sium carbonate, with water, and then the benzene was removed by distillation. Fractionation gave 5.2 g., 0.0253 mole, of XIII, 45% yield.

Anal. Calcd. for $C_{12}H_{18}SiO$: Si, 13.6; mol. wt., 206. Found: Si, 13.6; mol. wt., 202.

4-Trimethylsilyl-2-methyl-2-butanol.—To a rapidly stirred solution of methylmagnesium bromide, 0.51 equivalent, in 500 cc. of ether, there was added 30 g., 0.172 mole, of ethyl β-trimethylsilylpropionate over a period of fifteen minutes while cooling the reaction flask in an ice-bath. The cold reaction mixture was hydrolyzed with ice and water and the organic layer was separated. The aqueous layer was made slightly acid with hydrochloric acid and was extracted with two 100-cc. portions of ether. The combined organic layers were washed with 10% carbonate solution and dried over anhydrous sodium sulfate. Fractionation gave 17.3 g., 0.108 mole, of compound XIV, a yield of 63%.

Anal. Calcd. for $C_8H_{20}SiO$: Si, 17.5; mol. wt., 162. Found: Si, 17.7; mol. wt. in benzene, 165.

Compound XIV was also prepared from 4-trimethylsilyl-2-butanone. To a solution of methylmagnesium bromide, 0.41 mole, in 400 cc. of ether, there was added with stirring 33 g., 0.229 mole, of 4-trimethylsilyl-2-butanone during one hour. After refluxing had ceased, the reaction mixture was heated for an additional hour, hydrolyzed with ice and water, and the organic layer was separated. The aqueous layer was made slightly acid with hydrochloric acid and was then extracted with two 100-cc. portions of ether. The combined organic layers were washed with 5% carbonate solution and dried over sodium sulfate. After removal of the ether, fractionation gave 30.1 g., 0.188 mole, of 4-trimethylsilyl-2-methyl-2-butanol which had physical properties which checked those obtained on the material prepared from compound IV. The yield was 82%.

4-Phenyldimethylsilyl-2-methyl-2-butanol.—To a solution of methylmagnesium bromide, 0.43 mole, in 500 cc. of dry ether, there was rapidly added 25.5 g., 0.108 mole, of ethyl β-phenyldimethylsilylpropionate while cooling the reaction flask in an ice-bath. After stirring and refluxing for one hour, the product was poured into a mixture of ice and water, and the organic layer was separated. The aqueous layer was treated with hydrochloric acid until slightly acidic, and was then extracted with two 100-cc. portions of ether. The combined organic layers were washed with 5% sodium bicarbonate solution, with water, and were then dried over sodium sulfate. Fractionation gave 19.2 g., 0.0865 mole, of compound XV, 80% yield.

Anal. Calcd. for $C_{13}H_{22}SiO$: Si, 12.7; mol. wt., 222. Found: Si, 12.9; mol. wt. in benzene, 221.

4-Trimethylsilyl-2-methyl-2-chlorobutane.—Compound XIV, 6.7 g., 0.042 mole, was shaken with 100 cc. of concd. hydrochloric acid in a separatory funnel for fifteen minutes. The organic layer was then separated, washed with 5% bicarbonate solution followed by water, and was then dried over calcium chloride. Fractionation gave 3.6 g., 0.020 mole, of XVIII, 48% yield.

Anal. Calcd. for $C_8H_{19}SiCl$: Si, 15.7; Cl, 19.9. Found: Si, 15.8; Cl, 19.9.

Reaction of 4-Trimethylsilyl-2-butanone with Sodium Hypobromite.—In a 2-liter, three-necked flask equipped with a stirrer, dropping funnel, and a condenser, and surrounded by an ice–salt-bath, there was placed a solution of 57.2 g., 1.43 moles, of sodium hydroxide in 500 cc. of water. Bromine, 82.8 g., 0.52 mole, was then added at such a rate that the temperature remained below 0°. To this solution, over a period of one hour, while maintaining the temperature at 5°, there was added 25.0 g., 0.173 mole, of 4-trimethylsilyl-2-butanone. The reaction mixture was stirred at 0° for one hour and then for three hours at 25°. The lower organic layer was separated and the aqueous layer extracted with three 100-cc. portions of ether. Then the aqueous layer was then acidified with 75 cc. of concd. hydrochloric acid, the organic layer separated, and the aqueous layer extracted with three 100-cc. portions of ether. The combined organic layers from the acidified aqueous layer were dried over sodium sulfate and fractionated. There was obtained 10.3 g., 0.071 mole, of compound VI, b. p. 122° at 30 mm., n^{20}_{D} 1.4280, 41% yield.

Summary

1. The acetoacetic ester synthesis has been successfully applied to iodomethylsilanes.

2. Seventeen new silicon-containing esters, acids, ketones, alcohols, and halides, have been synthesized. In these compounds the functional group is linked to a carbon atom in the gamma relation to silicon: Si–C–C–C–X and Si–C–C–C=O, where X is halogen or hydroxyl.

STATE COLLEGE, PENNSYLVANIA

RECEIVED NOVEMBER 2, 1949

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS]

Partition Studies on Phenols. IV. Isolation of Indanols from Coal Hydrogenation Oils[1]

BY C. GOLUMBIC, E. O. WOOLFOLK, R. A. FRIEDEL AND M. ORCHIN

The hydrogenation of coal produces, among other products, a complex mixture of phenolic compounds. Because of their potential commercial value and the importance of oxygenated compounds in the study of the mechanism of the liquefaction of coal,[2] considerable effort has been devoted to the characterization of the phenolic fraction of coal hydrogenation oil. As a result, sixteen individual phenols have been isolated or identified, and the quantity of each in a particular mixture has been estimated or accurately determined.[3]

Of the many tools and techniques successfully employed in this work, the countercurrent distribution technique of Craig[4,5] was particularly useful, especially in the high-boiling range. Our pre-

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(1) Article not copyrighted.

(2) H. H. Storch, C. H. Fisher, C. O. Hawk and A. Eisner, Bur. Mines Tech. Paper 654, 50 pp. (1943).

(3) E. O. Woolfolk, M. F. Dull and M. Orchin, *Ind. Eng. Chem.*, in press; R. A. Friedel, L. Pierce and J. J. McGovern, *Anal. Chem.*, in press.

(4) L. C. Craig, *J. Biol. Chem.*, **155**, 519 (1944).

(5) L. C. Craig, C. Golumbic, H. Mighton and E. Titus, *ibid.*, **161**, 321 (1945).

vious work in this field[6,7,8] provided necessary background information and facilitated interpretation of the data obtained from the distribution of selected high-boiling phenolic fractions from coal hydrogenation oil. This report is concerned chiefly with the isolation and identification of indanols from these fractions.

Countercurrent Distributions.—The source of the material investigated and its separation into close-boiling numbered fractions have been described previously.[8] After orienting tests at different *p*H values to select the appropriate buffer,[7] each fraction (nos. 85, 99, 105, 117, 125, or 135) was distributed in the 54-tube Craig countercurrent instrument.[9] The immiscible phases were cyclohexane and 0.5 *M* alkaline phosphate buffer. The experimental distribution curves, when compared to theoretical curves,[10] showed that each fraction was a mixture of several compounds. Ultraviolet analysis of the contents of each tube of the distribution instrument was carried out at the wave lengths at which the original fraction exhibited selective absorption. By this means the presence of unusual components can often be detected. Thus, in fraction 85, whose distribution curve is given in Fig. 1, the compound responsible for band A_1 shows much stronger ultraviolet absorption at 276.5 mμ than at 289 or 285 mμ. This effect is not pronounced or is absent from the remainder of the components.

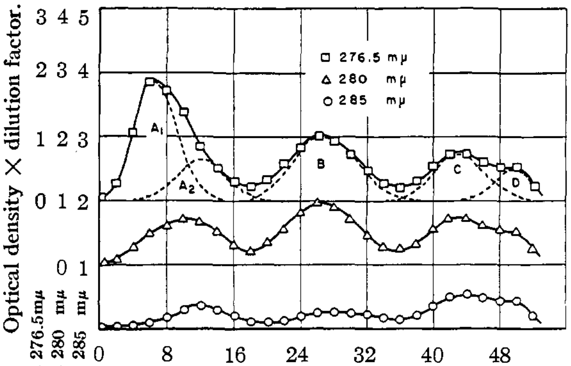

Fig. 1.—Distribution of fraction 85: ---, theoretical curves.

By the methods developed by Craig and coworkers,[19,11] the experimental distribution curves were used to calculate the percentage composition of each fraction. This estimation of composition is an approximate one but can be made exact when the ultraviolet extinction coefficients of the pure components have been determined. The partition coefficients of each component at the *p*H of distribution and at an acidic *p*H may also be determined.[12] These values are recorded in Table I, together with *pK* values of the major components of each fraction. Golumbic, *et al.*,[6] recently showed that the ionization constant of a phenol can be determined approximately when its distribution constants between a non-polar solvent, on the one hand, and an alkaline and neutral or acidic buffer phase, on the other, are known. It is thus possible without further isolation to describe the phenols present in each fraction in terms of at least one and in some instances, three, physical constants.

To determine definitive structural characteristics of the components of each fraction, ultraviolet and infrared absorption spectra were obtained for those distribution fractions which had a minimum of contamination resulting from overlapping bands. Thus, the material in tube 4 (band A_1) of fraction 85 gave an ultraviolet absorption curve which is identical with that of 4-indanol.[13]

On the basis of the value obtained for the partition coefficient of this component at the *p*H of distribution and at an acidic *p*H, as mentioned above, a scheme was devised for extracting it on a large scale from fraction 85. Five grams of the fraction was distributed between cyclohexane and an alkaline buffer adjusted so that the desired component would have a partition coefficient of 0.1–0.2. The buffer phase was then repeatedly washed with fresh solvent to remove the bulk of the other components in the fraction. From the alkaline phase, 4-indanol was isolated. With the identity of this compound established, its exact percentage in the fraction was calculated according to Williamson and Craig.[10] Isolation of the other components in fraction 85 was not attempted but considerable information on their structural characteristics was obtained and is recorded in Table I. The material in band A_2 gave an infrared spectrum identical with that of 3-methyl-5-ethyl-phenol. Infrared analysis indicated the presence of a 2,5-dialkylphenol structure in band D and the probable presence of a meta alkyl-substituted phenol in bands B and C.

By the same procedure, 5-indanol was detected in and isolated from fraction 99. A summary of the results obtained in the investigation of all six fractions is presented in Table I.

Experimental[14]

Isolation and Distillation of Tar-Acid Fraction.—Characteristics of the coal hydrogenation oil used as a source of tar acids and the alkaline extraction of this oil are described elsewhere.[3] After a preliminary vacuum distillation (2.5 mm.) of the alkali-soluble portion, it was subjected to precise fractional distillation under vacuum through a 91.4 cm., 25 mm. i. d. Podbielniak column

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[6] C. Golumbic, M. Orchin and S. Weller, THIS JOURNAL, **71**, 2624 (1949).

[7] C. Golumbic, *ibid.*, **71**, 2627 (1949).

[8] M. Orchin and C. Golumbic, *ibid.*, in press.

[9] L. C. Craig and O. Post, *Anal. Chem.*, **21**, 500 (1949).

[10] B. Williamson and L. C. Craig, *J. Biol. Chem.*, **168**, 687 (1947).

[11] L. C. Craig, H. Mighton, E. Titus and C. Golumbic, *Anal. Chem.*, **20**, 134 (1948).

[12] Y. Sato, G. T. Barry and L. C. Craig, *J. Biol. Chem.*, **170**, 501 (1947).

[13] R. A. Friedel, unpublished results.

[14] All melting points are corrected.

TABLE I

COUNTERCURRENT DISTRIBUTION ANALYSIS OF TAR-ACID FRACTIONS

Fraction	Distribution band	Approximate, %	Partition coefficients[d] k'	Partition coefficients[d] k	pK	Qualitative ultraviolet analysis	Qualitative infrared analysis	Probable composition
85[a]	A_1	44[e]	0.13	5.3	10.2	4-Indanol spectrum	4-Indanol	4-Indanol[f]
	A_2	11[e]	0.29	..	..	4-Indanol + a meta and/or ortho alkyl-substituted phenol	4-Indanol + 3-methyl-5-ethyl phenol	Mainly 3-methyl-5-ethyl-phenol
	B	30	1.0	..	..	Meta and/or ortho alkyl-substituted phenol	Meta-substituted phenol	Alkyl-substituted phenol
	C	15	3.9	..	..	Meta and/or ortho alkyl-substituted phenol	Meta-substituted phenol	Alkyl-substituted phenol
	D	5	10.0	..	..	Meta and/or ortho alkylphenols and some para-alkyl phenol	1,2,5 structure	Alkyl-substituted phenol
99[b]	A	44[e]	0.44	5.4	10.2	5-Indanol spectrum	5-Indanol	5-Indanol[f]
	B	30	3.1	21	..	*o*- or *m*-alkyl-substituted phenol	Meta alkyl and/or 3,5-dialkyl phenol	Alkyl-substituted phenol
	C	10	2.6	..	..	No definite structure discernible	Probably hydrocarbon	Unknown
105[a]	A_1	5	0.10	..	..	5-Indanol spectrum	....	5-Indanol
	A_2	50	0.26	13.2	10.2	5-Indanol spectrum	5-Indanol + unknown constituent	Probably 5-indanol homolog
	B	20	1.0	..	..	Phenols with para configuration	Meta, perhaps also 1,2,5 and 1,3,5 structures	*p*-Alkyl-substituted phenol
	C	20	2.1	..	.	Ortho and/or meta alkyl-substituted phenols	Apparently same as band B	Alkyl-substituted phenols
117[a]	A	30	0.23	13.5	10.1	5-Indanol spectrum	....	Probably 5-indanol homolog
	B	15[e]	1.12	..	..	*o*-Phenylphenol + alkyl-substituted phenol	*o*-Phenylphenol spectrum predominates	*o*-Phenylphenol[f] + alkyl substituted phenol
	C	40	9.6	..	..	Mixture, ortho and/or meta types	Probably ortho types	Alkyl-substituted phenols
125[c]	A	17[e]	1.41	..	..	*o*-Phenylphenol spectrum	....	*o*-Phenylphenol homolog
	B	50	9.8	..	..	Meta and/or ortho alkyl phenols	....	Alkyl-substituted phenols
135[c]	A	8[e]	0.03	..	..	*p*-Phenylphenol spectrum	....	*p*-Phenylphenol[f]
	B	15	1.0	..	..	5-Indanol spectrum	....	5-Indanol homolog
	C	70	...	..	..	Meta and/or ortho alkyl phenols + phenanthrene	....	Mainly alkyl-substituted phenols

[a] This countercurrent distribution was run at *p*H 11.90. [b] This countercurrent distribution was run at *p*H 11.26. [c] This countercurrent distribution was run at *p*H 12.54. [d] Partition coefficients at *p*H of distribution and at acidic *p*H, respectively. [e] Accurately determined value. [f] This compound was isolated.

operating at an efficiency of about 25 theoretical plates. A total of 136 fractions was collected, and the refractive index and density of each were determined. A detailed description of this distillation is given by Woolfolk, *et al.*[3] The physical properties of the fractions investigated in the present work are:

Fraction	Boiling range at 40 mm., °C.	$n^{20}D$	d^{20}_4
85	148–149	1.5485	1.048
99	155	1.5462	1.037
105	161–162	1.5470	1.028
117[a]	165–168	1.5585	1.047
125[a]	178–179	1.5532	1.027
135[a]	199–201	1.5605	...

[a] Distilled at 30 mm. pressure.

These fractions represent the six pronounced peaks in the refractive index-boiling point curve.[3]

Countercurrent Distribution and Spectrometry.—A 60-mg. sample was employed in each distribution, except for fraction 85, in which a 50-mg. sample was used. The detailed procedure for operating the Craig countercurrent distribution instrument has been reported previously.[4] At the end of each run, the material of each tube was acidified with hydrochloric acid and then shaken to permit the phenol in the buffer phase to pass into the cyclohexane layer. Ultraviolet measurements of this layer were made with the Beckman model DU quartz spectrophotometer. In those instances in which the entire ultraviolet spectra curves were desired, the Cary recording spectrophotometer was employed.

Infrared measurements were made on a Perkin–Elmer infrared spectrometer. Since the minimum sample usually required for infrared spectroscopy is about 100 mg., a micro-technique was devised for infrared examination of distribution fractions which may contain only 1–5 mg. of material. By simple evaporation of solvent from a very small piece of rock salt, a film of phenols was obtained which is adequate for determining the spectrum.

Isolation of 4-Indanol from Fraction 85.—Five grams of this fraction was dissolved in one liter of 0.7 *M* phosphate buffer of *p*H 12.1. This solution was extracted continuously with cyclohexane for six hours in a liquid–liquid extractor. The aqueous phase was removed, thoroughly shaken with three one-liter portions of fresh cyclohexane and then acidified with concd. hydrochloric acid. The liberated phenol was extracted with one liter of cyclohexane. The residue obtained upon evaporation of the cyclohexane consisted of 1.9 g. of crystalline material, which after recrystallization from petroleum ether (b. p. 30–60°), melted at 47–48°.

Anal.[15] Calcd. for $C_9H_{10}O$: C, 79.85; H, 7.51. Found: C, 79.68, 79.85; H, 7.58, 7.64.

Neutral equivalent of the aryloxyacetic acid: Calcd. for $C_{11}H_{12}O_3$: 192. Found: 192.

Since the melting point of this phenol (47–48°) and that of its aryloxyacetic acid (182°) are identical with these reported for 4-indanol and 4-indanyloxyacetic acid,[16] respectively, its identity is established.

Isolation of 5-Indanol from Fraction 99.—Ten grams of this was dissolved in 1 liter of 0.75 *M* phosphate buffer of *p*H 11.9. This solution was well shaken with 5 one-liter portions of cyclohexane, and then acidified with concd. hydrochloric acid. The liberated phenol was extracted with 1 liter of cyclohexane. Removal of the solvent left 1.9 g. of crystalline material, which, after two crystallizations from petroleum ether (b. p. 60–68°), melted at 52.4–

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(15) Analysis by Mr. G. L. Stragand, University of Pittsburgh, Pittsburgh, Pa.

(16) O. Kruber and W. Schneider, *Ber.*, **72**, 653 (1939).

53.8°. The aryloxyacetic acid of this phenol melted at 157.4–158.8°. These values are identical with those previously reported[17] for 5-indanol and 5-indanyloxyacetic acid, respectively.

Neutral equivalent, calcd. 192. Found: 192.

Selective Extraction of Fraction 105.—An extraction experiment similar to that for fraction 99, yielded an oil which could not be crystallized. The ultraviolet spectrum of this material was almost identical with that of 5-indanol but its aryloxyacetic acid had a neutralization equivalent of 207, which agrees with that of a methyl-5-indanol. Repeated crystallization of this derivative did not yield a constant-melting compound.

Selective Extraction of Fraction 117.—An extraction experiment analogous to that carried out for fraction 99, yielded crystalline material melting after repeated crystallization from petroleum ether at 49.4–55°. The substance had an ultraviolet spectrum typical of a 5-indanol but was obviously impure. Insufficient material was at hand for further purification.

Isolation of *p*-Phenylphenol from Fraction 135.—A portion of this fraction was dissolved in petroleum ether (b. p. 30–60°) and cooled at 0°. The crystalline material which separated was recrystallized from petroleum ether and finally from benzene–cyclohexane. The melting point of this substance, 163–165° was not depressed upon admixture with the authentic compound.

Acknowledgments.—The authors are indebted to Mr. George Goldbach for technical assistance and to Miss Marion Springer for infrared measurements.

Summary

A procedure, based on the countercurrent method, is presented for separation and characterization of complex phenolic mixtures. By this means, 4- and 5-indanol were isolated from a coal hydrogenation oil.

BRUCETON, PA. RECEIVED SEPTEMBER 29, 1949

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(17) O. Kruber and A. Marx, *Ber.*, **73B**, 1175 (1940).

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Low Temperature Autoxidation of Hydrocarbons: the Phenomenon of Maximum Rates[1,2]

BY ARTHUR V. TOBOLSKY,[3] DONALD J. METZ AND ROBERT B. MESROBIAN

Introduction

Recent chemical researches in the field of hydrocarbon oxidations have demonstrated that hydroperoxides appear as one of the first products of reaction.[4–6] Kinetic studies have shown that subsequent oxidation of the parent hydrocarbon is autocatalyzed by the decomposition of hydroperoxides which produces radical chain carriers for the chain reaction.[7–11] The decomposition of hydroperoxides also leads to the formation of secondary oxidation products such as ketones, aldehydes, acids, alcohols, water, carbon dioxide, etc.[10–12]

One of the simplest and most completely worked out autoxidation mechanisms is the one proposed by Bolland and Gee[9] for the oxidation of ethyl linoleate. At sufficiently high pressures of oxygen (greater than 40 mm.) and in the range where a sufficiently high concentration of hydroperoxide has been built up so that hydroperoxide decomposition is the important chain initiation step, they proposed the mechanism

$$2\text{ROOH} \xrightarrow{k_1} \text{R}\cdot + \text{RO}_2\cdot + \text{H}_2\text{O} \qquad (1\text{A})^{12\text{a}}$$

$$\text{R}\cdot + \text{O}_2 \xrightarrow{k_2} \text{RO}_2\cdot \qquad (\text{A}) \quad (2\text{A})$$

$$\text{RO}_2\cdot + \text{RH} \xrightarrow{k_3} \text{ROOH} + \text{R}\cdot \qquad (3\text{A})$$

$$\text{RO}_2\cdot + \text{RO}_2\cdot \xrightarrow{k_6} \text{ROOR} + \text{O}_2 \qquad (4\text{A})$$

(where RH represents ethyl linoleate—C=C—CH—C=C— and the H in question is the one that detaches most easily, due to the activating influence of the double bonds).

The rate of oxidation of ethyl linoleate was taken by Bolland and Gee to be identical with the rate of step 3A, since under their mild conditions of oxidation, every molecule of oxygen absorbed by the substrate could be identified as hydroperoxide

$$d[\text{ROOH}]/dt = k_3[\text{RO}_2\cdot][\text{RH}] \qquad (1)$$

Although we shall find it necessary to modify equation (1) to account for results obtained under relatively severe oxidation conditions (high temperatures, presence of activators, strong light

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(1) Presented before the Division of Petroleum Chemistry at the 115th, April, 1949, meeting of the American Chemical Society in San Francisco.

(2) The work described in this paper first began during the tenure of sponsorship by the Office of the Quartermaster General under Contract QM-1180 with the Polytechnic Institute of Brooklyn and was completed during sponsorship by the Office of Naval Research under Contract N6onr-26309.

(3) Assistant Professor of Chemistry, Princeton University and Adjunct Professor of Chemistry, Polytechnic Institute of Brooklyn.

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(10) F. F. Rust and W. E. Vaughan, U. S. Patents Nos. 2,396,206 and 2,396,217.

(11) P. George and A. D. Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946).

(12) H. Zuidema, *Chem. Rev.*, **38**, 197 (1946).

(12a) The R· shown on the right side of Eq. 1A is assumed to result from either a chain transfer step of RO· with RH or by self dismutation of the RO· to R·.