

and 1,3 isomers, the 1,1-dichloropropene has been measured in benzene solution by two other investigators.^{5,13} The values obtained, 1.69 and 1.73, are in reasonable agreement with the figure reported here (1.79).

The moment observed for the 3,3-dichloropropene (1.92) is in reasonable agreement with the value of 1.86 obtained by vectorial addition of the moment for dichloromethane to that for propylene.

The moment observed for the 2,3-dichloropropene is 1.99. This may be calculated by vectorial addition of the moments for methyl chloride (1.85) and vinyl chloride (1.44) provided the angle between the two vectors is known. Free rotation about the carbon-carbon single

bond in this molecule is prevented by steric hindrance. The average angle between the vectors given above as calculated from the experimental moment is 105°.

Summary

The electric moments of all seven of the isomeric dichloropropenes and of *trans*-1-chloropropene (37° isomer) have been measured in benzene solution at 30°.

The dipole moments of the 1,2 isomers indicate beyond question that the 93° isomer has the *cis* configuration, while the 76° isomer is the *trans* form. The moments for the other dichloropropenes are compared with literature or calculated values.

(18) deBruyne, Davis and Gross, *Physik. Z.*, **33**, 719 (1932).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Intramolecular Displacement of Carboxylate Ion. I. Formation of 1-Phenyl-1,2-dihydronaphtho(2,1-b)furan

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Displacement of the carboxylate ion from an alkyl ester of a carboxylic acid with consequent alkylation of the entering group is sometimes possible to accomplish when a hydrolytic medium is avoided. However, the most characteristic reaction of esters in aqueous alkali is hydrolysis with cleavage at the carbonyl carbon-alkoxy oxygen bond. We wish to describe an unusual instance in which intramolecular displacement of a carboxylate ion predominates under conditions normally expected to lead to hydrolysis.

Alkyl esters of carboxylic acids do serve as alkylating agents, but not to an extent comparable with alkyl halides, sulfates and sulfonates. Tertiary amines displace the carboxylate ion from methyl esters,² the ease of displacement being dependent, in part at least, on the strength of the acid from which the ester is derived. Inversion on the carbon atom bearing the acyloxy group is postulated. Dialkyl phthalates³ react with potassium phenoxides at 190–200° to produce the alkyl ethers of the phenols. The use of a phenoxide derived from an aminophenol, *e. g.*, *N*-methyl-*p*-aminophenol, not only results in *O*-alkylation but also more or less *N*-alkylation. Methyl benzoate and sodium methoxide at 175° give a 55% yield of dimethyl ether,⁴ but other esters of benzoic acid do not behave similarly. Grignard reagents are alkylated by esters of car-

boxylic acids provided the attack at the carbonyl group is sufficiently hindered by the steric effect of adjacent groups, and, apparently, provided the group attached to the alkoxy oxygen is capable of resonance stabilization as a carbonium ion.⁵

Intramolecular displacement of a carboxylate ion from an ester of a carboxylic acid, with inversion, is postulated by Fieser and Huang-Minlon⁶ in their interpretation of the course of the Serini reaction. The present paper reports an intramolecular displacement of carboxylate ion that by contrast is unique with respect to the reaction conditions used.

During the course of another investigation, 2-(2-hydroxy-1-naphthyl)-2-phenylethanol (I) was obtained. When this phenol-alcohol was treated with phthalic anhydride, the ester (II) was formed. By heating in a dilute sodium bicarbonate solution the ester (II) was slowly converted into the cyclized product, 1-phenyl-1,2-dihydronaphtho(2,1-b)furan (III). Addition of dilute sodium hydroxide to the bicarbonate solution of the ester also produced the furan, slowly at room temperature and very rapidly with gentle heating. As the concentration of added sodium hydroxide was increased, the hydrolysis to give the phenol-alcohol (I) became appreciable, but it did not appear possible to cause the ester to undergo hydrolysis to the exclusion of cyclization. The phenol-alcohol was not cyclized by dilute alkali, showing that hydrolysis did not precede cyclization.

(1) Based on a portion of a thesis submitted by Mr. Leonard H. Jules in partial fulfillment of the requirements for the degree of Master of Science.

(2) Willstätter and Kahn, *Ber.*, **35**, 584 (1902); Hammett and Pfuger, *This Journal*, **55**, 4079 (1933).

(3) King and Wright, *J. Chem. Soc.*, **155**, 1168 (1939).

(4) Adickes, Müllenheim and Simson, *Ber.*, **66**, 1904 (1933); Magnani and McElvain, *This Journal*, **40**, 813 (1938).

(5) Fieser and Heymann, *ibid.*, **64**, 376 (1942); Wilson, Roberts and Young, *ibid.*, **71**, 2019 (1949); Arnold and Searles, *ibid.*, **71**, 2021 (1949).

(6) Fieser and Huang-Minlon, *ibid.*, **71**, 1840 (1949).

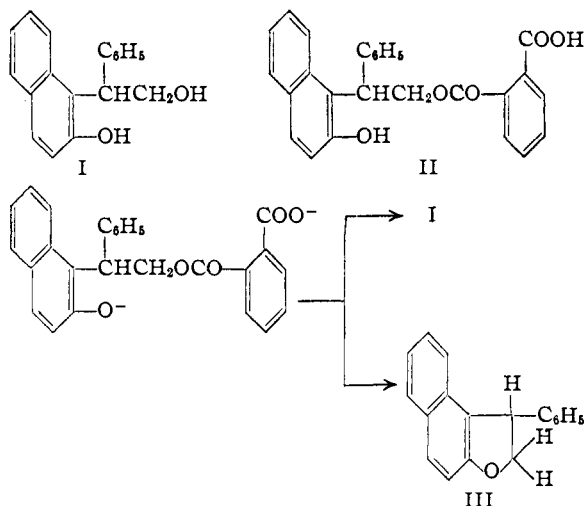


Table I contains data giving the yields of I and III obtained at different alkali concentrations.

TABLE I
EFFECT OF ALKALI CONCENTRATION ON THE HYDROLYSIS OF II

Concn., moles/l. ^a	Yield, %	
II	III	I
NaOH		
0.0833	93.5	0
.0833	81.3	9.5
.0833	67.1	24.6

^a See experimental details for comments on these values. Note that the value given here for the sodium hydroxide added to the bicarbonate solution of the ester has not been corrected for the reaction with the free phenolic group.

It is apparent that the ester (II) is much more inclined to react by cyclization than by hydrolysis. The cyclization is not dependent upon hydroxyl ion concentration if adequate alkali is present to form the naphthoxide anion. On the other hand the rate of hydrolysis is dependent upon the hydroxyl ion concentration, and an increase in the latter can sufficiently increase the rate to give a considerable amount of hydrolysis.

The present example of intramolecular displacement of carboxylate ion is not diagnostically reliable since the role, if any, played by the phenyl group beta to the ester linkage is not revealed with certainty. A cyclization often takes place more easily than does the same type of reaction leading to a linear molecule, because the atoms directly involved are more favorably located with respect to each other for intramolecular than for intermolecular reaction. When a new ring is formed having adjacent atoms in common with a ring already existing, the intramolecular reaction is often even more favored. In the molecule here under investigation, the close proximity of the naphthoxide anion to the alpha carbon atom of the alkoxy group is believed to be responsible for the observed rapid rate of carboxylate displacement relative to hydrolysis. The part played by the phenyl group and the generality of this type of intramolecular displacement is now being studied.

Experimental⁷

Preparation and Cyclization of the Acid Phthalate (II) of 2-(2-Hydroxy-1-naphthyl)-2-phenylethanol.—A solution of 2-(2-hydroxy-1-naphthyl)-2-phenylethanol (I) (1.0 g., 0.0038 mole), phthalic anhydride (2.2 g., 0.015 mole) and pyridine (1.2 g., 0.015 mole) in dioxane (25 cc.) was allowed to stand at room temperature for seventy-two hours. This solution was then added to 200 cc. of ether, washed with two 100-cc. portions of 10% hydrochloric acid, and extracted with three 100-cc. portions of 5% sodium bicarbonate. The combined basic extracts were acidified with dilute hydrochloric acid, and the ester was completely separated by extraction with two 100-cc. portions of ether. This solution was then dried over anhydrous sodium sulfate, and the ether evaporated under reduced pressure. Chloroform was added to the residue, and the mixture was heated to boiling, cooled and filtered. Evaporation of the solvent from the filtrate left a brown, viscous oil that did not crystallize. The oil was dissolved in hot benzene from which brown crystals separated on cooling. Recrystallization from benzene gave white crystals of the acid phthalate (II) which sintered slightly at 114° and melted at 119–120°. Analysis indicated the presence of a molecule of benzene of crystallization.

Anal. Calcd. for C₂₂H₂₀O₅: C, 78.35; H, 5.34. Found: C, 78.37; H, 5.41.

To a solution of this acid phthalate (II) (0.1081 g., 0.0022 mole) in 5% sodium bicarbonate (20 cc.) was added 10% sodium hydroxide (5 cc.). Although the solution became cloudy within two minutes at room temperature, the reaction was hastened by warming. The white precipitate was collected by filtration, washed with water and dried; weight 0.0525 g. (97%), m.p. 94–95°. This product, 1-phenyl-1,2-dihydronaphtho(2,1-b)furan (III), was identified by a mixed melting point determination with material from the acid-catalyzed cyclization of the phenol-alcohol (I).

Prolonged boiling of a 5% sodium bicarbonate solution of the ester also caused the formation of the furan. In another experiment, not described here, it was shown that the acetic acid ester would give the furan when treated with dilute sodium hydroxide.

Effect of Hydroxyl Ion Concentration on the Hydrolysis of the Acid Phthalate (II).—A solution of the phenol-alcohol (I) (2.64 g., 0.01 mole), phthalic anhydride (2.96 g., 0.02 mole) and pyridine (3 cc.) in dioxane (15 cc.), after standing for twenty-four hours at room temperature, was dissolved in 50 cc. of ether, washed with 5 cc. of concd. hydrochloric acid in 50 cc. of water, then washed with 50 cc. of water, and finally extracted with four 25-cc. portions of 4% sodium bicarbonate. Three such solutions so obtained were then treated with sodium hydroxide. (a) Addition of sodium hydroxide (1 g., 0.025 mole) in 20 cc. of water to the bicarbonate solution (120 cc. total volume), followed by gentle heating to 50–60° for thirty minutes, quickly gave 2.30 g. (93.5%) of the furan (III), m.p. 94–96°. Isolation of the furan was made simply by filtering off the solid, washing with water, and drying over calcium chloride in a vacuum desiccator. Addition of solid carbon dioxide to the filtrate from the furan separation caused any hydrolysis product (I) to separate. None was obtained in the present case. The ether solution from which the ester had been extracted by sodium bicarbonate was evaporated and the residue treated with 100 cc. of 0.8% sodium hydroxide. This gave an additional 0.15 g. (6.1%) of the furan, m.p. 93–96°. Thus, the ester was produced quantitatively, but it was not extracted completely from the ether solution by the bicarbonate. In constructing Table I it was assumed that esterification and extraction were quantitative; the stated yields are those obtained without recovery of the approximately 6% of ester retained in the ether. (b) Adding sodium hydroxide (4 g., 0.1 mole) in 20 cc. of water to the bicarbonate solution and proceeding as in (a) gave 2.0 g. (81.3%) of the furan, m.p. 95–96°, and a solid which, after one recrystal-

(7) All melting points are uncorrected. Microanalyses are by the Elek Micro Analytical Laboratories, Los Angeles, California.

lization from ethanol-water, weighed 0.25 g. (9.5%), m.p. 120–122°, and which was identified as the phenol-alcohol (I) by mixed melting point with authentic (I). (c) Addition of sodium hydroxide (15 g., 0.375 mole) in 20 cc. of water gave 1.65 g. (67.1%) of the furan (III), m.p. 94–96°, and 0.65 g. (24.6%) of the phenol-alcohol (I), m.p. 117–121°, both products being identified by mixed melting point determinations.

Preparation of 2-(2-Hydroxy-1-naphthyl)-2-phenylethanol (I).—The lactone of α -(2-hydroxy-1-naphthyl)-phenylacetic acid was prepared by a method similar to that given by Arventi.⁸ A mixture of 2-naphthol (35 g., 0.243 mole) and mandelic acid (25 g., 0.164 mole) was heated to 190–195° for one hour. After the mixture was cooled to incipient solidification, 50 cc. of ethanol was added and the insoluble lactone filtered off, washed with ethanol and dried to give 27.1 g. (63.5%), m.p. 180–185°. When recrystallized from glacial acetic acid, the lactone melted at 186–187° in agreement with the literature values.^{8,9}

The lactone (5 g., 0.0192 mole) was placed in the thimble of a Soxhlet extractor and reduced with lithium aluminum hydride (1.6 g., 0.042 mole) in 500 cc. of ether in the manner suggested by Nystrom and Brown¹⁰ for ether-insoluble compounds. The product, initially obtained as an oil, was crystallized from isopropyl alcohol and water after charcoal treatment to yield 4.8 g. (95%), m.p. 121–121.5°. Purifying recrystallizations from chloroform-carbon tetrachloride mixtures gave fine, white needles, m.p. 121.5–122°, of 2-(2-hydroxy-1-naphthyl)-2-phenylethanol.

(8) Arventi, *Ann. sci. univ. Jassy*, Pt. 1, **23**, 344 (1937).

(9) Bistrzycki and Flatau, *Ber.*, **30**, 124 (1897).

(10) Nystrom and Brown, *THIS JOURNAL*, **69**, 2548 (1947).

Anal. Calcd. for C₁₈H₁₆O₂: C, 81.79; H, 6.10. Found: C, 81.93; H, 6.26.

After 1 g. of this phenol-alcohol was refluxed with 50 cc. of 10% sodium hydroxide for one hour, it was recovered unchanged.

Preparation of 1-Phenyl-1,2-dihydronaphtho(2,1-b)furan (III) by Acid Catalysis.—A solution of 2-(2-hydroxy-1-naphthyl)-2-phenylethanol (I) (2.0 g.) and *p*-toluenesulfonic acid monohydrate (0.1 g.) in 100 cc. of benzene was refluxed for one hour with simultaneous removal of 50 cc. of benzene containing the water formed. Evaporation of the solvent and crystallization of the residue from ethanol-water gave long, white needles, 1.5 g. (80.6%), m.p. 95–96°, of 1-phenyl-1,2-dihydronaphtho(2,1-b)furan.

Anal. Calcd. for C₁₈H₁₄O: C, 87.77; H, 5.73. Found: C, 88.01; H, 5.89.

Summary

The intramolecular displacement of carboxylate ion from the ester (II) of 2-(2-hydroxy-1-naphthyl)-2-phenylethanol to form 1-phenyl-1,2-dihydronaphtho(2,1-b)furan (III) was observed to proceed under hydrolytic conditions at a faster rate than hydrolysis, a result believed to arise from a favorable spatial situation. This behavior was shown to be an outstanding example of facile alkylation by alkyl esters of carboxylic acids.

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[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

The Synthesis of Some Alkylated Cyclohexenones and Aromatic Compounds

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The present paper briefly describes the details of synthesis of some cyclohexenones and aromatic compounds according to a general method previously outlined.³

Condensation of the methiodide of 1-N-morpholinobutanone-3 with ethyl sodio- α -acetyl isovalerate in absolute ethanol yielded ethyl Δ^1 -*p*-menthen-3-one-4-carboxylate, from which by decarboxylation under alkaline conditions *dl*-piperitone was obtained in 50% yield over-all. Mannich and Fournau⁴ previously failed to condense 1-dimethylaminobutanone-3 usefully with ethyl α -acetyl isovalerate in presence of small amounts of alkali, so that the advantage of using the Mannich base methiodide, a method due to du Feu, McQuillen and Robinson⁵ is again emphasized. Piperitone has been already synthesized by Walker⁶ from the not very accessible β -chloroethyl methyl ketone.

A similar condensation of the methiodide of a 3-dialkylaminomethyl-4-methylpentanone-2 with

ethyl sodio-acetoacetate to ethyl Δ^1 -*p*-menthen-3-one-6-carboxylate, followed by decarboxylation, should also yield piperitone. An attempt to effect such a synthesis starting from methyl isobutyl ketone failed because this ketone condensed with paraformaldehyde and morpholine hydrochloride to the hydrochloride of 1-N-morpholino-5-methyl-hexanone-3, the methyl group adjacent to carbonyl being attacked rather than the methylene group, in line with the experience of Mariella.⁷ Condensation of the methiodide of this base with ethyl sodio-acetoacetate, followed by decarboxylation under alkaline conditions yielded 1-isobutyl- Δ^1 -cyclohexen-3-one, as shown by dehydrogenation with palladium-charcoal to *m*-isobutyl-phenol and oxidation of the methyl ether of this to *m*-methoxybenzoic acid. Reduction of 1-isobutyl- Δ^1 -cyclohexen-3-one yielded an oily pleasant-smelling mixture of stereoisomeric 1-isobutylcyclohexan-3-ols,

Condensation of the methiodide of 1-N-morpholino-4-methylpentanone-3 with ethyl sodio- α -acetyl propionate, followed by decarboxylation under alkaline conditions gave a product from which *dl*-carvenone (Δ^3 -*p*-menthen-2-one) was obtained in poor yield.

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(3) Downes, Gill and Lions, *Aust. J. Sci.*, **3**, 147 (1948).

(4) Mannich and Fournau, *Ber.*, **71**, 2090 (1938).

(5) du Feu, McQuillen and Robinson, *J. Chem. Soc.*, 53–60 (1937).

(6) Walker, *ibid.*, 1585 (1935).

(7) Mariella, *THIS JOURNAL*, **69**, 2670 (1947).