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# Carboxylation of Phenol Derivatives. XXII.[1] Formation of Alkali Alkyl Carbonate by the *O*-Carboxylation of Alcohol in the Presence of an Alkali Salt of a Weak Acid

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*O*-Carboxylation of the alcohol (ROH) occurred to give alkali alkyl carbonate in a good yield when carbon dioxide was introduced into the mixture of an alkali salt of a weak acid, alcohol, and acetone (or THF) at room temperature under atmospheric pressure. Such alkali salts as PhOM, *p*-$R'C_6H_4OM$ ($R'=CH_3$, $CH_3O$, or Br), $Et_2NCSSM$, NaCN, and $C_6H_4(CO)_2NK$ (M=K or Na) were effective. The mixture of $HOC_6H_4COOM$ and ROCOOM was obtained from the reaction using $MOC_6H_4COOM$ as an alkali salt. However, the mixture was composed of equimolar amounts of *p*-$HOC_6H_4COOM$ and ROCOOM when *p*-$MOC_6H_4COOM$ was used. In this reaction, two mechanisms have been examined.

Alkali alkyl carbonates, which are known as carboxylating agents of alkali phenoxide, are usually prepared by the introduction of carbon dioxide into the alcohol solutions of alkoxides which are obtained from a metallic alkali and alcohol or by the removal of the formed water from alkali hydroxide and alcohol at an azeotrope with alcohol.[2]

It has been well known that hydroxybenzoic acids are formed when alkali phenoxide is heated under carbon dioxide pressure at a high temperature and, on the other hand, the complex is formed when alkali phenoxide is brought into contact with carbon dioxide at a low temperature. The latter reaction has been studied by many authors.[3]

During the investigation of the complex, we discovered a new reaction that forms alkali alkyl carbonates from alcohol and carbon dioxide in the presence of an alkali salt of a weak acid.

## Results and Discussion

When carbon dioxide was introduced into the methanol solution of alkali phenoxide, precipitates of alkali methyl carbonate were formed in good yields. This reaction was further examined and generalized as Eq. 1: where, AM represents an alkali salt of a weak acid.

$$AM + ROH + CO_2 \rightarrow AH + ROCOOM \qquad (1)$$

The results with many alklali salts of weak acids are summarized in Tables 1 and 2.

Potassium and sodium hydroxides cannot be used as alkali sources because the water formed in the reaction decomposes the alkali alkyl carbonates according to Eq. 2:

$$ROCOOM + H_2O \rightarrow ROH + MHCO_3 \qquad (2)$$

Alkali salts of weak acids, such as the sodium salt of phenol, *p*-cersol, *p*-methoxyphenol, *p*-bromophenol, diethyldithiocarbamic acid, or hydrogen cyanide and the potassium salt of phenol, diethyldithiocarbamic acid, or phthalimide, are effective, while alkali salts such as the sodium salt of nitrous acid, thiocyanic acid, sulfurous acid (mono salt), or hydrogen sulfide (di- and mono-salts), and potassium thiocyanate are not. The p$K_a$'s of most of the parent acids of the uneffective alkali salts are lower than 7.2. For example, the p$K_a$'s of some parent acids (in water at 25 °C) are as follows:[4] thiocyanic acid, 0.85; sulfurous acid, p$K_1$=1.90, p$K_2$=7.20; nitrous acid, 3.29; hydrogen sulfide, p$K_1$=6.88, p$K_2$=14.15. Among the parent acids of effective alkali salts, the strongest acid, is *p*-bromophenol, whose p$K_a$ at 25 °C is 9.24 (*cf.* hydrogen cyanide, 9.32; phthalimide, 9.90, phenol, 9.99. Although there is no data for the p$K_a$ of diethyl dithiocarbamic acid, it may be a weaker acid than *p*-bromophenol). Therefore, it can be concluded that an alkali salt whose parent acid has a p$K_a$ of more than about 9 will be effective.

In most reactions, acetone or tetrahydrofuran (THF) was used as a solvent. Alkali phenoxides dissolve considerably in methanol and ethanol, but these salts and other alkali salts are practically insoluble in other higher alcohols. In addition, potassium methyl carbonate dissolves to some extent in methanol at room temperature (see Table 4). Acetone and THF were good solvents for the sodium and potassium salts of phenol and *p*-substituted phenols.

The products prepared according to Eq. 1 were confirmed to be alkali alkyl carbonates by the elementary analyses and by the comparison of each IR spectrum with that of an authentic sample. However, the elementary analyses of the carbon and hydrogen atoms of the potassium alkyl carbonates, in most cases, did not accord with the calculated values within ± 1%, and are not listed in Table 2.

Introduction of carbon dioxide into a mixture of sodium phenoxide, isobutyl alcohol, and acetone, followed by the addition of an excess of methanol, gave fine crystallines. The main component of the crystallines was found to be sodium methyl carbonate. The reaction of Eq. 3 might occur after the reaction of Eq. 1, where

$$i\text{-}C_4H_9OCOONa + CH_3OH \rightarrow CH_3OCOONa + i\text{-}C_4H_9OH \qquad (3)$$

AM, R, and AH are PhONa, *i*-$C_4H_9$, and PhOH, respectively. In addition, sodium benzyl carbonate and sodium dodecyl carbonate, which are prepared only with difficulty by the previous method, were

Table 1. Sodium alkyl carbonates (Eq. 1)

| Alkali salt (0.03 mol) | ROH[a] R | Solvent (100 ml) | Product | Yield (%) | Analyses (%)[b] C | H | Na |
|---|---|---|---|---|---|---|---|
| PhONa | $CH_3$ | Acetone | $CH_3OCOONa$ | 98 | 24.39<br>(24.50) | 3.08<br>(3.08) | 23.20<br>(23.45) |
| PhONa | $C_2H_5$ | EtOH<br>(50 ml) | $C_2H_5OCOONa$ | 99 | 32.19<br>(32.16) | 4.59<br>(4.50) | — |
| PhONa | $i$-$C_4H_9$ | THF | $i$-$C_4H_9OCOONa$ | 63 | 40.80<br>(42.86) | 5.40<br>(6.47) | 15.54<br>(16.41) |
| PhONa | $i$-$C_4H_9$ | Acetone | $CH_3OCOONa$[c] | 58 | 25.47<br>(24.50) | 2.77<br>(3.08) | 25.34<br>(23.45) |
| PhONa | $s$-$C_4H_9$ | Acetone | $s$-$C_4H_9OCOONa$ | 69 | 38.65<br>(42.86) | 5.55<br>(6.47) | 17.40<br>(16.41) |
| PhONa | $n$-$C_5H_{11}$ | Acetone | $n$-$C_5H_{11}OCOONa$ | 93 | 46.30<br>(46.75) | 7.26<br>(7.19) | — |
| PhONa | $n$-$C_{12}H_{25}$ | Acetone | $n$-$C_{12}H_{25}OCOONa$ | 96 | 61.47<br>(61.82) | 9.71<br>(9.91) | — |
| PhONa | $C_6H_5CH_2$ | Acetone | $C_6H_5CH_2OCOONa$ | 58 | 55.39<br>(55.18) | 4.03<br>(4.05) | 13.24<br>(13.20) |
| $p$-$CH_3C_6H_4ONa$ | $C_2H_5$ | THF | $C_2H_5OCOONa$ | 91 | — | — | 19.61<br>(20.52) |
| $p$-$CH_3OC_6H_4ONa$ | $C_2H_5$ | EtOH<br>(50 ml) | $C_2H_5OCOONa$ | 94 | — | — | 20.56<br>(20.52) |
| $p$-$BrC_6H_4ONa$ | $C_2H_5$ | EtOH<br>(50 ml) | $C_2H_5OCOONa$ | 98 | — | — | 20.07<br>(20.52) |
| $Et_2NCSSNa$ | $CH_3$ | THF | $CH_3OCOONa$ | 51 | — | — | 23.48<br>(23.45) |
| $Et_2NCSSNa$ | $C_2H_5$ | THF | $C_2H_5OCOONa$ | 63 | — | — | 20.16<br>(20.52) |
| NaCN | $CH_3$ | MeOH<br>(50 ml) | $CH_3OCOONa$ | 81 | — | — | 23.06<br>(23.45) |
| $PhONa \cdot CO_2$[d] | $CH_3$ | Acetone | $CH_3OCOONa$ | 87[e] | 24.80<br>(24.50) | 3.18<br>(3.08) | 23.54<br>(23.45) |

a) At least 0.06 mol of alcohol was used. b) The calcd values are shown in parentheses. The Na% was evaluated by the titration of the $NaHCO_3$ in the product with 1 M HCl ($ROCOONa + H_2O \rightarrow ROH + NaHCO_3$). c) After introducing carbon dioxide into the mixture of sodium phenoxide, isobutyl alcohol, and acetone, 50 ml of methanol was added. The IR spectrum of the product obtained from this reaction was nearly identical with that of authentic sodium methyl carbonate. d) The complex was prepared according to the procedure described before (Ref. 1), but light oil was replaced with hexane. e) The yield is based on the PhONa initially used.

Table 2. Potassium alkyl carbonates (Eq. 1)

| Alkali salt (0.03 mol) | ROH[a] R | Solvent (100 ml) | Product | Yield (%) | Analysis[b] K (%) |
|---|---|---|---|---|---|
| PhOK | $CH_3$ | THF | $CH_3OCOOK$[c] | 79 | — |
| PhOK | $C_2H_5$ | EtOH<br>(50 ml) | $C_2H_5OCOOK$ | 87 | 31.0<br>(30.5) |
| PhOK | $n$-$C_3H_7$ | THF | $n$-$C_3H_7OCOOK$ | 98 | 27.1<br>(27.5) |
| PhOK | $n$-$C_4H_9$ | THF | $n$-$C_4H_9OCOOK$[c] | 96 | — |
| PhOK | $C_6H_5CH_2$ | $C_6H_5CH_2OH$ | $C_6H_5CH_2OCOOK$ | 88 | 20.9<br>(20.6) |
| $Et_2NCSSK$ | $CH_3$ | MeOH<br>(50 ml) | $CH_3OCOOK$[c] | 63 | — |
| $C_6H_4(CO)_2NK$[d] | $CH_3$ | Acetone | $CH_3OCOOK$ | 94 | 32.0[e]<br>(34.3) |
| $PhOK \cdot CO_2$ | $CH_3$ | Acetone | $CH_3OCOOK$ | 83 | 34.6<br>(34.3) |

a) At least 0.06 mol of alcohol was used. b) The calcd values are shown in parentheses. The K% was evaluated by the titration of the $KHCO_3$ in the product with 1 M HCl ($ROCOOK + H_2O \rightarrow ROH + KHCO_3$). c) The IR spectra of these products were in good agreement with those of authentic ones. d) Potassium phthalimide. e) Although the K% deviated 2.24% from the calcd value, the IR spectrum was nearly identical with that of potassium methyl carbonate.

easily obtained by the present reaction.

Kwan and his co-workers reported that a carbon atom with an active hydrogen is carboxylated by carbon dioxide in *N*,*N*-dimethylformamide in the presence of potassium phenoxide.[5)] However, the yields were less than 50%. In the present reaction an oxygen atom of alcohol is carboxylated to give alkali alkyl carbonate in good yield. As was mentioned already, not only alkali phenoxide but also many alkali salts of weak acids were available as alkali sources.

Two mechanisms for the present reaction, Eq. 1, can be considered. It is well known that alkali phenoxide forms a stable complex with carbon dioxide. We also reported that the complex is formed in good yield (about 80%) when the mixture of potassium phenoxide and light oil is stirred vigorously under a carbon dioxide atmosphere at room temperature for 30 min.[1)] It will be reasonable to assume that the first product formed in the present reaction of Eq. 1, where AM is alkali phenoxide, is a complex, because alcohol does not react with carbon dioxide at room temperature. Two complexes ($PhOK\cdot CO_2$ and $PhONa\cdot CO_2$) were prepared from potassium phenoxide and sodium phenoxide plus carbon dioxide, and then methanol was added to each complex. Potassium methyl carbonate and sodium methyl carbonate were obtained in good yields (see the last columns of Tables 1 and 2). Therefore, the complexes may be considered as intermediates in the present reaction and this reaction process can be expressed by two equations, (4) and (5). In Eq. 5 the oxygen atom of the alcohol would attack the

$$AM + CO_2 \rightarrow AM\cdot CO_2 \tag{4}$$

$$AM\cdot CO_2 + ROH \rightarrow ROCOOM + AH \tag{5}$$

carbon atom of the carbon dioxide of the complex, and as a result, phenol and alkali alkyl carbonate would be formed.

The second mechanism can be formulated as Eqs. 6 and 7:

$$AM + ROH \rightleftharpoons AH + ROM \tag{6}$$

$$ROM + CO_2 \longrightarrow ROCOOM \tag{7}$$

Equation 6 is equlibrium state, while Eq. 7 is substantially irreversible at room temperature.

It was reported that methyl ω-methoxyalkanoate was formed at high temperatures from the reaction shown in Eq. 8.[6)] Also when a mixture of sodium phenoxide (0.1 mol), benzyl chloride (0.1 mol), and methanol (100 ml) was refluxed for 2 h, benzyl methyl ether was obtained in 12% yield. These two facts support the assertion that at high temperature a considerable amount of sodium methoxide is formed by the equilibrium shown in Eq. 9, although both methyl

$$p\text{-}CH_3OOCC_6H_4ONa + Cl(CH_2)_nCOOCH_3 \xrightarrow{\text{in MeOH}} p\text{-}CH_3OOCC_6H_4O(CH_2)_nCOOCH_3 + NaCl \tag{8}$$

$$p\text{-}RC_6H_4ONa + CH_3OH \rightleftarrows p\text{-}RC_6H_4OH + CH_3ONa \quad (R{=}H \text{ or } CH_3OOC\text{-}) \tag{9}$$

*p*-hydroxybenzoic acid ($pK_a$=8.47 at 25 °C) and phenol ($pK_a$=10.0 at 25 °C) are considerably stronger acids than methanol ($pK_a$=15.5 at 25 °C).[7)] However, at room temperature, where the present reactions were carried out, the equilibrium will lie further to the left if we consider the $pK_a$ values. Therefore, the second mechanism may be less important than the first one. Alkali alkyl carbonate will be formed mainly by the first mechanism.

The mixture of sodium cyanide or sodium diethyldithiocarbamate and cyclohexane was stirred under a carbon dioxide atmosphere; the insoluble product was filtered. After the carbon dioxide had been replaced by nitrogen, methanol and acetone (solvent) were added into the product, but sodium methyl carbonate was not obtained. However, we noticed that these alkali salts absorbed carbon dioxide under atmospheric pressure. The difference between alkali phenoxides and other alkali salts may be as follows: although alkali phenoxide can form a stable complex with carbon dioxide,[1)] the other salts can not form such stable complexes. However, when an alcohol exists, the oxygen atom of the alcohol would attack the positively charged carbon atom of the carbonyl group of the complex and give alkali alkyl carbonate.

The difference of the reactivity toward sodium phenoxide in acetone between butyl alcohol and isobutyl alcohol was examined. The butyl alcohol reacted about 30 times faster than the isobutyl alcohol and 40 times faster than *s*-butyl alcohol. The oxygen atom of the branched alcohol must have difficulty in approaching the carbon atom of the carbonyl group of the complex. Therefore, the large differences of the reactivity between butyl alcohol and the branched alcohols ($i\text{-}C_4H_9OH$ and $s\text{-}C_4H_9OH$), and between isobutyl alcohol and *s*-butyl alcohol are attributed to the steric hindrance of the branched alcohol. The electronic effect of the alkyl group of alcohol would scarcely influence its reactivity because the difference of the electronic effect between the three alkyl groups, especially between the butyl and isobutyl groups, will be small.

Both di-alkali salts of salicylic acid and *p*-hydroxybenzoic acid may be employed as an alkali source. These results are summarized in Table 3. It was found that the content of *p*-hydroxybenzoic acid in each precipitate was in good agreement with the value calculated on the assumption that the precipitate is composed of equimolar amounts of mono-potassium salt or mono-sodium salt of *p*-hydroxybenzoic acid and potassium methyl carbonate or sodium methyl carbonate respectively, when the di-potassium salt or the di-sodium salt of *p*-hydroxybenzoic acid is used as an alkali source. However, the content of salicylic acid in each precipitate deviated significantly from the calculated value and, moreover, differed in every run when *p*-hydroxybenzoic acid was replaced with salicylic acid.

Alkali salts of *p*-hydroxybenzoic acid and salicylic acid can be well dissolved in methanol, but the solubility of sodium methyl carbonate is poor, only 1.0 g in 50 ml of methanol (see Table 4).

The results summarized in Table 3 can be explained as follows: when carbon dioxide is introduced into the methanol solution of the di-potassium salt of *p*-hydroxybenzoic acid, potassium methyl carbonate and potassium *p*-hydroxybenzoate are formed. Further introduction

Table 3. Reactions using di-alkali salts of POB or SA[a]

| Alkali salt[b] (g) | | ppt (g) | POB or SA (wt%)[c] in product pptd | | Analyses (%)[d] | |
|---|---|---|---|---|---|---|
| | | | | | C | H |
| POB di-K | 4.94 | 2.75 | 51.9 | (47.6) | — | — |
| POB di-K | 5.07 | 2.78 | 52.0 | (47.6) | — | — |
| POB di-Na | 5.00 | 4.44 | 54.2 | (53.5) | 40.67 | 3.61 |
| POB di-Na | 2.89 | 3.27 | 55.8 | (53.5) | 40.74 | 3.37 |
| SA di-K | 6.50 | 0.37 | 76.1 | (47.6) | — | — |
| SA di-Na | 6.12 | 2.12 | 38.5 | (53.5) | 41.34 | 3.02 |

a) POB = *p*-Hydroxybenzoic acid, SA = Salicylic acid; di-K = di-potassium salt, di-Na = di-sodium salt. b) These salts are dissolved in 50 ml of methanol. c) The values in parentheses were calculated on the assumption that the precipitates were composed of equal molar amounts of mono-alkali salt of POB or SA and alkali methyl carbonate. For example, [POB(Mw. 138.1)] × 100/[POB mono-K(Mw. 176.2) + $CH_3OCOOK$ (Mw. 114.1)] = 47.6(%). The determination of POB or SA was carried out by the UV technique. d) Calcd for (POB or SA mono-Na + $CH_3OCOONa$): C, 41.88%; H, 3.12%.

Table 4. Solubilities of alkali salts in methanol

| Alkali salt[a] | Solubility[b] (g) | Alkali salt | Solubility (g) |
|---|---|---|---|
| POB di-K | 12.0 | POB di-Na | 9.7 |
| POB mono-K | 10.0 | POB mono-Na | 5.0 |
| SA di-K | 6.5 | SA di-Na | 4.7 |
| SA mono-K | 7.0 | SA mono-Na | 10.5 |
| $CH_3OCOOK$ | 9.5 | $CH_3OCOONa$ | 1.0 |

a) See Table 3. b) Solubilities are defined as the amounts which dissolved easily in 50 ml of methanol at room temperature.

of carbon dioxide gives the complex composed of potassium *p*-hydroxybenzoate, carbon dioxide, and potassium methyl carbonate and the complex precipitates. However, carbon dioxide may escape from the complex during drying *in vacuo* after filtration. A similar explanation can be applied to the reaction using the di-sodium salt of *p*-hydroxybenzoic acid as an alkali source. There are other facts which support the above idea. When the methanol solutions of potassium *p*-hydroxybenzoate and of potassium methyl carbonate or the same solutions of sodium *p*-hydroxybenzoate and of sodium methyl carbonate were mixed, no precipitates were formed in either case. However, when carbon dioxide was introduced into each solution, precipitates were formed immediately from both.

The difference of the reactivity between the di-alkali salts of salicylic acid and of *p*-hydroxybenzoic acid was also observed in the Williamson ether syntheses. In the Williamson ether syntheses of the di-alkali salt of salicylic acid or *p*-hydroxybenzoic acid and benzylchloride in methanol at reflux temperature for 2 h, methyl benzyl ether was formed. Although di-alkali salts of *p*-hydroxybenzoic acid gave methyl benzyl ether only in about 4% yield, di-potassium and di-sodium salts of salicylic acid gave the same product in 67 and 47% yields, respectively. In addition, when the di-potassium salt of salicylic acid was recrystalized from methanol, the precipitate was the mono-potassium salt of salicylic acid (potassium salicylate). On the basis of these data, it was speculated that the di-potassium salt of salicylic acid easily changes into potassium salicylate. The reason may be due to the chelating structure of the salicylate; that is, the alkali atom of mono-alkali salicylate will be considerably neutralized and therefore the bonding force between the alkali atom of mono-alkali salicylate and the oxygen atom of carbon dioxide must be extremely weak.

## Experimental

*Authentic Alkali Alkyl Carbonate.* Metallic potassium or sodium was dissolved in anhydrous alcohol and then carbon dioxide was introduced with vigorous stirring. From this mixture, excess alcohol was evaporated off at about 100 °C *in vacuo.*

*Syntheses of Alkali Alkyl Carbonates by the Present Reaction.* A typical example is as follows. Into a 200 ml four-necked flask, provided with a mechanical stirrer, a thermometer, and a gas-inlet tube whose top was connected to a calcium chloride tube, were placed sodium phenoxide (3.48 g, 0.03 mol), anhydrous methanol (3 ml), and anhydrous acetone (50 ml, as a solvent of sodium phenoxide). A sufficient volume of dry carbon dioxide was slowly introduced into the stirred acetone solution and white precipitates soon formed. These precipitates were collected on a glass filter, washed with dry ether, and then dried in *vacuo* at room temperature: yield, 98.0%.

In the preparations of the branched alkyl alkali carbonates, the mixture became a slurry when carbon dioxide was introduced into the mixture of sodium phenoxide, alcohol, and solvent (acetone or THF). Therefore, these carbonates might partially decompose into alcohol and sodium hydrogen carbonate by contact with the moisture in the air, since rapid filtration was very difficult. Another possibility is that these carbonates contain some amounts of solvent, because of the difficulty of the complete evaporation of the solvent from these carbonates in a slurry-state. Owing to the above reasons, the values of the elementary analyses of the branched alkyl alkali carbonates would deviate more than 1% from the calculated values.

*Competitive Reactions.* Carbon dioxide was introduced into a mixture of isobutyl alcohol (0.10 mol), butyl alcohol (0.10 mol) and sodium phenoxide (0.021 mol) in acetone (100 ml); the precipitates were filtered, washed with ether, and then decomposed with water into alcohols and sodium hydrogen carbonate. The resulting alcohol were extracted with ether, and butyl alcohol and isobutyl alcohol were determined by gas chromatography (internal standard compound, cyclohexane; instrument, Yanagimoto G80; column, PEG 20 M, 2.25 m; temp, 98 °C). The ratio of butyl alcohol/isobutyl alcohol was 33.

Similarly, the reaction was carried out using the mixture of *s*-butyl alcohol (0.10 mol), butyl alcohol (0.10 mol), sodium phenoxide (0.021 mol), and acetone (100 ml); the alcohols derived from sodium butyl carbonates were determined by gas chromatography (column temp, 90 °C). The ratio of butyl alcohol/*s*-butyl alcohol was 41.

*Reactions using Di-alkali Salts of Hydroxybenzoic Acids as Alkali Sources.* An example is as follows. Five grams of di-sodium salt of *p*-hydroxybenzoic acid were dissolved in 50 ml of anhydrous methanol; into this mixture dry carbon dioxide was introduced. Within several minutes, white precipitates formed. After 30 min, the precipitates were filtered and dried *in vacuo* at room temperature: yield was 4.44 g. When di-potassium salt of salicylic acid was used, the formation of the precipitates was slower. Generally speaking, the readiness of the formation of the precipitates decreased in the following order: di-sodium salt of *p*-hydroxybenzoic acid>di-sodium salt of salicylic acid>di-potassium salt of *p*-hydroxybenzoic acid>di-potassium salt of salicylic acid.

*The Formation of the Complex from Mono-alkali Salt of* p-*Hydroxybenzoic Acid, Potassium Methyl Carbonate, and Carbon Dioxide.* Into a four-necked flask with a mechanical stirrer, 10.27 g of monopotassium salt of *p*-hydroxybenzoic acid and 50 ml of methanol were placed, and into this mixture carbon dioxide was introduced. The precipitates (perhaps mono-potassium salt of *p*-hydroxybenzoic acid) were filtered off. To the filtrate, a solution of 7.55 g of potassium methyl carbonate in 60 ml of methanol was added and then carbon dioxide was introduced. The precipitates were filtered and dried *in vacuo*: yield was 5.61 g. The content of *p*-hydroxybenzoic acid was 50.9% (determined by UV technique[2]). This value was in good agreement with the calculated one (47.6%, see Table 3), within experimental error. Therefore, this product must be composed of nearly equimolar amounts of mono-potassium salt of *p*-hydroxybenzoic acid and potassium methyl carbonate.

A similar reaction was carried out using sodium *p*-hydroxybenzoate and sodium methyl carbonate. The resulting content of *p*-hydroxybenzoic acid was 50.3%. This value is also in good agreement with the calculated one (53.5%, see Table 3), within experimental error.

*Reactions of Alkali Salts with Benzyl Chloride.* Into a 200 ml three-necked flask, with a mechanical stirrer and a reflux condenser whose top was connected to a calcium chloride tube, were placed 9.10 g of di-sodium salt of salicylic acid (0.05 mol), 6.35 g of benzyl chloride (0.05 mol), and 100 ml of methanol. The mixture was refluxed with vigorous stirring for 2 h. The volume of the solution was reduced to about half by evaporation of the methanol. The insoluble product was filtered off and then methyl benzyl ether was determined by gas chromatography (internal standard compound, dimethylaniline; column, PEG 20 M, 2.25 m; temp, 200 °C).

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