40% reacted, for *cis*-2,3-dichloro-2-butene between 11 and 23% reacted and for *trans*-2,3-dichloro-2-butene between 6 and 20% reacted. Because of the very slow rate of reaction, data were obtained only for a relatively low percentage reaction. Straight lines were also obtained for *cis*-1,2,3-trichloro-2-butene between 27 and 72% reacted and for *trans*-1,2,3-trichloro-2-butene between 40 and 74% reacted. The data are given in Table II.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

The Equilibrium between the *o*-Allenylphenoxide and 2-Benzofurylmethyl Anions

BY RUSSELL GAERTNER

Evidence is presented to establish that the product of the reaction of 2-(chloromethyl)-benzofuran with magnesium is *o*-allenylphenol. In addition to giving several reactions typical of its functional groups, this compound undergoes a novel base-catalyzed ring closure under mild conditions to give 2-methylbenzofuran. The data are best correlated by a theory involving an equilibrium between the benzofurylmethyl and *o*-allenylphenoxide anions. This appears to be the first demonstration of such an equilibrium between "aromatic" and acyclic systems.

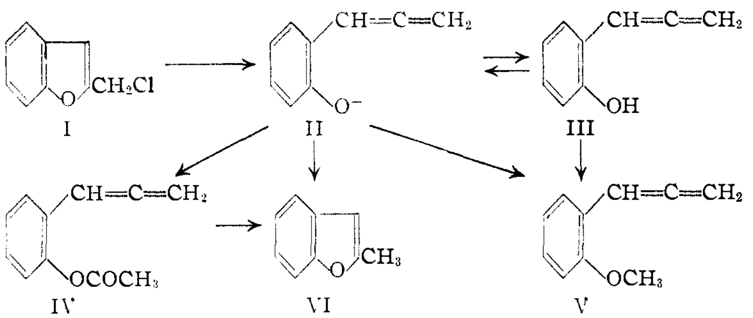
It was shown recently[1] that 2-thenylmagnesium chloride undergoes rearrangements to give 2-methyl-3-substituted-thiophenes when treated with typical reactants. In an attempt to extend the investigation to 2-furfuryl chloride using the cyclic reactor, only polymeric products resulted before hydrolysis. In the hope that this difficulty could be avoided, the corresponding benzofuran derivative has been investigated, with the unexpected results described in this report.

The synthesis of 2-(chloromethyl)-benzofuran (I) allows no uncertainty concerning its structure. Coumarilic acid was reduced with lithium aluminum hydride and the resulting 2-benzofurylcarbinol was converted to the halide by the action of thionyl chloride.

Conversion of the chloride (I in chart A) in the cyclic reactor appeared to proceed normally. However, the ethereal solution failed to yield a carboxylic acid when treated with carbon dioxide. Although its properties suggested that an unsaturated phenol was present, all efforts to isolate this compound were unsuccessful. It polymerized exothermically when simple distillation *in vacuo* was attempted. Even aspiration of solvents at ice temperatures left only a brittle resin. Its unsaturated derivatives also soon polymerized in contact with air but could be distilled and characterized by working rapidly. The phenol (III) was stable in dilute solution in ether or as the anhydrous ethereal magnesium phenoxide (II) prepared in the cyclic reactor.

By hydrogenation of the phenol a 69% yield of *o*-*n*-propylphenol was obtained; its phenylurethan was identical with an authentic sample. The unsaturated phenol was converted by conventional methods to its phenylurethan and acetate (IV). The analytical results and quantitative hydrogenation of both compounds (to derivatives of *o*-*n*-propylphenol) indicated the presence of two double bonds. These facts suggested three possible structures: *o*-propargyl-, *o*-propynyl- or *o*-allenylphenol. Migration of multiple bonds in the presence of bases is well known; however, rearrangement under such mild conditions to yield a compound in which the unsaturation is not conjugated with the benzene ring would be unprecedented. The choice between the allenyl and propynyl structures was made in part on the basis of an oxidation[2] with permanganate in pyridine, which produced *no* acetic acid. These data, together with the well-known ease of polymerization of phenylallene, point to the allenylphenol structure, which alone is also consistent with other reactions and the absorption spectra of this series of compounds.

CHART A



The rearrangement to *o*-allenylphenol might have been predicted by recognizing that 2-(chloromethyl)-benzofuran is a β-haloether as well as an arylmethyl halide. The cleavage of the former type of compound by reactive metals is the basis for the familiar Boord synthesis[3] of olefins. There is an interesting precedent for this scission of the "aromatic" benzofuran nucleus in the observation of Reichstein and Baud[4] that *o*-ethynylphenol was a product of the reaction of 3-bromobenzofuran with magnesium.

An attempt to methylate *o*-allenylphenol in alkaline solution with dimethyl sulfate led to unexpected results. Although small amounts (13% yield) of *o*-methoxyphenylallene (V) were obtained in this way (when the reaction mixture was cooled),

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(1) Gaertner, This Journal, 73, 3934 (1951); *ibid.*, 72, 4326 (1950).

(2) Young, Ballou and Nozaki, *ibid.*, 61, 12 (1939). The procedure was originally designed for the analysis of mixtures of allylbenzene and propenylbenzene.

(3) Dykstra, Lewis and Boord, *ibid.*, 52, 3396 (1930); see also Amstutz, *J. Org. Chem.*, 9, 310 (1944), for a discussion of the mechanism of these reactions and a number of interesting examples.

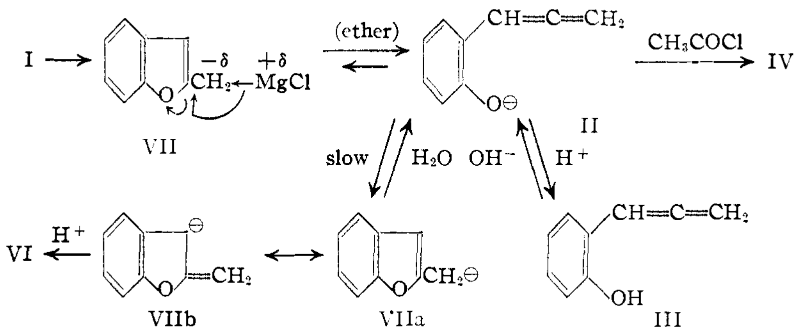
(4) Reichstein and Baud, *Helv. Chim. Acta*, 20, 892 (1937). See, concerning the similar behavior of 3-benzofuryllithium, Gilman and Melstrom, This Journal, 70, 1655 (1948).

the principal product was a lower-boiling liquid with the properties of *2-methylbenzofuran* (VI). Both aqueous alkali and triethylamine catalyzed this transformation. The best yield (81%) of VI was obtained from *o*-allenylphenyl acetate (IV) by a sodium methoxide-catalyzed transesterification in methanol. 3-Acetyl-2-methylbenzofuran served as a solid derivative[5] of VI obtainable by acetylation of either the lower-boiling liquid or authentic[6] 2-methylbenzofuran. *o*-Methoxyphenylallene (V) was also obtained by methylating the phenol with diazomethane, a reaction which proceeded very slowly until boron trifluoride was added.

The ultraviolet absorption spectra of these compounds are presented in Fig. 1. Extinction coefficients for *o*-allenylphenol were based on evaporation of an aliquot of the ethereal solution and undoubtedly are too small. With this exception, the data are in agreement with the chemical evidence. The effect of a double bond conjugated with the benzene ring is apparent, as are the differences between the spectra of compounds possessing this structural feature and that of allylphenyl (which closely resembles the curve for phenol itself). The close correspondence between the spectrum of authentic 2-methylbenzofuran and that obtained through the allenylphenol confirms their identity. From the more sharply defined maxima and minima in the curve for the latter, one may infer that it is the purer of the two samples.

The reaction of 2-(chloromethyl)-benzofuran with alkali cyanides was of interest since furfuryl chloride is known to yield 2-cyano-5-methylfuran in this reaction.[7] This reaction did not proceed in a straightforward manner; when aqueous solvents were used hydrolysis occurred, but in dioxane–acetone mixtures a poor yield of 2-benzofurylacetonitrile resulted. It was hydrolyzed by alkali to the corresponding known acid. A second, higher-melting compound isolated from the reaction mixture resisted alkaline hydrolysis and has not been characterized. There was no indication that rearrangement had occurred.

CHART B



Theoretical Discussion

An assumption which seems to correlate all of the above facts is the postulation of the existence of a slow equilibrium between the *o*-allenylphenoxide and the benzofurylmethyl anions with the former predominating, as shown in Chart B. The initial cleavage is thought to occur by way of the intermediate Grignard reagent (VII), which is polarized as indicated, allowing the pictured electron-pair shifts to proceed; the phenoxide (II) is produced. II must predominate over VII in ethereal solution, because of the nature of the product (IV) of the reaction with acetyl chloride and the failure of the attempted carbonation, although traces of products corresponding to the Grignard reagent might have escaped detection. Rapid hydrolysis with acids of the ethereal solution then yields the phenol (III) although there was always some 2-methylbenzofuran in these reaction mixtures (corresponding to VII?). In aqueous solution, bases reconvert the phenol (III) to its phenoxide (II) and the equilibrium[8] between II and VIIa–VIIb is slowly established. The query concerning to which double bond the phenoxide adds is meaningless since the resulting carbanion is a resonance hybrid of two major contributing structures, VIIa and VIIb. The carbanion is rapidly converted by proton donors to its very weak "acid," 2-methylbenzofuran (VI), driving the reaction to completion. The contribution of VIIa is predominant, due to the stabilization of the benzofuran nucleus by resonance (exclusive of contributing structures involving the exocyclic atom). Thus the expected product of reaction with proton donors is 2-methyl-

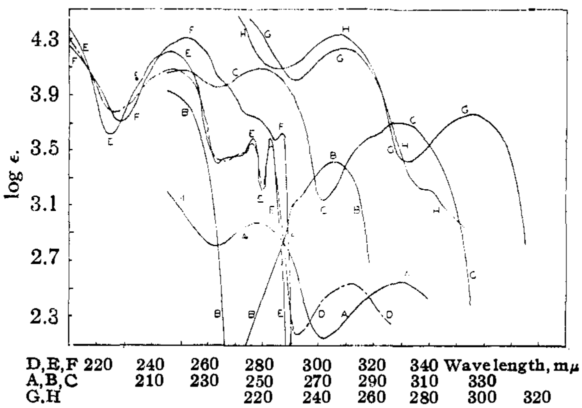


Fig. 1.—Ultraviolet absorption spectra in ethanol. Key: A, II; B, *o*-allylphenol; C, *o*-propenylphenol; D (broken line), authentic[6] 2-methylbenzofuran; E, VI; F, I; G, V; H, IV.

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(5) Stoermer and Barthelmes, *Ber.*, **48**, 62 (1915), reported that the picrate melted at 72–74°. A single attempt to prepare this compound gave needles with a wide melting range (74–80°).

(6) The detailed directions of Adams and Rindfusz, THIS JOURNAL, **41**, 648 (1919), for the reaction of *o*-allylphenyl acetate dibromide with alcoholic alkali were followed. See Claisen, *Ber.*, **53**, 322 (1920), for the identification of the product as 2-methylbenzofuran.

(7) Runde, Scott and Johnson, THIS JOURNAL, **52**, 1284 (1930); Reichstein, *Ber.*, **63**, 749 (1930); Reichstein and Zschokke, *Helv. Chim. Acta*, **15**, 1124 (1932).

(8) The use of the term "equilibrium" in this connection deserves comment. This is clearly not a case of resonance, since movement of more than electrons is implied in this conversion. For the allenyl group *per se* is linear, *i.e.*, the three carbon atoms lie in a straight line. These same three atoms form a definite obtuse angle in VIIa ⟷ VIIb. One of the familiar restrictions placed on resonance is that shifts in the positions of atomic nuclei are excluded. This distinction between a true resonance hybrid and an equilibrium is thus significant.

benzofuran—corresponding to VIIa—rather than α-methylenecoumarane—corresponding to VIIb.

Although several older syntheses of the benzofuran nucleus might have this mechanism in common, such a suggestion is unnecessary and probably incorrect.[9] In summary, the ring closure reported here is unique in that it involves *an equilibrium between an "aromatic" system—the benzofurylmethyl carbanion—and an acyclic structure—the o-allenylphenoxide ion,* both anions being stabilized by resonance in excess of that inherent in their benzene nuclei.

Acknowledgment.—The author is indebted to the Graduate School for a grant-in-aid for the 1950–1951 academic year without which this work would not have been possible.

Experimental Part[10]

2-Benzofurylcarbinol.—Solid coumarilic acid[11] (32.4 g.) was added in small portions through a large-bore condenser to a stirred mixture of 12.3 g. of lithium aluminum hydride and about 350 ml. of absolute ether. After hydrolysis with 10% sulfuric acid, the carbinol[12] (25.2 g., 85% yield) was isolated; b.p. 112–113° (1.1 mm.); $n^{20}\text{D}$ 1.5834; d^{20}_4 1.203; *MR* (calcd.) 40.66 (obsd.) 41.35. The compound was converted to its phenylurethan, m.p. 110.6–111.6°.

2-(Chloromethyl)-benzofuran (I).—To a mixture of 60 g. of purified thionyl chloride and 50 ml. of toluene, stirred in an ice-bath, was added slowly 34 g. of the alcohol. The temperature was raised slowly and finally the mixture was heated under reflux for an hour. The toluene and excess reagent were removed at the aspirator, and the residual dark-colored oil was distilled *in vacuo*. A total of 31.2 g. (81.7%) yield of a colorless mobile oil distilled at 81–82° (0.9 mm.). The residue in the pot should not be overheated since it began to evolve hydrogen chloride at about 150°. Dissolved hydrogen chloride hastened the decomposition of the product which was otherwise stable if stored in the refrigerator. It slowly evolved hydrogen chloride and turned black after several days at room temperature.

When several drops of triethylamine were added as a stabilizing agent, crystallization occurred. After recrystallization from hexane, it formed platelets, m.p. 35–36°.

Anal. Calcd. for C_9H_7ClO: C, 64.88; H, 4.24. Found: C, 64.96; H, 4.40.

The properties of the supercooled liquid were: $n^{20}\text{D}$ 1.5917; d^{20}_4 1.235; *MR* (calcd.) 44.00 (obsd.) 45.64. It reacted rapidly, but not instantaneously, with alcoholic silver nitrate.

In a larger run, 75 g. of coumarilic acid was reduced and the crude alcohol was converted directly to the halide, 51.7 g. (74% based on the acid) being isolated. Two attempts to prepare this compound from benzofuran by the action of a solution of *s*-trioxane in acetic and hydrochloric acids were unsuccessful, although a trace of the desired product seemed to be present; resinification predominated.

Reaction of 2-(Chloromethyl)-benzofuran with Magnesium. *o*-Allenylphenol (III).—Use of the cyclic reactor in this Laboratory has been described earlier.[1] In the present case, its application was even more convenient since a column of amalgamated magnesium turnings could be used for several small runs. There was no fouling of the metal, and reinitiation was also unnecessary; a crystal of iodine promoted restarting. The apparatus was used and maintained with a nitrogen atmosphere.

Titration of an aliquot of the ethereal solution (Solution A) from 10.0 g. of halide indicated the presence of 105% of the theoretical amount of magnesium hydroxide; the end-point was not sharp. The Gilman test was negative. Several runs were also made in the conventional manner with mechanical stirring; since the yield of products described below was then somewhat lower (by 5–10%) than with the cyclic reactor, the latter was employed in all of the reported experiments, unless otherwise specified. Hydrolysis was always carried out by adding ice, followed quickly with dilute hydrochloric acid. This ethereal solution of the phenol, obtained by several extractions and back-extractions, is Solution B. An attempted carbonation of Solution A failed to yield any compound extractable by sodium carbonate solution. However, a phenolic product was partially extracted from ether by 20% sodium hydroxide solution. In subsequent runs when it was desired to effect complete extraction, the amount of ether was held to a minimum and several volumes of petroleum ether (30–60° unsaturate free) were added in the extractions. The phenol was then completely removed after three treatments with 10-ml. portions of alkali; such extractions were carried out very rapidly, with backwashing, in the presence of ice when it was desired to retain the phenoxide structure. The alkaline aqueous solution is Solution C.

Acidification of Solution C in the presence of ice and solvents freed the phenol; when the solvents were aspirated from the ice-bath, the residual oil appeared quite mobile until the last traces of solvents were removed. At this instant, the flask became warm and only a hard resinous cake resulted. In one experiment, an attempt was made to follow evaporation of solvents with distillation of the phenol from the ice-bath into a receiver cooled in Dry Ice in a short-path still maintained at about 0.01 mm. Again polymerization occurred.

However, the phenol seemed quite stable in Solution B. No attempt was made to obtain an analytical sample, nor could any constants be determined. Yields of derivatives were calculated from the weight of the chloride converted, which will be given in parentheses.

A 20-ml. aliquot of Solution B containing 0.3046 g. (determined by aspiration of solvents from a 10-ml. portion of the solution—undoubtedly too high) of the phenol was mixed with 40 ml. of reagent pyridine and aspirated to remove the ether, successive additions of pyridine being made to maintain the volume at about 40 ml. This and subsequent operations were conducted with a Kjeldahl splash trap in place. Another 35 ml. of pyridine was added, followed by 6.0 g. of potassium permanganate.[2] This mixture was heated at 40° for eight hours with stirring (magnetic stirrer). The solvent was completely removed at the aspirator with stirring. Then 50 ml. of 2 *N* sulfuric acid was added, followed by just sufficient solid oxalic acid to destroy the excess permanganate. The steam distillate (100 ml. was collected with concurrent addition of water to the pot) did not change the indicator to its acid color. Thus no acetic acid was produced; the terminal methyl group was absent.

b. **Hydrogenation.**—Direct hydrogenation of either Solution A or B proceeded erratically. Consistent results and the best yield of *o*-*n*-propylphenol were obtained by warming Solution B (5.00 g.) with Raney nickel catalyst (an old sample), removing the metal by filtration, adding about 200 ml. of ethanol, and distilling to remove most of the ether. In the presence of 0.3 g. of Adams platinum oxide catalyst, this solution absorbed 60% of the theoretical amount of hydrogen required for two double bonds per molecule. Apparently some hydrogenation occurred during the treatment with Raney nickel, which of course carries adsorbed hydrogen. Usual methods gave 2.81 g. (69%

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[9] A number of syntheses which might involve dehydrohalogenation to substituted allenes have been reviewed by Elderfield and Meyer in Elderfield, "Heterocyclic Compounds," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 17–18. However, some examples include compounds in which no hydrogen is available for elimination, and they must therefore proceed by displacement of halogen (including vinyl halogen), etc., by phenoxide. Mechanisms involving allenes also contradict the finding of Adams and Rindfusz (ref. 5) that 2-(bromomethyl)-coumarane was an intermediate in the synthesis of 2-methylbenzofuran. No evidence has been advanced previous to the present work, to the author's knowledge, that phenoxide adds to allenic, allyl or propenyl unsaturation. The cyclization of *o*-allylphenols is commonly acid-catalyzed (Tarbell, in Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 18).

[10] Melting points are corrected; boiling points are not. Microanalyses were performed by Mr. Charles W. Beazley, Micro-Tech Laboratories, Skokie, Illinois. In several instances, a composite result of several experiments is reported to avoid undue length. Properties of previously described compounds were in agreement with the reports in the literature, unless otherwise noted.

[11] Fuson, Kneisley and Kaiser, "Organic Syntheses," **24**, 33 (1944).

[12] Normant, *Bull. soc. chim.*, **12**, 609 (1945), obtained the alcohol (phenylurethan, m.p. 111°) by a less direct method. See also reference 18.

yield) of an oil boiling principally at 107–108° (18 mm.). It was saturated to hydrogen over platinum and was converted to the phenylurethan, m.p. 109.5–110.2°. A mixture with an authentic sample (m.p. 110.2–111.0°) of the phenylurethan[13] of *o*-*n*-propylphenol exhibited no depression. In other runs, platinum was ineffective and slow absorption of hydrogen was catalyzed by palladium-on-charcoal, but the product (58% yield) was still unsaturated and its phenylurethan melted over a wide range; separation of the isomers by recrystallization could not be effected. Once the product prepared by this method had been distilled, it was hydrogenated smoothly over platinum and contained 36% of allyl- and/or propenylphenol; the final product was pure *o*-*n*-propylphenol.

c. **Phenylurethan** of **III**.—To the dry Solution B (2.00 g.) was added 1.55 g. of phenyl isocyanate, 3 ml. of pyridine and 3 ml. of triethylamine. After aspiration of most of the ether at room temperature, hexane was added, the diphenylurea removed by filtration, and concentration continued. Upon cooling, rosetted white crystals separated, m.p. 125–129°. The melting point could not be improved by further recrystallization, although it was raised to 129–140°, and then to 140–170°. The compound apparently polymerized partially with each successive treatment.

Anal. Calcd. for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21. Found: C, 76.62; H, 5.33.

The crude product (0.302 g.) in ethanol absorbed just 2.0 moles of hydrogen, giving in another run in ether the phenylurethan of *o*-*n*-propylphenol.

***o*-Allenylphenyl Acetate (IV)**.—Solution A (10.0 g.) was treated with 15 ml. of reagent acetyl chloride, heated under reflux one hour, and hydrolyzed. The acetate, a mobile colorless liquid (7.80 g., 74.5% yield), boiled at 85–91° (1.1 mm.). The analytical data and properties were determined with a sample obtained by reaction of the halide (5.0 g.) with 1.0 g. of magnesium turnings in the conventional manner, followed by treatment with acetyl chloride; the yield of material of constant refractive index in three fractions was 3.23 g. (62%); b.p. 89–90° (0.9 mm.); $n^{20}D$ 1.5649; d^{20}_4 1.093; *MR* (calcd.) 50.06, (obsd.) 51.91.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.95; H, 6.04.

Although a considerable amount of polymeric material remained in the pot, precautions designed to minimize polymerization seemed to have little effect. The pure material stored in air became quite viscous after several days but did not set to a resin. A fresh sample was hydrogenated smoothly over platinum oxide in ethanol, absorbing 1.97 moles of the gas. The resulting solution was hydrolyzed by adding a pellet of sodium hydroxide and heating. The crude phenol was converted to *o*-*n*-propylphenyl phenylurethan.

A single attempt to prepare the acetate by passing ketene through the ethereal solution of the phenol was unsuccessful, although the reaction appeared to proceed satisfactorily. At the distillation stage, the product polymerized violently, exothermically, and completely.

***o*-Methoxyphenylallene (V) and 2-Methylbenzofuran (VI). Methylation of *o*-Allenylphenol. A. Dimethyl Sulfate**.—Solution C (5.00 g.) was stirred and maintained near 0° while 6.3 g. of dimethyl sulfate was added dropwise. Stirring was continued for an hour and dilute ammonia was added. Distillation at 0.4 mm. of the alkali-insoluble material gave three fractions: 36–62° (0.73 g., $n^{20}D$ 1.5612); 62–62.5° (0.23 g., $n^{20}D$ 1.5810); 62.5–63 (0.57 g., $n^{20}D$ 1.5876, 13% yield). The last fraction was pure *o*-methoxyphenylallene (V); d^{20}_4 1.028; *MR* (calcd.) 45.49, (obsd.) 47.82. A portion was submitted for analysis without redistillation.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.77; H, 6.97.

It polymerized rapidly in contact with air. Material prepared in this way and stored in the refrigerator overnight absorbed only 1.41 moles of hydrogen and was more viscous than the very mobile fresh distillate. It soon set to a hard resin. An impure sample of the methyl ether was subjected to oxidation with alkaline potassium permanganate. The only product, isolated in low yield, was *o*-methoxybenzoic acid; m.p. 99–101°. It was identical with authentic material (m.p. 100–101.5°) prepared by methylation of salicylic acid.

A hint concerning the nature of the low-boiling fraction was obtained from the observation that the alkaline aqueous layer from the methylation procedure, when warmed briefly, yielded 0.82 g. of the same compound; b.p. 69–70° (10 mm.) or 196° (746 mm.); $n^{20}D$ 1.5597.

In another run conducted at room temperature, in which only a trace of methyl ether was obtained, the same pure compound was isolated; b.p. 31–33° (0.5 mm.); $n^{20}D$ 1.5602; d^{20}_4 1.057; *MR* (calcd.) 39.14, (obsd.) 40.93.

Anal. Calcd. for C_9H_8O: C, 81.79; H, 6.10. Found: C, 81.58; H, 6.08.

These data agree satisfactorily with the properties of 2-methylbenzofuran.[14]

B. **Diazomethane**.—When Solution B (300 ml., principally petroleum ether) (10.23 g.) was treated with a solution of diazomethane prepared[15] from 15 g. of nitrosomethylurea in 200 ml. of ether, evolution of nitrogen was impracticably slow. Addition of small amounts of methyl alcohol and triethylamine seemed to have no effect. However, vigorous evolution of nitrogen followed the dropwise addition of a total of about 1 ml. of 45% boron trifluoride etherate.[16] The yellow solution became milky in appearance and a polymeric gum separated. Acetic acid was added, the solution was decanted, and rapid extractions were performed with 40% potassium hydroxide solution.

The methyl ether (b.p. 61.5–65° at 0.4 mm.; 1.81 g., 20% yield; $n^{20}D$ 1.5874) was the principal product. The forerun (0.91 g.) was mainly methylbenzofuran. From the alkaline extracts, by warming, was obtained 2.27 g. of the latter; b.p. 68–70° (8 mm.), $n^{20}D$ 1.5603. No systematic attempt was made to improve the yield of *o*-methoxyphenylallene obtainable by either of these procedures. A freshly prepared sample of the ether was hydrogenated over platinum oxide; 2.10 double bonds per molecule were indicated.

Characterization of 2-Methylbenzofuran.—For comparison with the low-boiling product described above, 2-methylbenzofuran (V) was prepared according to the directions of Adams and Rindfusz.[6] The picrate[5] did not separate from alcoholic solution; when a solution of the compound and picric acid in petroleum ether and chloroform was allowed to evaporate, canary yellow needles (m.p. 74–80°) separated.

Authentic 2-methylbenzofuran was acetylated according to the general method of Farrar and Levine.[17] When a mixture of 3.0 g. with 2.5 g. of acetic anhydride was treated with 1.0 g. of anhydrous stannic chloride, the product, 3-acetyl-2-methylbenzofuran, was a colorless viscous liquid (b.p. 108–110° at 1.0 mm., 1.95 g.) which solidified, m.p. 45–47°. The crude product of acetylation of the unknown liquid melted at 47–49° and did not depress the value for the authentic ketone. A sample was recrystallized from hexane and sublimed twice at 80° (0.2 mm.), m.p. 47.4–49.4°.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.85; H, 5.78. Found: C, 75.80; H, 5.88.

Preparation of 2-Methylbenzofuran (VI). A. From *o*-Allenylphenol (III).—In addition to the isolation of this compound from methylation mixtures, described above, a brief study was made of its production by basic catalysts directly from the phenol.

A current of dry purified nitrogen was passed through Solution B (6.00 g., clear amber in color) to remove residual solvents. Then heating and slow stirring were commenced from the initial temperature of 5°. Up to 25°, the solution became increasingly milky in appearance, and a layer began to form above it from 25 to 35°. At 45° the formation of the layer was essentially complete and the aqueous layer became clear at 65°. The time required to attain 80° was 30 minutes; heating to 100° during a like period completed the process. The product weighed 2.98 g. (b.p. 71–72.5°

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[13] The hydrogenation of allylphenol and the phenylurethan (m.p. 111°) of the product have been described by Claisen, *Ann.*, **418**, 88 (1919). Hexane was a more convenient solvent than formic acid for recrystallization of the derivative.

[14] v. Auwers, *Ann.*, **422**, 133 (1921).

[15] Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 166, note 3.

[16] See Newman and Beal, THIS JOURNAL, **72**, 5161 (1950), concerning the action of this catalyst on solutions of diazoketones in alcohols.

[17] Farrar and Levine, *ibid.*, **72**, 4433 (1950).

at 9 mm.; n^{20}D 1.5602; 62.7% yield). A trace (0.38 g.) of material remained in the original solvent layer; from the alkaline solution by acidification and extraction was isolated 0.63 g. of a gum.

To the dry Solution B (5.00 g.) was added 10 ml. of triethylamine. The ether was removed by slow distillation, the residue was heated under reflux for three hours, and then acidified with dilute hydrochloric acid. Only a trace was alkali-soluble. The methylbenzofuran weighed 2.34 g. (b.p. 75–77° at 12 mm.; n^{20}D 1.5629; 59% yield).

B. **From *o*-Allenylphenyl Acetate (V).**—To a solution prepared by dissolving 2.3 g. of sodium in 70 ml. of absolute methanol was added 6.33 g. of the freshly distilled acetate. The color changed to deep amber and the mixture became warmer. It was heated under reflux for 11 hours and the bulk of the solvent was removed by distillation. The odor of methyl acetate was unmistakable. The residue was acidified and extracted with ether. Two rough fractionations gave a total of 3.88 g. of 2-methylbenzofuran (b.p. 77–80° at 14 mm.; n^{20}D 1.5583; 81% yield). The residue (0.47 g.) was not characterized.

An attempt to transmetallate 2-methylbenzofuran by heating with ethylmagnesium bromide failed; the starting material was recovered after treatment of the mixture with acetyl chloride.

Reaction of 2-(Chloromethyl)-benzofuran with Alkali Cyanides.—Five grams of the chloride was heated under reflux for two hours with 4.9 g. of powdered sodium cyanide in 50 ml. of reagent acetone. An equal volume of water was added and heating continued for six hours. The product did not crystallize from hexane. It was hydrolyzed by heating with 10 g. of potassium hydroxide in aqueous ethanol. The 2-benzofurylacetic acid,[18] m.p. 99.5–100.5°, weighed 1.27 g. (24%) after recrystallization from hexane. The neutral fraction contained 2-benzofurylcarbinol (about 0.8 g.) isolated as the phenylurethan.

The chloride (5.0 g.) was heated under reflux with mechanical stirring for seven hours with 6.5 g. of potassium cyanide in 25 ml. of acetone and 25 ml. of purified dioxane. All but 10 ml. of the solvents was removed by distillation, and water was added to the residue. After extraction into ether, distillation of this solvent, and addition of petroleum ether (70–90°) and benzene, 0.70 g. of light tan crystals separated. Recrystallization produced fine white needles, m.p. 161.8–162.4°. The compound resisted attempted hydrolysis with alcoholic alkali and has not been identified.

Anal. Found: C, 80.17; H, 4.95; N, 3.22.

The residue from distillation of the benzene–petroleum ether filtrate above did not crystallize. Distillation yielded, after a small forerun of unchanged chloride, a total of 1.25 g. boiling at 95–110° (0.5 mm., principally at 105–110°). 2-Benzofurylacetonitrile formed colorless needles from hexane, m.p. 58.5–59.7°.

Anal. Calcd. for $C_{10}H_7NO$: C, 76.42; H, 4.49. Found: C, 76.53; H, 4.33

The nitrile was hydrolyzed to 2-benzofurylacetic acid by alcoholic alkali.

Ultraviolet Absorption Spectra.—The measurements for Fig. 1 were made on a Beckman model DU spectrophotometer. Samples of easily polymerizable materials were freshly distilled and the measurements were completed within a few hours. The *o*-allenylphenol from 1.67 g. of chloride was made up to 100 ml. with ether. Evaporation at the aspirator of a 10-ml. aliquot left 0.1523 g.; although some impurities are undoubtedly included in this figure, it was the only available basis for the calculation of extinction coefficients. A 2-ml. aliquot of this solution was diluted to 25 ml. with 95% ethanol, and 2 ml. of that mixture again made up to 25 ml. with ethanol. Solutions of *o*-propenylphenol and *o*-allylphenol were prepared similarly. The other spectra were determined with ethanol as the solvent.

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[18] Reichstein and Reichstein, *Helv. Chim. Acta*, **13**, 1275 (1930), reported a constant of 98–99° for the compound, obtained by a more indirect method, which, however, was not open to the possibility of rearrangement.

[CONTRIBUTION FROM POLYCHEMICALS DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO., INC.]

Synthesis of 3-Amino-1,2-propanediol and 2,3-Diamino-1-propanol

BY R. C. SCHREYER

Synthesis of 3-amino-1,2-propanediol and 2,3-diamino-1-propanol from methoxyacetaldehyde and hydrogen cyanide involving no halogen containing compounds has been described. A number of substituted propionitriles and propylamines have been reported.

Syntheses of 3-amino-1,2-propanediol and 2,3-diamino-1-propanol were desired which involved no halogen containing compounds. 3-Amino-1,2-propanediol has been prepared by amination of hydroxypropylene oxide[1] or 3-chloro-1,2-propanediol[2] with aqueous ammonia. Abderhalden and Eichwald[3] have reported the synthesis of 2,3-diamino-1-propanol by amination of β,γ-dibromopropyl methyl ether followed by cleavage with hydrogen bromide.

In this investigation methoxyacetaldehyde–water azeotrope, obtained by the air oxidation of methoxyethanol over silver, was the starting material for the syntheses of the desired intermediates. 3-Methoxy-2-hydroxypropionitrile (I) was formed by treatment of methoxyacetaldehyde with hydrogen cyanide. Attempts to hydrogenate the cyanhydrin directly to 3-methoxy-2-hydroxypropylamine (IV) were not successful due to decomposition. The hydroxyl group of the cyanhydrin was protected by reaction with ethylal and a trace of acid to form 3-methoxy-2-ethoxymethoxypropionitrile (II). Hydrogenation of (II) to (III) then proceeded in high yields. The ethoxymethoxy group was removed by processing with ethanol in presence of acid to give (IV). 3-Amino-1,2-propanediol (V) was obtained by cleavage of the ether linkage with hydrochloric acid.

2,3-Diamino-1-propanol (VIII) was obtained by amination of (I) to 3-methoxy-2-aminopropionitrile (VI) followed by hydrogenation to 3-methoxypropylenediamine (VII) and cleavage of the ether linkage.

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Experimental

3-Methoxy-2-hydroxypropionitrile.—Hydrogen cyanide (290 ml.) was added portionwise to a stirred mixture of 515 g. of methoxyacetaldehyde–water azeotrope (13% H_2O) and 1 g. of pyridine, maintaining the temperature at 50–60°. The addition time was 2 hours. The mixture was cooled

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(1) L. Smith and T. Nilsson, *J. prakt. Chem.*, **162**, 63 (1943).

(2) Girdler Corp., French Patent 808,024, Jan. 27, 1937.

(3) E. Abderhalden and E. Eichwald, *Ber.*, **49**, 2101 (1916).