maxima at 3625 and 3545 cm.$^{-1}$ will be noticed indicating OH stretching frequencies of both "free" and internally H-bonded OH groups.[20]

Although a number of approximate coincidences of wave lengths of infrared absorption bands will be noticed in comparing the spectra of compounds assigned closely related structures in the above discussion, it is thought that more data on compounds of known similar structures should be available before further generalizations are made relating particular bands to particular structural features.

ALBANY 6, CALIFORNIA

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[20] L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

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

Nuclear Structure of the Water-soluble Polycarboxylic Acids from the Oxidation of Bituminous Coal: The Hydrogenolysis Reaction[1]

BY JACOB ENTEL

RECEIVED FEBRUARY 4, 1954

To ascertain the nature of the nuclei of the yellow, water-soluble, polycarboxylic aromatic acids produced by the controlled oxidation of aqueous alkaline suspensions of bituminous coals these acids have been subjected to a series of reactions which have converted the carboxyl groups to methyl groups, and which have led to the isolation and identification of individual compounds. Herein is described the application of this series of reactions. Phthalan, 5-methylphthalan, 2-methylcyclohexanemethanol, 1,2,3,4-, 1,2,3,5- and 1,2,4,5-tetramethylbenzene have been isolated and identified from the fraction boiling at 195–207° (760 mm.) which was obtained from the hydrogenolysis of the butyl esters of these acids. Since further work on this problem is not planned for the near future, the results of preliminary investigations of those hydrogenolysis fractions boiling above 207° (760 mm.) are also presented. From these fractions pentamethylbenzene has been isolated and identified. Two compounds—4,5- and 4,7-dimethylphthalan—have been isolated, but it has not been possible to determine which of these compounds is the 4,5- or 4,7-dimethylphthalan. The data also indicated the presence of such compounds as polymethylbiphenyls, polymethylphthalans, polymethylhexahydrophthalyl alcohols, lactones of polymethyl-2-hydroxybicyclohexyl-2′-carboxylic acid and polymethylcyclohexanemethanols. The significance of these compounds in establishing the nuclear structure of the acids obtained from the alkaline oxidation of coal is discussed.

In the controlled oxidation of aqueous alkaline suspensions of bituminous coals, yellow, water-soluble, polycarboxylic aromatic acids are produced in yields of 50–60% by weight of coal charged.[2] These acids have been the subject of extensive investigations because of their potential commercial value and their significance in structural studies on coal.

In order to ascertain the nature of the nuclei to which the carboxyl groups are attached, these acids have been subjected to the following series of reactions: (1) esterification, (2) hydrogenolysis of the resulting esters, (3) precision fractional distillation of the hydrogenolysis products, (4) adsorption of selected distillation fractions on selective adsorbents, (5) precision fractional distillation of the products obtained by the adsorption procedure and (6) identification of individual compounds by chemical, spectroscopic and other physical means. The procedures, results and discussion of steps 1–3 inclusive have been described in detail elsewhere.[2]

The data obtained from the fractional distillation of 1920 g. of the hydrogenolysis products of the butyl esters of these acids[2] indicated that this material consisted essentially of a mixture of three classes of compounds: (a) oxygenated materials, (b) aromatic hydrocarbons and (c) alicyclic hydrocarbons. Initial separation of this mixture of classes from each other facilitates the isolation and identification of the individual compounds which comprise these hydrogenolysis products. The feasibility of effecting this type of separation by adsorption on bentonite and silica-gel has been shown.[3]

In this work primary interest was in those materials with boiling ranges higher than the previously identified trimethylbenzenes.[2] Accordingly, the fractions which were obtained from the fractional distillation of 1920 g. of hydrogenolysis materials[2] and which boiled above 195° at 760 mm. pressure were composited as shown in Table I, preparatory to separation by adsorption on bentonite and silica-gel.

TABLE I

PROPERTIES OF THE COMPOSITE DISTILLATION FRACTIONS OF THE HYDROGENOLYSIS PRODUCTS

Fraction	B.p., °C./760 mm.	Mol. wt. range	Wt., g.
I	195–207	126–140	87
II	212–263	144–174	180
III	280–317	186–218	173
IV	>320	220–250	213
V	.....	250–300	145
Residue	.....	Avg. 545	598

This paper describes the work up of fraction I, *in toto*, to show the feasibility of the previously outlined series of reactions in isolating and identifying individual components of the hydrogenolysis products of the esters of the acids obtained by the oxidation of bituminous coals. As work on this problem has been postponed indefinitely, the results of a preliminary investigation of fractions II–V inclusive are also presented.

Experimental

Selective Adsorption.—22.6 g. of durene (1,2,4,5-tetramethylbenzene) was removed from fraction I by fractional freezing. The remaining 64 g. was dissolved in 640 ml. of pentane and subjected to a bentonite–silica gel adsorption sequence[3] with results shown in Fig. 1.

The bentonite column was developed with anhydrous ether after 1800 ml. of pentane had failed to elute the oxy-

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[1] Presented in part before the Division of Gas and Fuel Chemistry, American Chemical Society, April 21, 1953, Pittsburgh, Penna.

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

[3] J. Entel, C. H. Ruof and H. C. Howard, *Anal. Chem.*, **25**, 616 (1953).

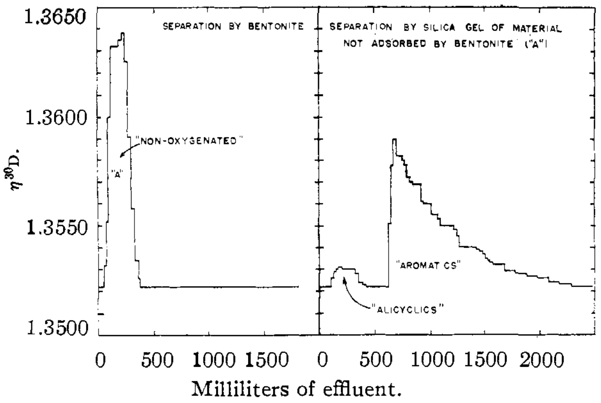

Fig. 1.—Separation of composite fraction I by adsorption.

genated material. Difficulty in eluting the adsorbed material of fractions III–V from the silica gel column led to the replacement of this adsorbent by activated alumina (Alcoa Grade, F-20, 80–200 mesh). Final traces of adsorbed material were removed from the bentonite columns by extraction of the adsorbent with acetone (Mallinckrodt Analytical Reagent Grade) in a Soxhlet extractor. A material balance obtained after removal of the solvents by distillation is shown in Table II.

Fractional Distillation.—All distillations were done in a vacuum model Piros–Glover spinning band column (H. S. Martin and Co., Evanston, Ill.). The complexity due to the many isomers possible and the scarcity of material available precluded investigation of the silica gel non-adsorbed material (alicyclic hydrocarbons) of fraction I. The plots of the distillation data and the individual components isolated and identified from the bentonite- and silica gel-adsorbed materials of fraction I are shown in Figs. 2 and 3. Preliminary distillation of fractions II and III was begun but has been halted indefinitely.

Results and Discussion

From the aromatic hydrocarbon material of fraction I, 30 g. of durene (1,2,4,5-), 10 g. of isodurene (1,2,3,5-) and 15 g. of prehnitene (1,2,3,4-tetramethylbenzene) were recovered and unequivocally identified by comparison of the following properties with those of the respective authentic compounds: boiling and/or melting point, refractive index, ultimate composition, chemical derivatives (picrates and aroylbenzoic acids), alkaline permanganate oxidation and identification of the subsequent benzenecarboxylic acid, and infrared and ultraviolet spectra. Six grams of 2-methylcyclohexanemethanol was recovered and identified from the oxygenated material of fraction I by comparison of the refractive index, ultimate composition, boiling point and infrared spectrum with those previously described for the authentic compound.[4] Approximately 1 g. of phthalan, contaminated with 2-methylcyclohexanemethanol was isolated and identified by stannic chloride adduct formation and comparison of the infrared and ultraviolet spectra with those previously published for phthalan.[4] A 4-g. mixture of equal amounts of a monomethylphthalan and 2-methylcyclohexanemethanol was isolated from fraction I. Alkaline permanganate oxidation of this material gave 1,2,4-benzenetricarboxylic acid. Of all the monomethylphthalans possible, only 5-methylphthalan can give this acid upon oxidation.

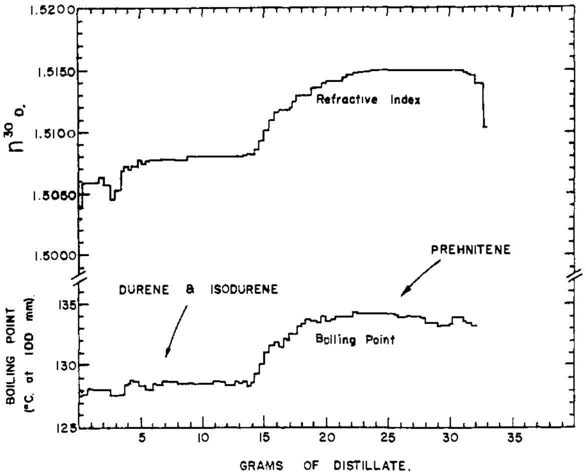

Fig. 2.—Fractionation of aromatic hydrocarbons from composite fraction I.

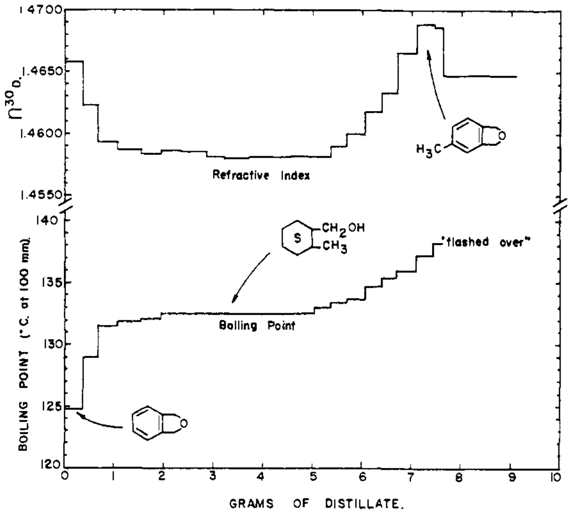

Fig. 3.—Fractionation of material adsorbed by bentonite from composite fraction I.

From the aromatic hydrocarbon material of fraction II, pentamethylbenzene (7 g.) was identified by the methods previously described for the tetramethylbenzenes of fraction I. From the oxygenated material of fraction II a fraction consisting of a monomethylphthalan containing a maximum of 10% of a dimethylcyclohexanemethanol as an impurity was isolated: b.p. 104° (20 mm.), n^{30}D 1.5266, d^{30}_4 1.03. This monomethylphthalan, 12 g., was shown to be 5-methylphthalan by alkaline permanganate oxidation to 1,2,4-benzenetricarboxylic acid. A total of 20 g. of two dimethylphthalans containing small amounts of impurities, and with the following physical properties was isolated: b.p. 122.5° (20 mm.), n^{30}D 1.5288, d^{30}_4 1.03; and b.p. 126.5° (20 mm.), n^{30}D 1.5347, d^{30}_4 1.04. Infrared spectra, Fig. 4, show these to be two distinctly different compounds, each of which gave 1,2,3,4-benzenetetracarboxylic acid upon alkaline permanganate oxidation. Of all the possible dimethylphthalans only 4,5- and 4,7-dimethylphthalan can give this acid upon oxidation. It is not possible from the available data to state with

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[4] J. Entel, C. H. Ruof and H. C. Howard, THIS JOURNAL, **74**, 441 (1952).

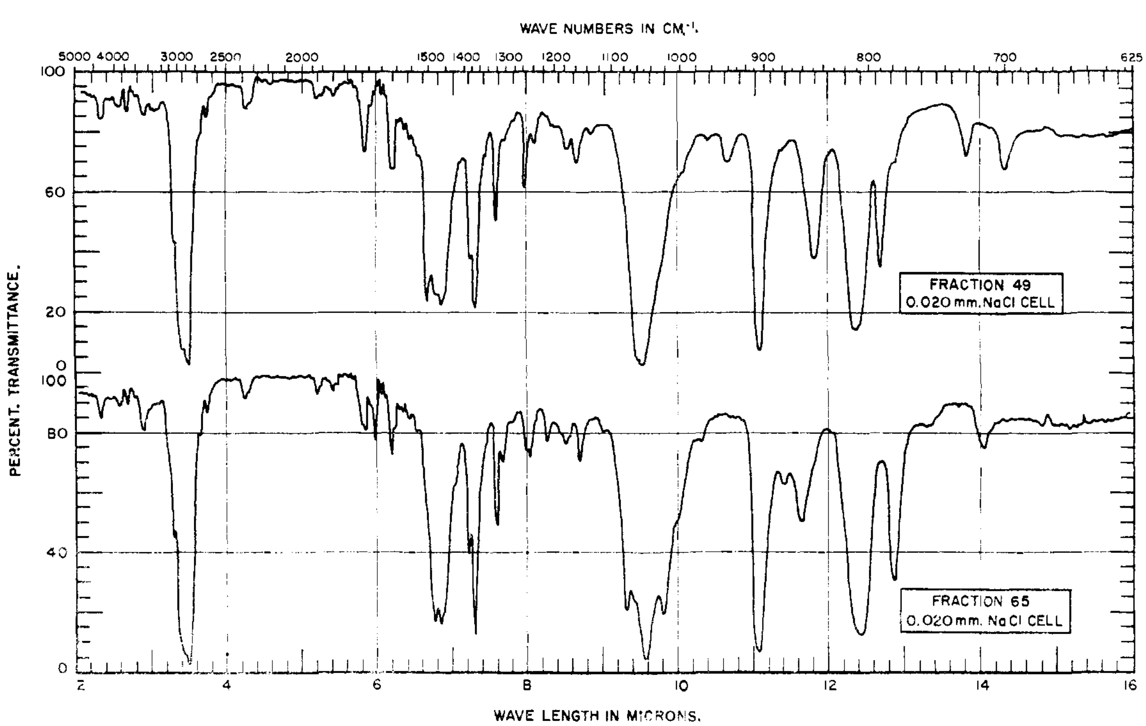

Fig. 4.—Infrared spectra of two dimethylphthalans.

certainty which of those two materials is the 4,5- or 4,7-dimethylphthalan.

Data indicated the presence in fractions II and III of significant quantities of materials with the properties of polymethyl derivatives of: biphenyl, lactone of 2-hydroxybicyclohexyl-2′-carboxylic acid, phthalan, cyclohexanemethanol and phthalyl alcohol.

Significance of the Compounds Isolated.—The isolation of alicyclic hydrocarbons from these hydrogenolysis products is of limited significance since some hydrogenation of ring systems undoubtedly occurs during the hydrogenolysis reaction. The presence of 1,2,4,5-, 1,2,3,5- and 1,2,3,4-benzenetetracarboxylic acid in the mixture of acids obtained by the oxidation of a bituminous coal is proved by the isolation of the analogous hydrocarbons from these hydrogenolysis products, *i.e.*, durene, isodurene and prehnitene. The significance of the isolation of phthalans is uncertain in establishing the nuclear structure of these acids. Work previously reported[5] has shown it possible to synthesize phthalans by hydrogenolysis of the type of esters known to be present in the mixture of esters of these acids from coal. On the other hand, evidence exists which indicates that the phthalan nucleus may have been present in the esters of these acids prior to hydrogenolysis and possible synthesis, *i.e.*, formation of adducts with stannic chloride and the presence of a considerable amount of oxygen in non-determinable groups.[5]

TABLE II

ADSORPTION MATERIAL BALANCES (FRACTIONS I–V INCLUSIVE)

	I Wt. % of charge	II Wt. % of charge	III Wt. % of charge	IV Wt. % of charge	V Wt. % of charge
Bentonite-adsorbed (oxygenated)	32.8	65.6	31.8	54.4	52.8
Silica gel-non-adsorbed (alicyclics)	2.4	2.1	..	..	..
Silica gel-adsorbed, pentane-eluted (aromatics)	64.8	24.6	..	..	..
Silica gel-adsorbed, ether-developed (oxygenated)	..	4.6	..	..	..
Alumina-non-adsorbed (alicyclics)	..	..	0.5	..	..
Alumina-adsorbed, ether-developed (aromatics)	..	..	63.6	45.6	44.8
Loss	0	3.1	4.1	0	2.4

The carbinols isolated most probably are secondary hydrogenolysis products of phthalans.[5] The lactones of polymethyl-2-hydroxybicyclohexyl-2′-carboxylic acids isolated from these hydrogenolysis products are hydrogenated analogs of the lactone of 2-hydroxybiphenyl-2′-carboxylic acid which was isolated from the decarboxylation products of the acids produced by the oxidation of coal.[6] This is confirmatory evidence for the presence of lactone structures in these acids.

The data obtained from this work are insufficient to allow an unequivocal statement of the presence of polymethylbiphenyls in these hydrogenolysis products. However, unpublished work by this author has shown the presence of biphenyl in the low temperature decarboxylation products of the acids produced by the oxidation of coal and may be regarded

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(5) C. H. Ruof, J. Entel and H. C. Howard, THIS JOURNAL, **74**, 3440 (1952).

(6) J. Entel, C. H. Ruof and H. C. Howard, *ibid.*, **75**, 3038 (1953).

as confirmatory evidence for the presence of biphenylpolycarboxylic acids in the acids obtained by the oxidation of coal. The nuclei isolated in this work, phenyl, biphenyl, phthalan and "lactone," not only are indicative of the nuclear structure of the acids produced by the oxidation of coal, but may also represent some of the fundamental units which comprise the coal structure, and which were resistant to further degradation by the methods employed in this work.

Acknowledgment.—The author wishes to express his appreciation to Dr. H. C. Howard of the Coal Research Laboratory for assistance in operating the Piros-Glover distillation column. Absorption spectra were run on the Baird infrared and the Cary ultraviolet recording spectrophotometers of the Mellon Institute, Pittsburgh, Pa. The ultimate analyses were performed by the Huffman Microanalytical Laboratories, Denver, Colorado.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Hofmann Degradation of *cis*- and *trans*-2-Phenylcyclohexylamines

BY RICHARD T. ARNOLD AND PAUL N. RICHARDSON[1]

RECEIVED MARCH 11, 1954

Pure *cis*- and *trans*-2-phenylcyclohexylamines have been prepared and characterized. Thermal decomposition of the quaternary hydroxides from each of these substances gave 1-phenylcyclohexene as the sole identifiable hydrocarbon. The data may be explained in terms of the current views relative to the mechanism of the Hofmann degradation.

Recent studies relative to the mechanism of the Hofmann degradation[2-4] have shown quite conclusively that this reaction involves a bimolecular, ionic, *trans* elimination. The elucidation of the structures assigned to the isomeric menthylamines[5] and 3α- and 3β-dimethylaminoallopregnanes[6] is based upon these considerations.

During the course of another investigation we were obliged to prepare pure *cis*- and *trans*-2-phenylcyclohexylamines (III and IV, respectively). This was accomplished by means of a Curtius degradation on carefully purified *cis*- and *trans*-2-phenylcyclohexanecarboxylic acids (I and II, respectively) since it is well recognized that no change in configuration takes place during this transformation.[7,8] Compounds I and II have been synthesized by Gutsche[9] and Alder and co-workers.[10]

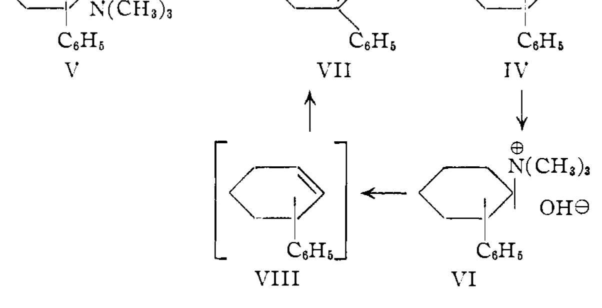
Although the latter investigators encountered difficulty in the *cis* → *trans* isomerization of methyl 2-phenylcyclohexylcarboxylate and reported no yield for this step, we have found that the *trans* ester may be obtained readily in 96% yield. This modified route would appear to be more practical than that employed by Gutsche.[9]

We have now established that 2-phenylcyclohexylamine prepared by the reduction of 2-phenylcyclohexanone oxime with sodium and alcohol,[11] or *via* the Diels–Alder reaction of ω-nitrostyrene and butadiene[12] has the *trans* configuration.

No difficulty was experienced in transforming the geometric isomeric primary amines into the corresponding tertiary compounds by methylation with formaldehyde and formic acid[13] and these were converted in the usual fashion to the isomeric quaternary salts and hydroxides.

A reaction scheme is

$C_6H_5—CH=CH—CH=CH_2 + CH_2=CH—CO_2H$



Assuming *trans* elimination, and recognizing that the most acidic hydrogen atom in the quaternary bases is attached to C_2 which holds the phenyl group, 1-phenylcyclohexene (VII) should be derived from V and 3-phenylcyclohexene (VIII) from VI.

However, examination of the ultraviolet spectra and refractive indices of the hydrocarbon samples produced from each isomeric quaternary base proved them to be essentially indistinguishable

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[1] Taken from the Ph.D. thesis of Paul N. Richardson, April, 1952.

[2] M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw and L. I. Wolff, *J. Chem. Soc.*, 2093 (1948).

[3] D. H. R. Barton, *Experientia*, **6**, 316 (1950).

[4] W. E. Doering and H. Meislich, THIS JOURNAL, **74**, 2099 (1950).

[5] N. L. McNiven and J. Read, *J. Chem. Soc.*, 153 (1952).

[6] R. D. Haworth, J. McKenna and R. G. Powell, *ibid.*, 1110 (1953).

[7] L. W. Jones and E. S. Wallis, THIS JOURNAL, **48**, 169 (1926).

[8] G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 460.

[9] C. D. Gutsche, THIS JOURNAL, **70**, 4150 (1948).

[10] K. Alder, H. Vagt and W. Vogt, *Ann.*, **565**, 135 (1949).

[11] J. V. Braun, H. Gruber and G. Kirschbaum, *Ber.*, **55**, 3664 (1922).

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[13] W. S. Emerson and F. W. Neumann, *ibid.*, **63**, 972 (1941).