I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," Japanese Edition (translated by K. Fukui *et al.*), Kodansha Co., Ltd., (1978), pp. 40-77.
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