Copolymer E was prepared by solution polymerization, at 50% by volume in methanol, of an equimolar mixture of the two monomers. Azo-bis-isobutyronitrile (0.05%) was used as catalyst; the polymerization temperature was 70°. After 80 minutes, the viscous polymer solution was diluted with methanol, cooled and precipitated into an excess of acetone. The resin was washed with methyl ethyl ketone, and purified by twice redissolving in a 90–10 methanol–water mixture, precipitating in acetone, and hardening the precipitate by washing with methyl ethyl ketone. The polymer was finally vacuum dried. Conversion to polymer was 11%.

Copolymers C, G and F were prepared by solution polymerization in 50% aqueous methanol, using potassium persulfate as catalyst. Copolymers A, B, D and H were prepared by polymerization in dilute aqueous HCl solution (*p*H 1.2), using potassium persulfate as catalyst. Conversions were not permitted to exceed 25%. These copolymers were purified in essentially the same manner as copolymer E, minor variations being required because of solubility differences. Copolymer composition was determined by Kjeldahl analysis for nitrogen. Copolymers A, B, D and H were isolated as the hydrochlorides.

The viscosity data of Figs. 2 and 3 were determined in a dilution viscometer of the type previously described.[5] These curves were obtained at constant resin concentration; successive dilutions were made with a solution having the same resin concentration as that in the viscometer, but differing in the concentration of HCl, NaCl, buffer or other component undergoing variation. In the vicinity of the isoelectric point, solutions exhibited a very pronounced foaming tendency, which could be completely eliminated by addition of traces of 2-ethylhexanol. Another surface phenomenon, which affects the viscosity results to some extent, is a small amount of adsorption of the resin on glass surfaces.

The viscosity data of Figs. 5–12 were obtained in a similar dilution viscometer. Dilution was made with concentrated acid or alkali solutions; hence the resin concentration changed slightly during each dilution experiment. This was corrected for. Acid and base additions were run separately, in order to avoid the introduction of neutral electrolyte. Small concentrations of neutral salt were present, of course, in the cases of copolymers A, B, D and H, which had been isolated as the hydrochlorides. It would have been preferable to have measured the *p*H of the solutions inside the viscometers at the time of the viscosity measurement. Because this was difficult to arrange, parallel neutralizations were run outside the viscometers for *p*H determination. Since no buffers were used in this series of experiments, extreme care had to be taken to avoid absorption of CO_2, which would have resulted in sizable *p*H and viscosity drifts. All air taken into the viscometers was drawn through a Caroxite CO_2 absorption bulb.

Electrophoresis data were obtained with a Tiselius apparatus (Perkin–Elmer Company). The acetate–diethyl barbiturate buffer-system recommended by Michaelis[8] was used, since it covers a wide range of *p*H without introducing multivalent ions. Resin solutions containing 0.6 g./100 ml. were prepared in the buffers, and were dialyzed for 4 days against large volumes of buffers with an ionic strength of 0.057. Cell currents were 4.0–6.2 milliamps. at 6.3–7.9 volts/cm. Both ascending and descending boundaries were photographed and the mobility *u* (cm.^{2}/volt sec.) was calculated from their average displacements.

[8] L. Michaelis, *Biochem. Z.*, **234**, 139 (1931).

MIDLAND, MICHIGAN RECEIVED JULY 27, 1951

[CONTRIBUTION FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Nature of Oxygen in Coal: Preparation and Properties of Phthalan[1]

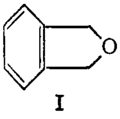
BY JACOB ENTEL, CLARENCE H. RUOF AND H. C. HOWARD

Phthalan has been produced in yields of 89% by dehydration of phthalyl alcohol over alumina at 300°. It readily absorbs oxygen from the atmosphere to form a crystalline peroxide, $C_{16}H_{14}O_4$; reacts with stannic chloride to form a crystalline adduct containing two molecules of the ether for each molecule of the tin salt; and readily adds hydrogen over Raney nickel catalyst at 150° to form hexahydrophthalan. It has been subjected to hydrogenolysis over copper–chromium oxide catalyst at 250, 300 and 350° and the products determined quantitatively by infrared and ultraviolet spectra and other physical properties; 2-methylcyclohexanemethanol and *o*-methylbenzyl alcohol were synthesized for comparison purposes. The similarity of the properties of phthalan to those of coal and its degradation products suggest that a part of the oxygen in coal may occur in phthalan type structures.

The controlled oxidation of suspensions of bituminous coals in aqueous alkali converts about 50% of the carbon to a mixture of water-soluble polycarboxylic acids. In addition to the benzenecarboxylic acids which have been definitely identified, there are present acids in which the nuclei are larger than the benzene ring and in which part of the oxygen is in non-determinable groups. Oxygen-rich fractions of the hydrogenolysis products of the esters of the acids have many chemical and physical properties characteristic of the cyclic ether structures, benzofuran and dihydrobenzofuran, but possess a few properties inconsistent therewith, which suggests the isomeric structure, phthalan.[2] The present work was undertaken to provide information necessary for definite characterization of phthalans and to test their amenability to hydrogenolysis. Such knowledge has hitherto been unavailable.

Discussion

Phthalan (I) has been prepared previously[3,4] in poor yield by heating *o*-xylylene bromide with potassium hydroxide. In the present work phthalan has been prepared in 89% yields by the dehydration of phthalyl alcohol over alumina at 300° in analogy to the formation of methyltetrahydrofuran from 1,4-pentanediol.[5] Attempts to dehydrate phthalyl alcohol at 145° (3 mm.) by distillation or by refluxing with sirupy phosphoric acid yielded unchanged phthalyl alcohol and a red resin, respectively.


I

The phthalyl alcohol was prepared in 94% yield

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[1] Presented before the Fuel, Gas and Petroleum Chemistry Section of the XIIth International Congress of Pure and Applied Chemistry, Sept., 1951, New York, N. Y.

[2] C. H. Ruof, T. R. Savich and H. C. Howard, THIS JOURNAL, **73**, 3873 (1951).

[3] R. Willstätter and H. Veraguth, *Ber.*, **40**, 965 (1907).

[4] For a discussion of phthalan and its homologs, *cf.* R. C. Elderfield, "Heterocyclic Compounds," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 83–91.

[5] E. Beati and G. Mattei, *Ann. chim. applicata*, **30**, 21 (1940).

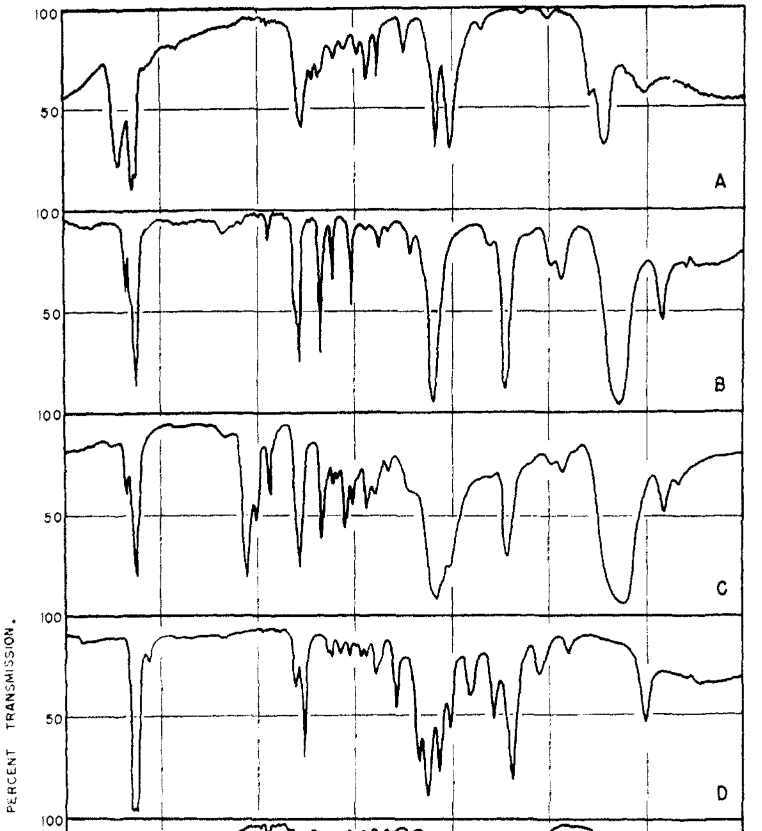
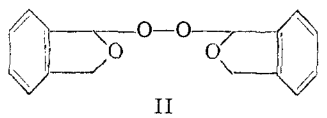


Fig. 1.—Infrared spectra: A, phthalyl alcohol ("nujol mull"); B, phthalan (0.014-mm. cell); C, phthalan heated 43 hours in air (0.02-mm. cell); D, hexahydrophthalan (0.014-mm. cell); E, phthalan peroxide ("nujol mull"); F, *o*-methylbenzyl alcohol ("nujol mull"); G, 2-methylcyclohexanemethanol (0.014-mm. cell).

by the reduction of phthalyl chloride by lithium aluminum hydride. The chloride was preferred to the anhydride[6] because of its ease of introduction into the reaction mixture.

The infrared spectrum (Fig. 1) of phthalan demonstrates the absence of carbonyl and hydroxyl groups and the presence of an ortho-substituted benzene ring, while the ultraviolet spectrum (Fig. 2) indicates a benzene ring. In addition to the spectral data, the ultimate analysis, molecular weight, molar refraction, failure of chemical tests for carbonyl groups, oxidation to *o*-phthalic acid by alkaline permanganate, methods of synthesis and non-identity with 2,3-dihydrobenzofuran[7] definitely establish structure I for phthalan.

When refluxed in air and light for 43 hours, phthalan is converted to a dark red resin, *cf.* Figs. 1 and 2 for spectra; however, it can be fractionally distilled *in vacuo* or in an inert atmosphere, *viz.*, nitrogen, without evidence of decomposition. On exposure to the atmosphere it readily absorbs oxygen; adequate protection against the atmosphere is therefore required for all analytical samples. The rate of this oxygen absorption is several hundred-fold less than that of alkaline pyrogallol under similar conditions. However, thin films of phthalan, when exposed to air for one day, are completely converted to a white crystalline peroxide whose ultimate analysis, molecular weight, infrared and ultraviolet spectra (Figs. 1 and 2) and iodometric titration suggest structure II.



II

Two molecules of phthalan or its hexahydro derivative readily react with one molecule of stannic chloride to form crystalline adducts.[8]

Phthalan readily adds hydrogen with saturation of the benzene ring. Hydrogenolytic rupture of the heterocyclic ring may also occur. In this work phthalan has been hydrogenated over Raney nickel at 150–160° to give hexahydrophthalan. It has been subjected to hydrogenolysis over copper–chromium oxide catalyst at 250, 300 and 350° for 12-hour periods and the products have been identified by precision fractional distillation and comparison with infrared and ultraviolet spectra, *cf.* Figs. 1 and 2, and other physical properties of the possible products; *o*-methylbenzyl alcohol and 2-methyl-

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[6] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 1197 (1947).

[7] J. Entel, C. H. Ruof and H. C. Howard, *ibid.*, **73**, 4152 (1951).

[8] C. H. Ruof and H. C. Howard, "Stannic Chloride Adducts with Coal Degradation Products," presented before the Gas and Fuel Division, American Chemical Society, 118th National Meeting, Chicago, Ill., Sept. 4–8, 1950.

cyclohexanemethanol have been synthesized for comparison purposes.

The amounts of the different components in the reaction products were estimated quantitatively from the refractive indices and quantitative infrared spectra of the individual fractions. From the analyses thus obtained, the composition of the products was calculated to be as shown in Table I.

TABLE I

HYDROGENOLYSIS PRODUCTS OF PHTHALAN (COPPER-CHROMIUM OXIDE, 12 HOURS)

	Weight % yield of products 250°	300°	350°
Phthalan	49	1	0
Hexahydrophthalan	30	34	12
2-Methylcyclohexanemethanol	5	5	15
o-Xylene	15	54	42
1,2-Dimethylcyclohexane	1	6	31

The persistence of significant amounts of unchanged phthalan and of hexahydrophthalan in the products of hydrogenolytic reactions at temperatures as high as 350° shows the much greater stability of this type of oxygen heterocycle as compared with the normal benzofurans.[7] The marked stability of phthalan on hydrogenolysis, its adduct-forming property, its thermal instability in contact with air and its ready addition of oxygen are properties exhibited by coal and its degradation products and suggest that a part of the oxygen in coal may occur in phthalan type structures.

Experimental

Preparation of Phthalyl Alcohol.—Sixty-five grams (1.7 moles) of lithium aluminum hydride (Metal Hydrides, Inc.) was added to 2 liters of anhydrous ether (Mallinckrodt) in a 3-necked 5-liter flask equipped with mercury sealed stirrer, dropping funnel and reflux condenser. After refluxing for four hours to dissolve the lithium aluminum hydride completely, a solution of 303 g. (1.5 moles) of freshly distilled phthalyl chloride in 600 ml. of ether was added cautiously with reflux. After the addition was complete the reflux was continued for 12 hours. After hydrolysis with excess of cold 30% sulfuric acid, the product was exhaustively extracted with ether and the ethereal solution was washed with a solution of sodium carbonate. The ether was removed by distillation and the residual yellow oil was evacuated in a desiccator until crystals appeared. The crystals were removed by filtration; several additional crops were obtained from the mother liquor by the same procedure. The crystalline products were combined, washed with warm pentane and dried to give 195 g. (94% yield) of colorless crystals of phthalyl alcohol, m.p. 63–64°,[8] diacetate, m.p. 35–36°.[6]

Preparation of Phthalan. **(a) Willstätter's Method.**—*o*-Xylylene bromide and potassium hydroxide were mixed, fused and steam distilled as directed[3]: yield of phthalan, b.p. 191°, $n^{25}\text{D}$ 1.5440, was 13% of theoretical.

(b) Dehydration of Phthalyl Alcohol.—Efforts to dehydrate the phthalyl alcohol by distillation at 145° (3 mm.) or by refluxing with 85% phosphoric acid gave unreacted alcohol and a red resin, respectively.

Melted phthalyl alcohol, 276 g., from several preparations was dehydrated at 300° by passing the vapor through a heated glass tube packed with $^1/_4''$ mesh activated alumina. The product consisted of 240 g. of reddish-brown oil and 36 ml. of water; it was steam distilled from a 10% aqueous sodium hydroxide solution: yield 214 g. (89% yield) of phthalan. Unreacted phthalyl alcohol, 20 g., was recovered from the portion non-volatile with steam.

After having been dried over anhydrous sodium sulfate the phthalan was fractionated *in vacuo* in a 15-plate column, b.p. 106° (36 mm.). A sample for physical property measurements was then refractionated in a column of 50 theoretical plates at atmospheric pressure in a dry nitrogen atmosphere, b.p. 191° (740 mm.) and 106° (36 mm.), $n^{25}\text{D}$ 1.5440, $d^{25}{}_4$ 1.0873, f.p. +6.0°. A "heart cut" sample for ultimate analysis was removed from the column and immediately sealed under dry nitrogen in an aluminum foil coated ampule to protect it from air and light.

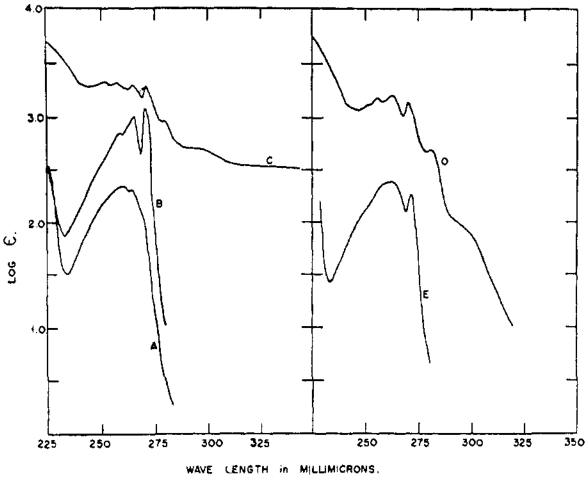

Fig. 2.—Ultraviolet spectra: A, phthalyl alcohol (in absolute ethanol); B, phthalan (in isoöctane); C, phthalan heated 43 hours in air (in absolute ethanol); D, phthalan peroxide (in 95% ethanol); E, *o*-methylbenzyl alcohol (in isoöctane).

Anal. Calcd. for C_8H_8O: C, 79.97; H, 6.71; molar refraction, 34.97; mol. wt., 120. Found: C, 80.00; H, 6.75; molar refraction, 34.84; mol wt., 122 (cryoscopically in benzene).

When samples of phthalan were exposed to air prior to analysis the carbon content was always lower than theoretical as a result of reaction with oxygen.

Preparation of Phthalan Peroxide.—Samples of phthalan were placed in thin films on watch glasses and exposed to air and light. After one day all the phthalan had been converted to a white crystalline solid which was then recrystallized from ether, m.p. 137.5–139.5°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.09; H, 5.22; mol. wt., 270. Found: C, 70.95; H, 5.32; mol. wt., 268 (cryoscopically in benzene).

The product has no absorption peaks for carbonyl or hydroxyl groups in the infrared spectrum (*cf.* Fig. 1). Iodometric titration indicates 2.04 equivalents of iodine liberated by each molecular weight; theoretical for peroxide of structure II, 2.00.

Formation of Adducts with $SnCl_4$.—Phthalan, 5 ml. (5.4365 g.), was dissolved in 100 ml. of pentane in a 270-ml. centrifuge cup and 5 ml. of anhydrous stannic chloride, 11.130 g., in 100 ml. of pentane was added with the immediate formation of a heavy white precipitate. The reaction mixture was allowed to stand several days over solid potassium hydroxide in a desiccator which was open to the atmosphere through a drying tube. The precipitate was then centrifuged and washed twice with fresh pentane and dried *in vacuo:* yield 11.88 g. The precipitate was then analyzed for tin tetrachloride by a modification of the method of Sisler[9] in which the amount of ammonium nitrate used was increased from 1.0 to 5.0 g.

Anal. Calcd. for $(C_8H_8O)\cdot SnCl_4$: $SnCl_4$, 68.44. $(C_8H_8O)_2\cdot SnCl_4$: $SnCl_4$, 52.02. Found: $SnCl_4$, 51.5, 52.8.

Hexahydrophthalan was treated in a similar manner to give its stannic chloride adduct.

Anal. Calcd. for $(C_8H_{14}O)\cdot SnCl_4$: $SnCl_4$, 67.37. $(C_8H_{14}O)_2\cdot SnCl_4$: $SnCl_4$, 50.79. Found: $SnCl_4$, 51.8, 52.0, 52.0, 51.9.

When the hexahydrophthalan adduct was prepared and filtered through a fritted filter disk in an inert atmosphere, the tin tetrachloride analyses were still higher than theoretical, 51.8 and 52.0.

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[9] H. H. Sisler, H. H. Batey, B. Pfahler and R. Mattair, THIS JOURNAL, **70**, 3822 (1948).

Heating the adducts with dilute acids or bases regenerated the phthalan and hexahydrophthalan.

Preparation of Hexahydrophthalan.—Phthalan, 106 g. (0.9 mole), was hydrogenated over 4 ml. of Raney nickel catalyst at 150–160° for 12 hours with an initial cold pressure of 1700 p.s.i.g. The product was fractionated through a column of 50 theoretical plates. The yield of hexahydrophthalan with a strong menthol odor was 107 g. (96%), b.p. 179° (740 mm.), $n^{25}\text{D}$ 1.4683, $d^{25}{}_4$ 0.9727, f.p. glass.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18; molar refraction, 36.40. Found: C, 76.13; H, 11.27; molar refraction, 36.08.

Hydrogenolyses of Phthalan.—The hydrogenolyses of phthalan were run at reaction temperatures of 250, 300 and 350 ± 5° for 12 hours in a 1080-ml. stainless steel rocking autoclave which was heated by an external electric furnace. In all three runs 5 g. of copper–chromium oxide catalyst, 80 g. of phthalan (0.67 mole) and 1625–1725 p.s.i.g. of hydrogen pressure were charged to the autoclave. Hydrogen absorptions corresponded to 1.6, 2.9 and 4.0 moles of hydrogen per mole of phthalan at 250, 300 and 350°, respectively. The bomb was cooled to room temperature after reaction and the products filtered free of catalyst and fractionated in a column of 50 theoretical plates. The fractions were then analyzed quantitatively by means of their infrared spectra and other physical properties; a summary of the yields of the various products is presented in Table I.

Preparation of *o*-Methylbenzyl Alcohol.—A mixture of 185 g. (1 mole) of *o*-xylyl bromide and 123 g. (1.5 moles) of fused sodium acetate dissolved in a minimum volume of boiling glacial acetic acid was refluxed for 24 hours. Without isolating the resulting *o*-xylyl acetate, the crude reaction mixture was neutralized and then made alkaline with an excess of 400 ml. of 20% sodium hydroxide solution. After refluxing 8 hours the product was steam distilled; the distillate was extracted with ether, the ethereal extract was dried over anhydrous potassium carbonate and the ether distilled off. On refrigeration the *o*-methylbenzyl alcohol crystallized after which it was filtered free of oil and recrystallized from pentane: yield 105 g. (86% yield) of white needles, m.p. 36–37°; *o*-tolylcarbinyl-N-phenylcarbamate, m.p. 79–80°.[10]

Anal. Calcd. for $C_8H_{10}O$: OH, 14.0. Found: OH, 14.3, 14.0.

Preparation of 2-Methylcyclohexanemethanol.—(a) Hydrogenation of *o*-methylbenzyl alcohol over Raney nickel or palladium-on-charcoal gave high yields of *o*-xylene and 1,2-dimethylcyclohexane and only minor amounts of this compound.

(b) A mixture of 2-methylcyclohexanol and excess zinc chloride–hydrochloric acid reagent (1:1 molar ratio) was refluxed for 4 hours and cooled to room temperature. The upper phase was removed and washed with concentrated sulfuric acid, a saturated solution of sodium bicarbonate and then water and dried over anhydrous calcium chloride. The product, 2-methylchlorocyclohexane, was fractionated, b.p. 153–154° (735 mm.).

Into the ethereal solution of a Grignard reagent prepared from 148 g. (1.12 moles) of the halide, formaldehyde vapor from the thermal depolymerization of paraformaldehyde at 180–200° was bubbled until a negative Gilman test was obtained. After hydrolysis and steam distillation the reaction product was fractionated in a column of 50 theoretical plates and the yield was 70 g. (50% yield) of 2-methylcyclohexanemethanol, b.p. 194° (733 mm.), $n^{25}\text{D}$ 1.4610.

Anal. Calcd. for $C_8H_{16}O$: C, 75.00; H, 12.50; OH, 13.28. Found: C, 75.27; H, 12.66; OH, 13.22.

Only one isomer was isolated in the fractionation; this appears to be the form previously designated as *trans* by Skita.[11]

Acknowledgment.—We wish to express our thanks to Messrs. Joseph B. Simsic and Daniel T. Muth for their assistance. Absorption spectra were run on the Baird Infrared and Cary Ultraviolet Recording Spectrophotometers of the Mellon Institute, Pittsburgh, Pennsylvania, and microanalyses were performed by the Huffman Microanalytical Laboratories, Denver, Colorado.

PITTSBURGH, PENNA. RECEIVED JULY 13, 1951

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(10) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 412.

(11) A. Skita, *Ann.*, **431**, 9, 20 (1923).

[CONTRIBUTION FROM THE PURDUE UNIVERSITY CHEMISTRY DEPARTMENT AND THE PURDUE RESEARCH FOUNDATION]

The Ionization Constants of Some Fluorine-containing Alcohols[1,2]

BY E. T. MCBEE, W. F. MARZLUFF AND O. R. PIERCE

Diols of the general formula $HOCH_2(CF_2)_nCH_2OH$ where n is 1, 2, 3 or 4 were synthesized. The pK_a values of 2,2,3,3-tetrafluoro-1,4-butanediol were measured and found to be 12.1 ± 0.1 and 13.7 ± 0.2 while those of 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol were determined as 12.1 ± 0.1 and 12.8 ± 0.2. In addition, the pK_a value of 2,2,2-trifluoroethanol was measured and found to be 12.3 ± 0.05. The inductive effect of fluorine substitution beta to hydroxyl groupings can be calculated by empirical methods.

Discussion

Fluorine-containing diols were prepared for use in quantitative determinations of the effect of fluorine substitution on the acidity of hydroxyl groupings. Alcohols containing fluorine beta to the hydroxyl group were first prepared by Swarts[3a,b] who reported 1,1,1-trifluoro-2-propanol to be more acidic than phenol.[3a] Since work in this Laboratory had demonstrated that 2,2,2-trifluoroethanol was not acidic in nature, the ionization constants of 2,2,2-trifluoroethanol and diols containing fluorine were measured.

Diols of the general formula $HOCH_2(CF_2)_n$-CH_2OH, where n is 1, 2, 3, 4, were synthesized from the respective fluorine-containing acids. Octafluoroadipic acid was prepared by the oxidation of 1,2-dichloroöctafluorocyclohexene and hexafluoroglutaric acid was obtained by the oxidation of 1,2-dichlorohexafluorocyclopentene (Hooker Electrochemical Co.) using potassium permanganate.[4] The yield of the acid in each case was from 40 to 50%. Hexafluorocyclobutene was oxidized with potassium permanganate at autogenous pressures to give the desired tetrafluorosuccinic acid.[5] The

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(1) This paper represents part of a thesis to be submitted by W. F. Marzluff to the Graduate School, Purdue University, in partial fulfillment for the degree of Doctor of Philosophy. This work was supported by the Air Materiel Command, United States Air Force.

(2) Presented, in part, before the Fluorine Symposium, 118th Meeting of the American Chemical Society, Chicago, Illinois, September, 1950.

(3) (a) F. Swarts, *Bull. soc. chim. Belg.*, **38**, 99 (1929); (b) *Compt. rend.*, **197**, 1261 (1933).

(4) E. T. McBee and P. A. Wiseman, *Ind. Eng. Chem.*, **39**, 415 (1947).

(5) A. L. Henne and W. J. Zimmerschied, THIS JOURNAL, **69**, 283 (1947).