

Mechanism of the Kolbe-Schmitt Reaction. Part I. Infra-red Studies.

By J. L. HALES, J. IDRIS JONES, and A. S. LINDSEY.

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Examination of the infra-red absorption spectrum of the product obtained by carboxylation of sodium phenoxide (Kolbe-Schmitt reaction) shows that the sodium is attached to the carboxyl group, thus disproving Tijmstra's suggestion (*Ber.*, 1905, **38**, 1375) that the product has the metal oxide structure. Various reaction mechanisms are examined and some evidence is presented in support of the theory of cation-induced electrophilic replacement in the aromatic nucleus.

VARIOUS theories have been advanced to explain the mechanism of the carboxylation of alkali-metal aryloxides by carbon dioxide under pressure (Kolbe-Schmitt reaction). These postulate, respectively, initial formation of a metal aryl carbonate which subsequently rearranges (Schmitt, *J. pr. Chem.*, 1885, **31**, 397), direct carboxylation of the aromatic nucleus (Lobry de Bruyn and Tijmstra, *Rec. Trav. chim.*, 1904, **23**, 385; Tijmstra, *Ber.*, 1905, **38**, 1375; Schwenk *et al.*, *Chem. Ztg.*, 1929, **53**, 297, 333; Silin and Moschinskaya, *J. Gen. Chem., U.S.S.R.*, 1938, **8**, 810), alkali-metal-induced electrophilic replacement of nuclear hydrogen by carboxyl with migration of the alkali metal to the carboxyl group (Johnson, *J. Amer. Chem. Soc.*, 1933, **55**, 3029; Seel, *Angew. Chem.*, 1948, **60**, 300; cf. Henecka, "Chemieder β -Dicarbonylverbindungen," Springer-Verlag, Berlin, 1950, p. 164), and carboxylation of an *ortho*-metallated intermediate (Gilman, Arntzen, and

Webb, *J. Org. Chem.*, 1945, **10**, 374). The mechanism suggested by Gershzon (*J. Gen. Chem., U.S.S.R.*, 1943, **13**, 68) was later disproved (*ibid.*, 1946, **16**, 1485). A useful summary of current knowledge of the Kolbe-Schmitt reaction has been given by Wessely *et al.* (*Monatsh.*, 1950, **81**, 1071).

In the case of sodium phenoxide, direct substitution of carbon dioxide in the activated aromatic nucleus with retention of the metal-oxide structure (I; R = H) was postulated by Tijnstra (*loc. cit.*) whereas, according to the other views of the reaction, the product is a metal carboxylate (II; R = H). By a study of the infra-red absorption spectra we have sought to distinguish between these alternative structures. The preliminary results have already been reported (Hales, Jones, and Lindsey, *Chem. and Ind.*, 1954, 49).



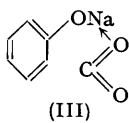
It is known that the asymmetric stretching of the ionised carboxyl group, $\nu_a (\text{C}^{\ominus}\text{O})$, gives rise to a strong absorption band near 1600 cm.^{-1} (see, *e.g.*, Thomas, *Discuss. Faraday Soc.*, 1950, **9**, 339). This is so for potassium phenylacetate (Davies and Thomas, *J.*, 1951, 2858) and we find likewise that sodium benzoate (1600 cm.^{-1}), sodium salicylate (1600 cm.^{-1}), and sodium *o*-methoxybenzoate (1613 cm.^{-1}) all give rise to strong bands in this region. Flett (*J.*, 1951, 962) has demonstrated that carboxylic acids give rise in general to five recognisable absorption bands, the first, due to associated OH, in the region 2700—2500, the others at ~ 1700 , 1420, 1250, and 900 cm.^{-1} , the 1700 and 1250 cm.^{-1} bands being the strongest. We have confirmed his results in the case of benzoic and salicylic acid; the spectrum of *o*-methoxybenzoic acid, which shows bands at 2605, 1689, 1669, 1412, 1258, and 921 cm.^{-1} , lends additional support. The doublet (1689, 1669 cm.^{-1}) here may possibly be due to a splitting of the single frequency owing to symmetry of the crystal lattice; alternatively two possible molecular configurations might exist in the solid state corresponding to the free and internally hydrogen-bonded hydroxyl groups (Davies, *Chem. and Ind.*, 1953, 614). Although Flett's work indicates that the strong 1258-cm.^{-1} band of *o*-methoxybenzoic acid arises from the carboxyl group, the position of the band falls well outside the limits of $1300 \pm 15 \text{ cm.}^{-1}$ suggested by Hadzi and Sheppard (*Proc. Roy. Soc.*, 1953, *A*, **216**, 247), and comparison with benzoic acid might suggest that the medium 1289-cm.^{-1} band arises from the carboxyl group. In the case of potassium hydrogen phthalate, bands indicating the presence of both ionised and non-ionised carboxyl groups are present, the relevant bands being 1603 (ionised) and 1669 cm.^{-1} (non-ionised) (cf. Davison, *Chem. and Ind.*, 1953, 408; Cardwell, Dunitz, and Orgel, *J.*, 1953, 3740). The absorption spectra of sodium phenoxide and disodium salicylate are also recorded in the Table. The spectrum of the former is in good agreement with that recently reported by Davies and Jones (*J.*, 1954, 120).

On the basis of these observations, therefore, it should be possible to distinguish between structures (I) and (II) (R = H). Thus a band due to phenolic OH at 3200—3500 cm.^{-1} would not be expected for a compound (I) but is likely for a compound (II; R = H). Both compounds, however, are likely to show some broad absorption in the region 2500—3100 cm.^{-1} . Comparison of the spectra of methyl salicylate and sodium methyl salicylate and of sodium salicylate and disodium salicylate shows that in both cases replacement of the hydrogen, bonded to the carbonyl group, by sodium results in a shift of 10—14 cm.^{-1} . On this basis a compound of structure (I; R = H) can be expected to give a carbonyl absorption band near 1650 cm.^{-1} whereas structure (II) would give a band near 1600 cm.^{-1} . Comparisons in the regions 1400—1465 and near 1250 cm.^{-1} are not likely to be very diagnostic since both structures are likely to give bands in these regions. The presence of a band in the 900—940 cm.^{-1} region is likely if (I) is the structure but not if it is (II).

Sodium phenoxide was carboxylated by three methods, (i) by heating "sodium phenyl carbonate" (Schmitt, *loc. cit.*) at 145° in a sealed tube, (ii) by direct pressure carboxylation at $125\text{--}135^\circ$, and (iii) by passing dry carbon dioxide through a phenolic solution of sodium phenoxide at 140° (cf. B.P. 384,619/1932). The absorption spectra of the products obtained by these procedures were all substantially similar to that of authentic mono-

sodium salicylate, and differed from that expected for a structure of type (I; R = H). The spectrum of the product obtained by method (ii) showed some weak absorption bands arising from the presence of small amounts of sodium carbonate and sodium hydrogen carbonate. These by-products could be removed in hot absolute acetone, the recovered product then possessing a spectrum closely similar to that of authentic monosodium salicylate. The carbonates arise from the presence of moisture which, despite rigorous drying of the starting materials, is picked up during the charging of the autoclave. In the other two methods moisture could more easily be excluded and only traces of carbonate were formed.

Schmitt (*loc. cit.*) showed that sodium phenoxide combines with an equimolecular amount of dry carbon dioxide at room temperature to form a compound which he considered to be sodium phenyl carbonate, $\text{PhO}\cdot\text{CO}_2\text{Na}$, and he postulated it as an intermediate in the carboxylation reaction. This compound, which is readily decomposed by water, completely dissociates at about 80° at atmospheric pressure (Tijmstra, *loc. cit.*). We have confirmed the fact that dry sodium phenoxide, when kept in contact with dry carbon dioxide for 7–10 days, takes up almost the theoretical quantity. Much of the absorbed carbon dioxide can be removed merely by applying a high vacuum and all can be removed at 80° *in vacuo*, sodium phenoxide being recovered unchanged. Since the material remains as a discrete microcrystalline powder during both the absorbing and the desorbing process, it is improbable that the crystal lattice undergoes sufficient distortion at room temperature to permit the large separation of the sodium and phenoxy-ions necessary for the formation of a new carbon-oxygen bond (as in $\text{PhO}\cdot\text{CO}_2\text{Na}$). It is known that sodium phenoxide readily forms chelate compounds with oxygenated substances, *e.g.*, with acetone (Segaller, *J.*, 1914, **105**, 114) and phenol (Gentsch, G.P. 156,761; *Chem. Zentr.*, 1905, I, 313); it is therefore likely that it will weakly chelate with carbon dioxide in a similar way. The infra-red absorption spectrum of the sodium phenoxide-carbon dioxide complex shows a medium-strength band, due to a carbonyl function, at 1684 cm^{-1} . Sodium methyl carbonate, $\text{MeO}\cdot\text{CO}_2\text{Na}$, a stable recrystallisable solid, has an absorption band, due to carbonyl, at 1630 cm^{-1} . Dimethyl carbonate and methyl phenyl carbonate possess carbonyl bands at 1748 and 1754 cm^{-1} respectively, indicating that the phenyl group has little effect on the position of the carbonyl band. These facts suggest that Schmitt's "sodium phenyl carbonate" is a complex which may be represented as (III). Davies (*Z. physikal. Chem.*, 1928, **134**, 57) has shown that this complex does not dissociate between 120° and 160° provided the pressure exceeds about 4 atmospheres.



Gilman, Arntzen, and Webb (*loc. cit.*) have suggested that, at the temperature of the Kolbe-Schmitt reaction, alkali-metal phenoxides tautomerise to the corresponding *ortho*-metallated structures and that these tautomers either react directly with carbon dioxide as does, for example, phenyl-lithium, or react with non-tautomerised alkali-metal phenoxide to produce *ortho*-metallated compounds which then react with carbon dioxide. Both of these views seem unlikely since it is well known that sodium phenoxide at temperatures above 120° reacts with alkyl halides to give, substantially, the corresponding alkyl phenyl ether (*e.g.*, Vincent, *Bull. Soc. chim.*, 1883, **40**, 106). We have confirmed this observation by adding *n*-hexyl bromide to sodium phenoxide at 150° and, by infra-red absorption analysis of the product, have shown it to contain at least 91% of *n*-hexyl phenyl ether. If tautomerism of sodium phenoxide had occurred at this temperature, appreciable quantities of *ortho*-substituted products should have been formed. Although benzyl chloride reacts with sodium phenoxide at 80° to give *ortho*-substituted products this is an anomalous reaction since diphenylmethyl bromide *ortho*-substitutes sodium phenoxide *even in the cold* (Claisen *et al.*, *Annalen*, 1925, **442**, 210). Moreover, Gilman *et al.* (*loc. cit.*) showed that treatment of lithium phenoxide with carbon dioxide at room temperature did not give any salicylic acid. The second view of Gilman and his collaborators is also disproved by the absence of any disodium salicylate in the carboxylation products.

The familiar effect of small amounts of water in reducing the extent of carboxylation in the Kolbe-Schmitt reaction may well be due to the stronger chelating power of water with

sodium phenoxide. Various authors (cf. Brady and Jakobovits, *J.*, 1950, 767) have commented on the specific effect of different alkali metals in carboxylation reactions, attributing it to differences in the chelating strengths of the metals. In this paper we have considered only the behaviour of sodium phenoxide but later we hope to deal with this phenomenon in more detail.

Phenol will only undergo carboxylation in the form of the alkali-metal phenoxide (Kolbe-Schmitt reaction) (cf. Kinney and Ward, *J. Amer. Chem. Soc.*, 1933, 55, 3796). In the Marasse modification of the reaction (G.P. 73,279/1893) where the free phenol is heated with anhydrous potassium carbonate and carbon dioxide under pressure it has been shown that phenoxide formation is a necessary prelude to reaction (Wessely *et al.*, *loc. cit.*). It therefore seems likely that this type of carboxylation involves electrophilic attack on the *ortho*-carbon atom (cf. Seel, *loc. cit.*). Presumably, a similar process can operate when carboxylation is carried out in phenol solution; here, one of the phenol molecules of the sodium phenoxide-phenol solvate would be displaced by a molecule of carbon dioxide with subsequent electrophilic attack on the *ortho*-position.

Although the experimental results described above show that Tijnstra's formulation (*loc. cit.*) of the reaction product as sodium salicyloxide (I; R = H) is no longer tenable, this does not rule out the possibility that his original hypothesis of direct nuclear carboxylation may still represent the first step in the reaction, and that subsequent interchange of hydrogen and sodium ions (or atoms) occurs, giving sodium salicylate as the final product. However an alternative reaction mechanism, based on the preliminary association of sodium phenoxide with carbon dioxide under pressure to form a complex, and involving intramolecular reaction with displacement of the *ortho*-hydrogen by electrophilic attack, appears to us to offer a more satisfactory scheme of reaction. The absence of disodium salicylate in the carboxylation products, already described, strongly supports the intra-

Infra-red absorption bands (cm.⁻¹). (Disubstituted derivatives are all *o*-compounds.)

$C_6H_4 \begin{matrix} \diagup OH \\ \diagdown CO_2Na \end{matrix}$	$C_6H_4 \begin{matrix} \diagup OH \\ \diagdown CO_2Me \end{matrix}$	$C_6H_4 \begin{matrix} \diagup ONa \\ \diagdown CO_2Me \end{matrix}$	$C_6H_4 \begin{matrix} \diagup OMe \\ \diagdown CO_2Na \end{matrix}$	$C_6H_4 \begin{matrix} \diagup OMe \\ \diagdown CO_2H \end{matrix}$	$C_6H_4 \begin{matrix} \diagup OH \\ \diagdown CO_2H \end{matrix}$	$C_6H_4 \begin{matrix} \diagup ONa \\ \diagdown CO_2Na \end{matrix}$
—	~3400 m(sh)	—	—	—	—	—
—	3185 s	—	—	—	3255 m(sp)	—
—	3058 s(sh)	—	—	—	—	—
2925 s	2967 s	2905 s	2950 s	2910 s	2950 s	2905 s
2875 s(sh)	2857 m	2865 s(sh)	2890 s(sh)	2875 s(sh)	2890 s(sh)	2840 s(sh)
—	—	—	—	—	2740 m	—
—	—	—	—	—	2610 m	—
—	1675 s	1661 s	—	1689 s(sh)	1664 s	—
—	—	—	1613 s	1669 s	—	—
1600 s(sh)	—	—	1597 m	—	—	1590 m
—	1610 m	1597 m	1592 s	1595 m	1610 s	—
1585 s	1585 m	—	1577 s	1580 m	1582 m	—
—	—	—	1548 m(h)	—	—	1550 m
—	—	1536 m	—	—	—	1529 m

PhONa	Ph·CO ₂ Na	Ph·CO ₂ H	$C_6H_4 \begin{matrix} \diagup CO_2H \\ \diagdown CO_2K \end{matrix}$	Assignments
—	—	—	—	OH (Bonded)
—	—	—	—	} { CH freqs. (from Nujol and compound *) Bonded OH submaxima
2935 s	2915 s	2950 s	2900 s	
2875 s(sh)	2875 s(sh)	2905 s(sh)	2855 s(sh)	} C=O of conjugated CO ₂ R (R = H or Me) C=O of ionic CO ₂ ⁻
—	—	2690 m	—	
—	—	2575 m	—	} Phenyl-ring vibrations
—	1600 s	1692 s	1669 w	
—	—	1605 m	1603 m(sh)	
1585 s	—	1585 m	1587 m	
—	1553 s	—	1567 m	
1555 m	—	—	—	

s = strong band 80—100% of strongest band in spectrum.

m = medium ,, 40—80% ,, ,, ,,

sp = sharp.

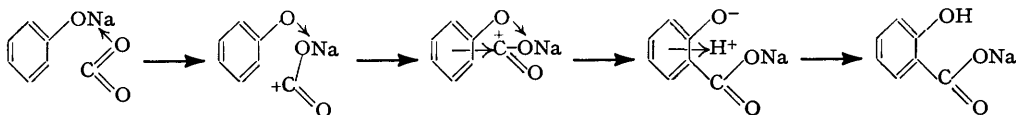
* The spectrum of methyl salicylate is that of the pure liquid.

sh = shoulder.

h = hump.

b = broad band.

molecular mechanism. The essential difference between the two mechanisms suggested appears to lie in the position of the displaced proton during the intermediate stage. According to the first mechanism a definite attachment of the proton to the carboxyl group as one stage of the reaction must be postulated, whereas, in the second, displacement of the proton on to the aromatic π -electron orbital (see below) would involve a close association of the proton with the aromatic nucleus during the intermediate stage. The latter mechanism will operate only if, in solid sodium phenoxide, the oxygen atom is coplanar with the benzene ring so that its "lone-pair" electrons can take part in a molecular π -electron orbital (cf. Coulson, "Valence," Oxford Univ. Press, 1952, p. 247). The reaction would then proceed according to the scheme outlined below (cf. Dewar, "The Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, pp. 168, 227—228). In this case the proton held by the π -electron system would migrate to the phenolic oxygen.



That the assumption made is valid, at least for sodium phenoxide in solution, is implied in the observation that the ultra-violet absorption spectrum of sodium phenoxide in ethanol (λ_{\max} , 219, 273 $m\mu$; $\log \epsilon$ 3.4, 2.8) differs from that of benzene (λ_{\max} , 198, 256 $m\mu$; $\log \epsilon$ 3.9, 2.4) and approaches that of aniline (λ_{\max} , 233, 285 $m\mu$; $\log \epsilon$ 3.9, 3.2) (cf. Maccoll, *Quart. Reviews*, 1947, 1, 45 and 56; Dewar, *op. cit.*, p. 201).

EXPERIMENTAL

Microanalyses were carried out by Miss M. Corner and her staff of this laboratory.

Infra-red Absorption Spectra.—Spectra were measured on a modified Hilger D 209 double-beam instrument (Hales, *J. Sci. Instr.*, 1949, 26, 359; 1953, 30, 52), the solid compounds being prepared as mulls in Nujol. Mulls of hygroscopic compounds were prepared in a "dry box." Compounds were prepared as follows.

Sodium Phenoxide.—(a) Clean sodium (4.6 g.) was converted into sodium sand in anhydrous sulphur-free toluene (300 ml.). Freshly distilled phenol (18.9 g.) in anhydrous toluene (50 ml.) was then added dropwise with stirring. After 4 hours' gentle refluxing the pasty mixture was allowed to cool and the product filtered off rapidly and washed with anhydrous toluene and finally with anhydrous ether. The snow-white powder was dried *in vacuo* in a desiccator (Found: C, 61.6; H, 4.8; Na, 19.95%; equiv., 116. Calc. for C_6H_5ONa : C, 62.1; H, 4.3; Na, 19.8%; equiv., 116). Ultra-violet absorption spectrum (in EtOH): λ_{\max} , 219, 273 $m\mu$ ($\log \epsilon$ 3.4, 2.8). Microscopic examination ($\times 600$) of the product suspended in liquid paraffin showed it to consist of rectangular crystals.

(b) Commercial sodium phenoxide was recrystallised twice from boiling anhydrous acetone. Dried *in vacuo* (over P_2O_5), it was a white powder which gradually discoloured in a desiccator. Some samples prepared in this way melted at *ca.* 60° but resolidified at higher temperatures. This may have been due to traces of acetone (Found: Na, 20.0%). The infra-red absorption spectrum of the product was closely similar to that of the product obtained as in (a).

Sodium Salicylate.—Salicylic acid (1.38 g.; "AnalaR") was dissolved in 0.1N-sodium hydroxide (100 ml.) and evaporated to dryness; the solid product was extracted (Soxhlet) with chloroform to remove traces of free acid and then dried at 100° (Found: C, 52.4; H, 3.45; Na, 14.6. Calc. for $C_7H_5O_3Na$: C, 52.5; H, 3.1; Na, 14.4%). The infra-red absorption spectrum of this compound was closely similar to that of a good-quality commercial sample.

Disodium Salicylate.—(a) Monosodium salicylate was neutralised with sodium hydroxide in water and the solution evaporated to dryness. Recrystallisation of the product from ethanol, washing with hot anhydrous acetone, and drying at 110° gave disodium salicylate (Found: Na, 25.7. Calc. for $C_7H_4O_3Na_2$: Na, 25.3%).

(b) Equimolecular quantities of sodium phenoxide and monosodium salicylate were heated at 240° *in vacuo* for 2 hr. The product was washed with anhydrous ether to remove phenol and with hot anhydrous acetone to remove unchanged starting materials. The product was dried at 150° *in vacuo* (Found: Na, 24.9%).

o-Methoxybenzoic Acid.—Prepared by Graebe's method (*Annalen*, 1905, 340, 210), this had m. p. 102° (Found: C, 62.9; H, 5.0. Calc. for $C_8H_8O_3$: C, 63.2; H, 5.3%).

Sodium o-Methoxybenzoate.—To *o*-methoxybenzoic acid (4 g.) in methanol (25 ml.) was added a solution of sodium hydroxide (1.05 g.) in methanol (15 ml.). The bulk of the methanol was removed under reduced pressure, anhydrous ether added, and the sodium salt filtered off, washed with ether, and dried at 110° *in vacuo* (P_2O_5) (Found: C, 55.0; H, 4.0; Na, 13.5. $C_8H_7O_3Na$ requires C, 55.2; H, 4.0; Na, 13.2%).

Sodium Methyl Salicylate.—To sodium (0.5 g.) dissolved in absolute methanol (25 ml.) was added a solution of freshly distilled methyl salicylate (3 g.) in methanol (25 ml.). After removal of the bulk of the methanol under reduced pressure, the solid product was filtered off and washed with cold absolute methanol, anhydrous ether, and finally boiling anhydrous benzene. It was dried at 120° *in vacuo* (Found: C, 55.2; H, 3.95; Na, 13.4. Calc. for $C_8H_7O_3Na$: C, 55.2; H, 4.0; Na, 13.2%).

Sodium Methyl Carbonate.—To a solution of sodium (1 g.) in absolute methanol (50 ml.) was added excess of solid carbon dioxide (10 g.) previously washed in methanol. The solid product was rapidly filtered off, recrystallised from absolute methanol (lustrous flakes), and dried *in vacuo* for 24 hr. (P_2O_5) (Found: Na, 24.0%; equiv., 98.0. Calc. for $C_2H_3O_3Na$: Na, 23.5%; equiv., 98.0).

Methyl Phenyl Carbonate.—To methyl chloroformate (40 g.) in benzene (100 ml.) was added dry powdered sodium phenoxide (17 g.), and the mixture was gently refluxed for 3 hr. The product recovered by distillation, after filtration from the sodium chloride, was redistilled, taken up in light petroleum (b. p. 40–60°), and filtered through a short column of alumina. Fractionation of the eluate gave methyl phenyl carbonate (10 g.), b. p. 120–121°/38 mm., $n_D^{18.5}$ 1.4972 (Found: C, 63.35; H, 5.4. Calc. for $C_8H_9O_3$: C, 63.2; H, 5.3%). The spectrum of this compound possessed an absorption band, due to carbonyl, at 1754 cm^{-1} .

Other Compounds.—Salicylic acid was "AnalaR" material, recrystallised and resublimed as white needles, m. p. 160–161°.

Potassium hydrogen phthalate was "AnalaR" material, dried at 110°.

Benzoic acid was "AnalaR" material, m. p. 122°.

Sodium benzoate was of reagent grade (B.D.H.), dried at 110°.

Dimethyl carbonate was of reagent grade (B.D.H.). The spectrum of this compound possessed an absorption band due to carbonyl, at 1748 cm^{-1} .

Kolbe-Schmitt Carboxylation Products.—(a) *Sealed tube technique.* A Carius tube containing dry sodium phenoxide (0.99 g.) was attached to a tube and tap system so that it could be successively evacuated and connected to a reservoir of dry carbon dioxide (dried over P_2O_5 for 72 hr.). After 96 hr. the theoretical amount of carbon dioxide (0.37 g.) had been absorbed. Dry air was admitted to the tube which was then sealed and heated for 2 hr. at 145°. After cooling, no large internal pressure was present. The product had a faint pink colour (Found: Na, 14.4. Calc. for $C_7H_5O_3Na$: N, 14.4%).

(b) *Autoclave technique.* A glass tube containing dry sodium phenoxide (1.98 g.) was placed in a steel autoclave (ca. 100 c.c.), and air was removed by flushing twice with carbon dioxide which had been dried for 72 hr. (P_2O_5) in a second autoclave (2 l.). The smaller autoclave was then filled with carbon dioxide at a pressure of 250 lb./sq. in. and heated at 125–135° for 3 hr. (1.25 hr. preheating). On opening of the autoclave it was found that some phenol (0.11 g.) had sublimed to the upper parts. The product (2.49 g.) was washed with a little anhydrous ether to give product (B). Part of this was treated with hot absolute acetone, and the soluble material (Found: Na, 13.8%) recovered by evaporating off the solvent at room temperature under reduced pressure. The infra-red absorption spectrum of the acetone-insoluble material showed it to be essentially a mixture of sodium carbonate and sodium hydrogen carbonate.

(c) *Carboxylation in phenol solution (method of B.P. 384,619).* Solid sodium hydroxide (0.41 g.) was dissolved in freshly distilled phenol (21 g.) by heating it at 140° with passage of dry nitrogen. The excess of water was removed azeotropically by distillation with dry xylene (30 ml.). Dry carbon dioxide was then passed briskly through the melt held at 140–150° for 14 hr. The product (1.24 g.) was recovered by addition of anhydrous ether, filtration, and thorough washing with ether.

Sodium Phenoxide-Carbon Dioxide Complex.—A tube containing dry, finely powdered sodium phenoxide (551 mg.) was evacuated and then connected to a reservoir of carbon dioxide which had been dried for several weeks (P_2O_5). After 7 days at room temperature 88% (183 mg.) of the theoretical amount of carbon dioxide had been absorbed. Standing in contact with carbon dioxide for a further 3 days led to no further absorption.

A mull of this complex in Nujol, prepared in a "dry box," showed a medium-strength band due to carbonyl at 1684 cm^{-1} .

A sample of the sodium phenoxide-carbon dioxide complex prepared in a similar way was subjected cautiously to a vacuum of 0.05 mm. of mercury. The powder became disturbed as it "degassed." The containing vessel was immersed in boiling benzene vapour and the vacuum of 0.05 mm. maintained for 3 hr. The residual powder possessed a spectrum closely similar to that of the original sodium phenoxide, and still appeared microcrystalline on microscopic examination.

Reaction of n-Hexyl Bromide with Sodium Phenoxide.—To dry, finely powdered sodium phenoxide (5.0 g.), heated at 160° for 30 min., was added *n*-hexyl bromide (50 ml.), and the mixture was refluxed for 8 hr. The solid sodium bromide (4.5 g.; theor., 4.4 g.) was filtered off and washed well with anhydrous ether. Extraction of the bulked ethereal filtrates with 20% sodium hydroxide solution led to the recovery, in the usual way, of a phenolic product (*a*) (0.25 g.) which partly crystallised. Distillation removed ether and unchanged *n*-hexyl bromide from the dried ethereal solution and gave the main product (*b*), b. p. 235—245° (6.55 g., 90.8%), leaving a still residue (*c*) (0.70 g.). Refractionation of (*b*) gave a good sample of *n*-hexyl phenyl ether, b. p. 240—241°, n_D^{20} 1.4928 (Found: C, 80.6; H, 10.1. Calc. for $C_{12}H_{18}O$: C, 80.9; H, 10.1), which gave no colour with ferric chloride solution. For *n*-hexyl phenyl ether Hurd and McNamee (*J. Amer. Chem. Soc.*, 1932, 54, 1648) give b. p. 125—128°/10 mm., n_D^{25} 1.4889. The infra-red absorption spectrum of this compound had a broad similarity to that of anisole, and possessed strong absorption bands at 1079 and at 1250 cm^{-1} indicative of the ether linkage (Tschamler and Leutner, *Monatsh.*, 1952, 83, 1502). Examination of the spectrum of product (*b*) showed it to be substantially the same product. Residue (*c*) contained unidentified impurities in addition to *n*-hexyl phenyl ether, while phenolic fraction (*a*) consisted largely of unchanged phenol.

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CHEMICAL RESEARCH LABORATORY,
D.S.I.R., TEDDINGTON, MIDDLESEX.

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