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Effect of Cation Capture by Crown Ether and Polar Solvent in the Carboxylation with CO_2 of Alkali Metal 2-Naphtholates under Ordinary Conditions†

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An efficient method for the carboxylation of sodium 2-naphtholate and potassium 2-naphtholate in benzene with 10 mol% of crown ether or aprotic polar solvents under 1 atm of carbon dioxide at 60 °C affords 2-hydroxynaphthalene-1-carboxylic acid in yields ranging from 14.6 to 43.8% and 26.7 to 66.0%, respectively.

A useful process for the carboxylation of alkali metal 2-naphtholates has been developed based on the principles of crown ether chemistry. Crown ethers have been exhaustively studied in the last 25 years.[1–3] These macrocyclic ligands are well known for their superb selectivity towards metal ions.[4,5] This modified carboxylation procedure occurs at a reasonable temperature and carbon dioxide pressure and is practical for the manufacturing of 2-hydroxynaphthalene-1-carboxylic acid (2-H-1-NA), which is useful as a chemical intermediate for dyes, heat-sensitive dyes, photographic materials, liquid crystals, chemical feedstock, *etc.*

It is well known that carboxylation of alkali metal naphtholates can be carried out under normal temperatures and pressures because a polar solvent is used.[6–9] However, we found that benzene together with a small amount of crown ether or polar solvent, which creates a homogeneous solution, could be used instread. Our reaction in essence is similar to the alkylation reaction of potassium phenoxide with butyl bromide using various crown ethers,[10] however only a 10 mol% of crown ether is needed. The reaction readily occurs at atmospheric pressure and at 60 °C for the carboxylation of potassium 2-naphtholate and sodium 2-naphtholate to give high selectivity and a relatively high yield of 2-H-1-NA. These solvation effects were clarified because crown ethers were used to separate the metal cation from the naphtholate anion, thereby increasing the charge of the free naphtholate anion, creating a homogeneous solution, and making a stronger nucleophilic reagent. Similar results were found using at trace amount of polar solvents, which solvate the potassium ion creating a solvent-separated ion-pair.

The results are shown in Table 1, and the yields were calculated after purification. The highest yields were achieved using the aliphatic crown ethers as compared to the other crown ethers because the oxygen basicity of the aliphatic crown ethers is higher than that of the aromatic-containing crown ethers. An increase in the basicity of the crown ether increases both its solvating and chelating ability.[11]

Table 1 Effects of crown ethers on the carboxylation of alkali metal 2-naphtholates (0.01 mol) in benzene (15 ml)[a]

Crown ethers (0.001 mol)	Alkali metal salt	Time (t/h)	Yield of 2-H-1-NA (%)
None	potassium	6	0.5
Dibenzo-18-crown-6	potassium	6	27.5
Benzo-15-crown-5	sodium	6	21.0
15-Crown-5	potassium	6	14.6
	sodium	6	43.7
18-Crown-6	potassium	5	43.8
	sodium	6	29.8

[a]Reaction temperature, 60 °C; atmospheric pressure of CO_2.

To support our proposal that the solvation and/or removal of the cation is necessary in benzene, polar aprotic solvents (0.001 mol) were added to the carboxylation reaction without the use of a crown ether (Table 2).[12] A polar solvent aids in solvating the alkali metal naphtholate, thereby creating a solvent-separated ion-pair. It acts in a similar way as a crown ether: increasing the alkali cation and oxygen intranuclear distance and creating a homogeneous solution.

Table 2 Effects of additive polar aprotic solvents on the carboxylation of potassium 2-naphtholate (0.01 mol) in benzene (15 ml)[a]

Additives (0.001 mol)	Time (t/h)	Yield of 2-H-1-NA (%)
None	6	0.5
DMSO	6	66.0
DMF	3	39.4
Ethylene carbonate	3	45.3
1,2-Dimethoxyethane	3	26.7
1,4-Dioxane	6	58.5
Nitrobenzene	3	50.5

[a]Reaction temperature, 60 °C; atmospheric pressure of CO_2.

The yields of 2-H-1-NA in polar aprotic solvents were greater than the crown ether yields when nitrobenzene, 1,4-dioxane, ethylene carbonate, or DMSO were added. For all of the solvents, except 1,4-dioxane and DMSO, the reaction time was shortened to 3 h. The greatest yield (66%) after purification was with DMSO; however, DMF, which is also a very polar solvent, unexpectedly gave much lower yields. The reason for this dichotomy is as yet unknown. The yields were probably lower with crown ethers because a crown ether can only react once to bind the cation; however, a polar solvent can make many solvent-separated ion-pairs through the course of the reaction.

In conclusion, the reaction of alkali metal naphtholates with CO_2 has been clarified through the use of crown ethers and polar solvents in benzene. The yields seem to vary with the solvating strength of the crown ether or polar solvent. The crown ether aids in the dissolution of the naphtholate salt to make a homogeneous solution similar in principle to polar solutions that solvate the cation-anion pair increasing their intramolecular distances. The anionic charge is then more pronounced on the oxygen and naphthalene ring, easing the electrophilic attack of CO_2, as supported by MNDO and Hückel calculations. Further experimentation and calculations are being performed to elucidate the mechanistic details.

Experimental

General Procedure for the Preparation of 2-H-1-NA.—A cylindrical Pyrex reactor was fitted with a Teflon stopper with two holes,

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one for a thermometer and the other one for a gas inlet tube. A gas burette was attached to the reaction apparatus to monitor the carbon dioxide uptake. A crown ether such as 18-crown-6 (0.001 mol) was used as received or a polar solvent such as DMSO (0.001 mol) was placed in the reaction apparatus with dry benzene (15 ml) and stirred. Dry potassium 2-naphtholate (0.01 mol), made from 2-naphthol and KOH, was then added to the flask and put under vacuum. Successful incorporation of K^+ into the crown ether was indicated by an immediate formation of a bright lavender solution. The reaction vessel was heated to 60 °C, then the inner atmosphere was substituted with carbon dioxide (1 atm). The reaction was stopped when the CO_2 was no longer being absorbed. The solution was evaporated to dryness under reduced pressure and the product was dissolved in water and made neutral to litmus to precipitate 2-naphthol, which was filtered off at 20 °C. The filtrates were acidified with H_2SO_4 to Congo Red at 55 °C and the precipitated 2-H-1-NA was filtered off at 18 °C, washed and centrifuged. The product was dried at 45 °C for 2 days. The products were identified by HPLC and mass spectrometry.

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