[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLORADO A. AND M. COLLEGE]

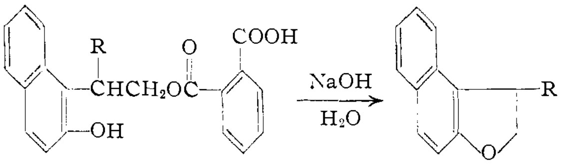
Intramolecular Displacement of Carboxylate Ion. III. Steric Facilitation

BY CYRUS O. GUSS AND ROBERT W. LERNER[1]

RECEIVED AUGUST 1, 1955

Carboxylic acid esters of structure I are prone to undergo displacement of carboxylate ion to form a dihydrofuran (II) when treated with aqueous alkali. It now has been demonstrated that the steric requirement of the group R in I has a large effect on the ease of displacement. No evidence of an inductive effect acting through R was detected. Mechanistically, this reaction is assumed to be the intramolecular analog of a bimolecular alkyl–oxygen fission.

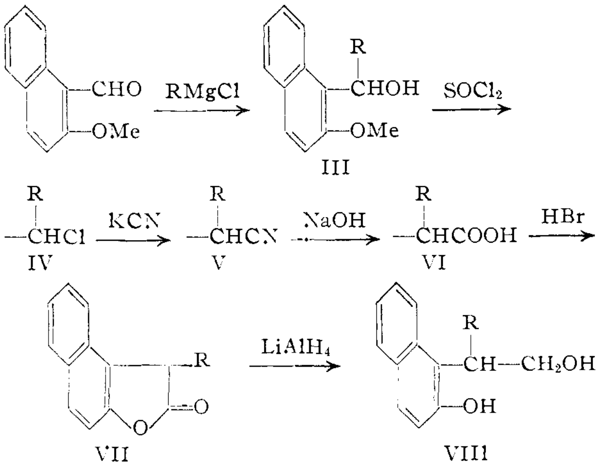
In two previous papers[2,3] several examples were reported in which the uncommon alkyl–oxygen fission of esters of carboxylic acids occurred in aqueous sodium hydroxide. All esters having structure I exhibited this behavior; other esters with similar structural features also gave dihydrofurans under the conditions usually used for alkaline hydrolysis. It was pointed out[2,3] that a plausible reason for the ease of displacement of carboxylate ion in these esters was to be found in the steric inhibition of rotation in the bond between the naphthalene ring and the carbon to which the group R is joined in I. For the ester where R is phenyl, a molecular model indicated the presence of nearly prohibitive interference between the *o*-position of this phenyl group and the 8-position of the naphthalene ring. This interference greatly restricted rotation in the aforementioned bond and, in so doing, held the phenolic group and the α-carbon of the alkoxy portion of the ester in close proximity to each other. Insofar as the model reflected the actual steric requirements in the molecule, this interpretation seemed to be worthy of consideration. All of the chemical evidence heretofore obtained has been in harmony with these assumptions. Thus, when R was hydrogen the relative amount of the dihydrofuran formed was markedly reduced compared with the amount formed when R was phenyl.[3] The present work was designed to make this presumed steric effect more apparent.



I II

There has been no cogent reason to assume that the loss of carboxylate ion from these esters proceeded by way of a unimolecular alkyl–oxygen fission of the type studied by Kenyon.[4] On the other hand, the structure seemed to be very favorable for the occurrence of the intramolecular analog of a bimolecular alkyl–oxygen fission, or an intramolecular SN2 reaction. Baddeley and Bennett[5] have examined the bimolecular kinetics involved in the reaction of various phenylethyl chlorides ($ArCH_2CH_2Cl$) with potassium iodide and found the relative rates to increase in the order Ar = phenyl, *p*-methoxyphenyl, *p*-iodophenyl, *p*-bromophenyl, *p*-chlorophenyl, *p*-fluorophenyl and *p*-nitrophenyl. The effect of these *p*-substituents was assumed to be purely inductive. It is apparent that in I, R = phenyl, a structure similar to the phenylethyl chlorides is present. Conceivably an inductive effect could act through R to alter the rate of displacement of carboxylate ion. Suitable esters were therefore synthesized in order to elucidate this point.

With but one exception, the phenol-alcohols which were precursors of the esters were obtained by reduction of the lactones resulting from the reaction of the appropriate 2-naphthol with mandelic acid or substituted mandelic acid.[2,3] This sequence worked very well when R was aromatic, but failed when R was aliphatic. In order to make I, R = cyclohexyl, the following route was utilized.



The phenol-alcohols were esterified with phthalic anhydride and taken up in aqueous sodium bicarbonate in the manner previously employed.[2,3] Treatment of these bicarbonate solutions of the esters with weak or strong sodium hydroxide solutions gave the results presented in Table I.

Discussion

These data clearly indicate a pronounced facilitation of the displacement reaction when R is increased in size. *Para* substituents on R do not exert a sufficient inductive effect to be unequivocally manifest, although when R is *p*-methoxyphenyl the cyclization reaction is somewhat higher than when R is phenyl. An inspection of a molecular model shows that the *p*-methoxy group and the 7-position of the naphthalene ring can give mutual interference

---

[1] Based on the thesis submitted by Robert W. Lerner in partial fulfillment of the requirements for the Master of Science degree, August, 1954. Scientific Series No. 464.

[2] C. O. Guss and L. H. Jules, THIS JOURNAL, **72**, 3462 (1950).

[3] C. O. Guss, *ibid.*, **73**, 608 (1951).

[4] J. Kenyon, S. M. Partridge and H. Phillips, *J. Chem. Soc.*, 85 (1936), and several subsequent papers.

[5] G. Baddeley and G. M. Bennett, *ibid.*, 1819 (1935); see also M. Simonetta and G. Favini, *ibid.*, 1840 (1954).

which, added to that of the phenyl ring and the 8-position, could account for the results obtained. Furthermore, the *p*-chlorophenyl group, on the basis of the work of Baddeley and Bennett,[5] would be expected to exert a greater inductive effect than the *p*-methoxyphenyl group and in a direction favorable to cyclization. This behavior is not observed.

The cyclohexyl group has somewhat greater steric requirements than a phenyl group; hence the greater ease of cyclization when R is cyclohexyl. Since the steric interference seems to occur between the 8-position of the naphthalene ring and the *o*-position of the phenyl group (R is phenyl), it is not surprising to find that the introduction of a methyl group at either position leads to exclusive cyclization even in strong alkali. The methyl group at the 8-position would not be expected to exert any effect on a unimolecular alkyl–oxygen fission,[4] thus pointing to a bimolecular type of reaction for a mechanistic interpretation of our results.

The evidence seems to be rather indicative, therefore, that an intramolecular analog of a bimolecular alkyl–oxygen fission is at hand. To our knowledge, these and the previous examples constitute the first reported instances of bimolecular alkyl–oxygen fission of carboxylic acid esters in aqueous alkali. In any event, this type of fission is definitely not common.

Acknowledgment.—The authors are grateful to the Research Corporation for a Frederick Gardner Cottrell grant in support of this work.

TABLE I

DISPLACEMENT OF CARBOXYLATE ION FROM THE SODIUM SALT OF I

	Yield, %		
	Weak[a] NaOH	Strong[b] NaOH	
R	Cyclized product	Cyclized product	Hydrol. product
Phenyl	93.5[e]	67.1	24.6
p-Chlorophenyl	86.0[e]	69.1	18.7
p-Methoxyphenyl	98.9[e]	76.0	21.9
Mesityl	..[c]	92.5	0
Cyclohexyl	..[c]	91.2	9.3
Phenyl[d]	..[c]	90.4	0

[a] The ester concentration was 0.083 mole per liter, and the added sodium hydroxide calculated to give a concentration of 0.208 mole per liter, uncorrected for reaction with the phenolic hydroxyl. [b] Same as for weak alkali except the sodium hydroxide concentration was 3.124 moles per liter. [c] Since the use of strong alkali, which was relatively unfavorable to cyclization, gave almost complete cyclization, the reaction was not run in weak alkali. [d] In this case the substance carried a methyl group in the 8-position of the naphthalene nucleus. [e] No hydrolysis was observed.

Experimental[6]

Preparation of the Lactones of α-Substituted-2-hydroxy-1-naphthaleneacetic Acids.—The lactones were prepared by heating the solid mixture of the mandelic acid with the 2-naphthol in an oil-bath at 150–210° for 30 minutes to an hour, the temperature and time depending on the particular combination of reactants. The evolution of water vapor was a good key to the progress of the reaction. A 50 to 100% excess of 2-naphthol was employed except in the reaction of mandelic acid with 8-methyl-2-naphthol where mandelic acid was the excess reactant. Ethanol was added to the cooled reaction mixture, and the insoluble product was filtered, washed with ethanol, and recrystallized from glacial and dilute acetic acid. Table II summarizes the pertinent data.

Preparation of β-Substituted-2-hydroxy-1-naphthalene-ethanols.—The reduction of the lactones was accomplished by adding the lactone in small portions to excess lithium aluminum hydride in dry ether, or by adding excess lithium aluminum hydride in small portions to a stirred slurry of the lactone in dry ether. After the reaction mixture had stood for about one hour, it was decomposed with dilute hydrochloric acid and worked up in the usual way. In the case of the 8-methyl compound, particular care was taken to keep the mixture cold during the decomposition. These phenol-alcohols were recrystallized from dilute ethanol. The data are presented in Table III.

TABLE II

LACTONES FROM 2-NAPHTHOLS AND MANDELIC ACIDS

Reactants	Yield, %	M.p., °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-Chloromandelic acid[a] and 2-naphthol	93.0	170–172	$C_{18}H_{11}O_2Cl$	73.35	73.10	3.76	3.91
p-Methoxymandelic acid[b] and 2-naphthol	89.9	146–148[c]					
2,4,6-Trimethylmandelic acid[d] and 2-naphthol	94.0	203–204[e]	$C_{21}H_{18}O_2$	83.42	83.24	6.00	6.17
Mandelic acid and 8-methyl-2-naphthol[f]	98.0	187–188.5	$C_{19}H_{14}O_2$	83.19	82.93	5.14	5.29

[a] Prepared by the method of S. Jenkins, THIS JOURNAL, **53**, 2341 (1931), m.p. 118–121°. [b] Prepared by the procedure of A. J. Bistrzycki, J. Paulus and R. Perrin, *Ber.*, **44**, 2596 (1911), m.p. 106–107°. [c] The foregoing authors report m.p. 145–146° for this lactone prepared by a similar but different method. [d] Prepared by the method of A. R. Gray and R. C. Fuson, THIS JOURNAL, **56**, 739 (1934), m.p. 151–154°. [e] This lactone appeared to be particularly susceptible to contamination by what was presumed to be the bislactone; see H. H. Wasserman, T. C. Liu and E. R. Wasserman, *ibid.*, **75**, 2056 (1953); H. H. Wasserman, H. W. Ackerman, H. H. Wotiz and T. C. Liu, *ibid.*, **77**, 973 (1955). [f] From anisole by the reaction sequence used by R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 1950 (1934), m.p. 66–68°.

Cyclization of the Phenol-alcohols to Dihydrofurans with *p*-Toluenesulfonic Acid.—This transformation was effected by refluxing the phenol-alcohol in benzene containing a small amount of *p*-toluenesulfonic acid for one to two hours. The benzene solution was then washed with dilute sodium hydroxide, dried over anhydrous potassium carbonate, and the benzene evaporated under reduced pressure. Dilute ethanol was used for the recrystallizations. Data relative to these products are given in Table IV.

Preparation of β-Cyclohexyl-2-hydroxy-1-naphthalene-ethanol (VIII).—The synthetic sequence leading to VIII began with the preparation of **α-cyclohexyl-2-methoxy-1-naphthalenemethanol (III)**. This compound was prepared by two different methods. **Method I** (Friedel–Crafts synthesis): A solution of cyclohexanecarbonyl chloride (106.5 g., 0.726 mole, b.p. 77–78° (19 mm.)) in carbon bisulfide (125 ml.) was added to a stirred mixture of 2-naphthyl methyl ether (118.5 g., 0.75 mole), carbon bisulfide (300 ml.) and anhydrous aluminum chloride (97 g., 0.73 mole) in appropriate apparatus over a period of 140 minutes. The mixture was allowed to stand 5 hours more, then added to iced concentrated hydrochloric acid (100 ml.) and the organic layer separated. This layer was washed with dilute sodium bicarbonate and then extracted with dilute sodium hydroxide. Addition of Dry Ice to this extract precipitated 19 g., m.p. 132–137°, of **cyclohexyl 2-hydroxy-1-naphthyl ketone**, formed by ether cleavage of the desired reaction product. Recrystallization from ethanol or petroleum ether, b.p. 60–71°, gave white needles, m.p. 136–137°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.29; H, 7.13. Found: C, 80.32; H, 7.23.

This phenol-ketone was remethylated with dimethyl sulfate and worked up with the main reaction product. The carbon bisulfide layer was dried over anhydrous sodium sulfate and the solvent evaporated to leave 166 g., m.p. 60–

---

(6) All temperature measurements are uncorrected

TABLE III

REDUCTION OF LACTONES TO PHENOL-ALCOHOLS

Substituted 2-hydroxy-1-naphthalene ethanols	Yield, %	M.p., °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
β-(*p*-Chlorophenyl)-	100	Glass[a]	$C_{18}H_{15}O_2Cl$	72.36	71.69	5.06	5.63
β-(*p*-Methoxyphenyl)-[b]		128–130					
β-Mesityl-	98	162–165	$C_{21}H_{22}O_2$	82.31	82.14	7.24	7.36
β-Phenyl-8-methyl-[c]	95	110–117	$C_{19}H_{18}O_2$	81.98	81.65	6.52	6.69
β-Cyclohexyl-	97	133.5–135	$C_{18}H_{22}O_2$	79.96	79.67	8.20	8.46

[a] This product was obtained as a colorless glass; all attempts to obtain a crystalline product failed. It was used in the crude form in all subsequent experiments. The material was soluble in aqueous sodium hydroxide and was precipitated from the alkaline solution by carbon dioxide, so there seemed no doubt that this was the desired compound. [b] Previously prepared by this reduction by C. O. Guss, R. Rosenthal and R. F. Brown, *J. Org. Chem.*, **20**, 909 (1955). [c] This phenol-alcohol behaved as if it cyclized very readily. For example, when the material was dissolved in hot ethanol and water was added to this solution by the usual technique for the use of solvent pairs, the melting point became less sharp. Repetition of this procedure eventually led to the isolation of the dihydrofuran that would result from the cyclization of the phenol-alcohol. Merely refluxing the phenol-alcohol in ethanol for several hours also gave the dihydrofuran. The material was best purified by dissolution in ethanol at room temperature, by addition of water to incipient cloudiness, and subsequent cooling in the refrigerator. The white needles on melting gradually changed after the initial softening to a brown liquid; the melting point range, as indicated, was rather wide.

TABLE IV

ACID-CATALYZED CYCLIZATION OF PHENOL-ALCOHOLS TO DIHYDROFURANS

Substituted-1,2-dihydronaphtho(2,1-b)furans	Yield, %	M.p., °C.	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1-*p*-Chlorophenyl-	100	94–96	$C_{18}H_{13}OCl$	77.00	76.99	4.67	4.80
1-*p*-Methoxyphenyl-[a]		104–106					
1-Mesityl-	100	143–144.5	$C_{21}H_{20}O$	87.45	87.51	6.99	7.15
1-Phenyl-9-methyl-	32	128–130	$C_{19}H_{16}O$	87.67	87.54	6.20	6.35
1-Cyclohexyl-	96.6	87–88	$C_{18}H_{20}O$	85.67	85.38	7.99	8.24

[a] Prepared by this method as previously reported by C. O. Guss, R. Rosenthal and R. F. Brown, *J. Org. Chem.*, **20**, 909 (1955).

100°. Recrystallizations from petroleum ether, b.p. 60–71°, gave white needles, 97 g. (50%), m.p. 105–108°. The pure **cyclohexyl 2-methoxy-1-naphthyl ketone** melted at 107.5–108.5°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.65; H, 7.64.

Reduction of the foregoing ketone (13.4 g., 0.05 mole) in dry ether (75 ml.) with lithium aluminum hydride (1 g., 0.026 mole) was carried out by adding the hydride in small portions. Sodium hydroxide (4 g.) in water (10 ml.) was used to decompose the reduction mixture. The ether solution gave 12.2 g. (90%) of white solid, m.p. 75–79°. A pure sample of this carbinol III melted at 77–79°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.77; H, 8.45.

The *p*-nitrobenzoate, from ethanol, melted at 124–126°.

Anal. Calcd. for $C_{25}H_{25}NO_5$: C, 71.58; H, 6.01. Found: C, 71.56; H, 6.26.

Method II (Grignard synthesis): To a solution of cyclohexylmagnesium chloride made from cyclohexyl chloride[7] (29.6 g., 0.25 mole) and magnesium (6.3 g., 0.26 gram-atom) in anhydrous ether (200 ml.) was added 2-methoxy-1-naphthaldehyde[8] (36 g., 0.2 mole) in dry benzene (125 ml.) over a 30-minute period. After an additional hour the mixture was decomposed with aqueous ammonium chloride. Following the addition of some dilute hydrochloric acid, the ether layer was separated, dried over anhydrous sodium sulfate, and the ether evaporated to obtain 54 g. of amber oil. A small sample of the oil, in dilute ethanol, gave a white solid, m.p. 77–79° alone or when mixed with III from the Friedel–Crafts route.

In the conversion of the carbinol to α-cyclohexyl-1-(chloromethyl)-2-methoxynaphthalene (IV), thionyl chloride (25 ml.) was added dropwise to the crude carbinol (54 g.) in dry benzene (150 ml.) over a 30-minute period. An initial cloudiness soon disappeared. The clear solution stood overnight before the benzene and excess thionyl chloride were removed at the water-pump. A clear, viscous brown oil (58 g.) remained. No attempt was ever made to effect a purification at this point.

Formation of **α-cyclohexyl-2-methoxy-1-naphthaleneacetonitrile (V)** from IV was dependent on the use of rather specific conditions. Thus, when IV (7.3 g. crude) in ethanol (10 ml.) was treated with potassium cyanide (2.0 g.) in water (2 ml.), the major product formed was **ethyl α-cyclohexyl-2-methoxy-1-naphthylmethyl ether**, m.p. 81.5–83°, from dilute ethanol as white plates.

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78. Found: C, 80.61; H, 8.98.

This is a characteristic behavior of the methoxybenzyl halides[9] to which IV is structurally similar. Acetone as the solvent instead of ethanol enabled the nitrile to be formed, provided the volume of acetone was large.[10] To the solution of the chloride IV (58 g. crude) in acetone (1250 ml.) was added potassium cyanide (26 g.) in water (400 ml.). This mixture was heated one hour at 35°, allowed to stand two hours, and then reduced one-half in volume at the water-pump without heating. Excess water was added, and the organic layer was taken up in ether and dried over anhydrous sodium sulfate. Evaporation of the ether left 61 g. of oil. It was possible to isolate the solid nitrile V from such a reaction, m.p. 113–114.5° from dilute ethanol. Ordinarily the crude nitrile was used in the subsequent hydrolysis step.

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.68; H, 7.58. Found: C, 81.57; H, 7.80.

In runs in which the amount of acetone and water was relatively much less, invariably there was obtained, in addition to some V, rather large amounts of material that did not contain nitrogen or chlorine; it was presumed to be **bis-(α-cyclohexyl-2-methoxy-1-naphthylmethyl) ether**, m.p. 200–201°, from petroleum ether, b.p. 60–71°.

Anal. Calcd. for $C_{36}H_{42}O_3$: C, 82.72; H, 8.10. Found: C, 82.53; H, 8.26.

The hydrolysis of the nitrile V to the acid VI was relatively difficult, as was anticipated in view of the inability of similar nitriles to be hydrolyzed.[11] The conversion was

---

(7) A generous sample was supplied by Arapahoe Chemicals, Inc.

(8) R. Adams and E. Montgomery, THIS JOURNAL, **46**, 1518 (1924).

(9) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 591.

(10) A. H. Cook, J. Downer and B. Hornung, *J. Chem. Soc.*, 502 (1941).

(11) Buu-Hoi and P. Cagniant, *Compt. rend.*, **219**, 455 (1944).

accomplished by refluxing the crude nitrile (61 g.) in triethylene glycol (200 ml.) with sodium hydroxide (20 g.) in water (20 ml.) in a copper flask for 12 complete days or until the slowly evolved ammonia could no longer be detected. The mixture was poured into water, in which it was nearly completely soluble, and the insoluble portion was removed by extraction with ether. Acidification of the aqueous layer with dilute hydrochloric acid precipitated a material that was taken up in ether and the solvent evaporated to leave 49.5 g. of oil. It was possible to isolate the lactone VII from this oil, so some cleavage of the methyl ether must have occurred during the hydrolysis step. However, the crude material, as just obtained, was refluxed 8 hours in a solution of concentrated hydrobromic acid (50 ml.) and glacial acetic acid (150 ml.). This mixture was poured into water and the nearly solid product taken up in ether, in which it was not highly soluble. The ether was evaporated, and the product, the **lactone of α-cyclohexyl-2-hydroxy-1-naphthaleneacetic acid (VII)**, was purified by recrystallization from dilute ethanol; 15.3 g. (28.7% based on 2-methoxy-1-naphthaldehyde), m.p. 134.5–135.5°, white needles.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.12; H, 7.00.

The data for the conversion of VII to VIII are in Table III.

In a prior synthetic excursion, **α-cyclohexyl-2-methoxy-1-naphthaleneacetic acid (VI)** was isolated in small yield from the carbonation of the appropriate Grignard reagent, m.p. 157–158°, from dilute ethanol.

Anal. Calcd. for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.36; H, 7.71.

When this acid was refluxed with hydrobromic acid in acetic acid, the lactone VII, m.p. 134.5–135.5°, was formed.

General Procedure.—The phenol-alcohol (0.01 mole) and phthalic anhydride (0.02 mole) were dissolved, with warming if necessary, in dry dioxane (15 ml.) containing dry pyridine (3 ml.). This solution was allowed to stand at room temperature for at least 24 hours for completion of the esterification reaction.

The mixture was dissolved in ether (50 ml.) and then extracted with dilute hydrochloric acid (5 ml. of concentrated acid in 50 ml. of water) to remove pyridine. After a wash with water (50 ml.) the ester was extracted with four 25-ml. portions of 4% sodium bicarbonate. In certain instances the sodium salt of the ester was insoluble, in which case a practical deviation from normal procedure was employed. Such deviations will be properly noted in the descriptions that follow. When the sodium salt was soluble, the combined extracts were treated with either "weak alkali" (1 g. of sodium hydroxide in 20 ml. of water) or with "strong alkali" (15 g. of sodium hydroxide in 20 ml. of water). The dihydrofuran that formed was filtered and purified. Any phenol-alcohol resulting from normal hydrolysis was isolated by the addition of Dry Ice to the filtrate from the removal of the dihydrofuran.

Formation of II, R = *p*-Chlorophenyl.—Extraction of the ester with sodium bicarbonate resulted in two liquid phases in the aqueous layer which, as such, was treated with the aqueous alkali. After addition of the weak alkali, the mixture was warmed to 60–70° for 90 minutes with mechanical shaking. There was formed 2.42 g. (86%), m.p. 91.5–94° crude, of 1-*p*-chlorophenyl-1,2-dihydronaphtho[2,1-b]furan, identical with the compound formed from the acid-catalyzed cyclization of the phenol-alcohol. No hydrolysis of the ester to the phenol-alcohol was observed. An additional 6.4% of the dihydrofuran was obtained by alkali treatment of the residue in the ether solution from which the ester had apparently been incompletely extracted.

When strong alkali was added to the bicarbonate extract, it produced a clear solution initially, but the dihydrofuran soon appeared, and, after warming, 1.94 g. (69.1%), m.p. 93–95° crude, of the dihydrofuran was isolated. Dry Ice treatment of the filtrate caused 0.56 g. (18.7%) of crude phenol-alcohol to separate as a brown oil.

Formation of II, R = *p*-Methoxyphenyl.—Addition of weak alkali to the clear bicarbonate extract and warming to 60–70° produced 2.73 g. (98.9%), m.p. 104–107° crude, of the dihydrofuran,[9] identical with that produced by the acid-catalyzed cyclization.[9] Strong alkali added to the bicarbonate extract gave 2.09 g. (76.0%), m.p. 105–109° crude, of the dihydrofuran, and, after addition of Dry Ice to the filtrate, 0.64 g. (21.9%) of hydrolysis product as a brown oil.

Formation of II, R = Mesityl.—When the ester was extracted from the ether solution with 4% sodium bicarbonate, the insoluble sodium salt of the ester precipitated. This salt was filtered, washed with water and dried, 4.56 g. (96%). The salt (4.77 g., 0.01 mole) was placed in water (100 ml.) and strong alkali added. At 60–70° and with mechanical shaking for two hours, 2.66 g. (92.5%), m.p. 142–144° crude, of the dihydrofuran was formed. A trace of hydrolysis product may have been present after Dry Ice treatment of the filtrate. Identity of the dihydrofuran was confirmed by mixed melting point with the product from the acid-catalyzed cyclization of the phenol-alcohol.

Formation of II, R = Cyclohexyl.—After it was found that the sodium salt of the ester was only partially soluble in the bicarbonate solution used for extraction, a modification was made in the usual procedure. The ether solution of the ester was evaporated, and 4% sodium bicarbonate (100 ml.) was added to the residue. To the slurry of the salt that formed was added the strong alkali. The momentarily clear solution gave, after warming, 2.3 g. (91.2%), m.p. 86–88° of crude dihydrofuran. Dry Ice added to the filtrate caused the separation of 0.25 g. (9.3%) of hydrolysis product, m.p. 50–130° crude, m.p. 130–134° after one recrystallization. The dihydrofuran here obtained did not depress the melting point of the dihydrofuran from the acid-catalyzed cyclization of the phenol-alcohol.

Formation of 1-Phenyl-9-methyl-1,2-dihydronaphtho[2,1-b]furan.—Addition of the strong alkali to the clear bicarbonate extract caused the dihydrofuran to form immediately, but the mixture was heated to 50–60° to ensure completion of the reaction. The dihydrofuran, 2.35 g. (90.4%), m.p. 125–130° crude, was identical with that from the acid-catalyzed cyclization of the phenol-alcohol. No hydrolysis product could be detected in the filtrate. The ether solution from which the ester had been extracted furnished 0.15 g. (5.8%) additional dihydrofuran when the residue from the evaporation of the ether was treated with dilute sodium hydroxide.

FORT COLLINS, COLORADO