semicarbazone of tetralone precipitated as white crystals (87%). The homogeneous alkaline residue, on acidification, precipitated benzoic acid, m. p. 119–120°, mixed m. p. 119–120°. In the case of benzoylhydrindone the diketone was not so soluble, however, and after 300 ml. of distillate had been collected, the undissolved diketone was filtered and weighed. The semicarbazone (77%) melted at 230–231° (reported m. p. 233°).[33] Acidification of the alkaline residue gave a 10% yield of a compound melting at 88–89° after recrystallization from alcohol, and which is presumed to be 1-benzoyl-2-(2-carboxyphenyl)-ethane.

Summary

1. The relative yields of the two possible acids and the relative yields of the series of para-substituted benzoic acids from the alkaline cleavage of para-substituted dibenzoylmethanes and para-substituted benzoylacetones have been related to the relative rates of alkaline hydrolysis of the corresponding ethyl esters.

2. Certain ε-acyl and ε-aroyl caproic acids have been prepared in satisfactory yield by the alkaline cleavage, involving ring opening, of α-acyl and α-aroyl cyclohexanones. Similarly, δ-acetylvaleric acid has been obtained from α-acetylcyclopentanone.

DURHAM, NORTH CAROLINA RECEIVED AUGUST 2, 1948

(33) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 361.

[CONTRIBUTION FROM KOPPERS COMPANY, INC., MULTIPLE FELLOWSHIP ON TAR SYNTHETICS, MELLON INSTITUTE]

Catalytic Alkylation of Indan and Tetralin by Olefins, Alcohols and Diethyl Ether

BY WALTER M. KUTZ, J. E. NICKELS, J. J. McGOVERN AND B. B. CORSON

This paper describes the alkylation of indan and tetralin by olefins, alcohols and diethyl ether in the presence of typical alkylation catalysts. The alkylation of tetralin by cyclopentene and cyclohexene[1] in the presence of aluminum chloride, and by ethylene[2] with phosphoric acid as catalyst has been reported; the alkylation of both indan[3] and tetralin[4] is claimed in patents.

The catalysts employed in the present work were alumina–silica, "solid phosphoric acid," aluminum chloride, sulfuric acid and hydrogen fluoride—continuous operation with the first two catalysts and batch operation with the last three.

Indan and tetralin underwent extensive condensation reactions under the influence of alumina–silica and aluminum chloride.[5] The high boiling products contained condensed ring systems as evidenced by their high refractive indices. This new condensation reaction of indan is being studied.

Monoalkyl indans and monoalkyltetralins can exist in two isomeric forms depending upon the location of the alkyl group with respect to the cycloparaffinic ring. All the monoalkylated products obtained in this investigation were isomer mixtures, and the isomer distribution in the mixtures depended upon the catalyst and/or conditions. For example, isopropylation of tetralin at 5° with concentrated sulfuric acid yielded approximately equal amounts of the 5- and 6-isomers, whereas isopropylation at 300° over alumina–silica produced mainly the 6-isomer.

The conventional method of establishing the structure of an organic compound involves the assumption that the sample contains only one species, and the acceptance of a minor yield of a known derivative as indicative of the structure of the original compound. Boiling point is often accepted as criterion of homogeneity without proof that the possible mixture is separable by the distillation employed. In the case of an acknowledged isomer mixture, the unjustified assumption is often tacitly made that the original isomer composition is preserved in the derivative, regardless of yield. We have attempted to avoid these suppositions.

The isomeric compositions of the monoalkylindan mixtures obtained in the present study were established by the ultraviolet absorption spectra of the mixed benzenetricarboxylic acids produced by permanganate oxidation. Inasmuch as the average yield of acid was 80%, the isomer composition of the mixed acids was fairly representative of the isomer composition of the antecedent hydrocarbon mixture. The composition of the monoalkyltetralins could not be established in similar manner because of poor oxidation yields. For example, a fifty–fifty mixture of 5- and 6-isopropyltetralins gave a 25% yield of mixed acids containing 80% of hemimellitic acid and 20% of trimellitic acid. The isomer compositions of the monoalkyltetralins were established by the ultraviolet and infrared absorption spectra of the monoalkylnaphthalenes obtained by sulfur dehydrogenation of the alkyltetralins (also by the melting point of the picrate in the case of the *t*-butylnaphthalenes). Spectroscopic technique is ideally suitable for the analysis of isomer mixtures, a task which is usually difficult and often impossible by conventional methods.

Incidentally, the statement of Tsukervanik and Terent'eva[6] that 1-monoalkylnaphthalenes are

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(1) Pokrovskaya and Suschik, *J. Gen. Chem.* (*U. S. S. R.*), **9**, 2291 (1939); Pokrovskaya and Stephantseva, *ibid.*, **9**, 1953 (1939).

(2) Ipatieff, Pines and Komarewsky, *Ind. Eng. Chem.*, **28**, 222 (1936).

(3) German Patent 80,158 (1895).

(4) U. S. Patents 1,667,214 (1928); reissue 17,548 (1928); 1,741,472 (1929); 1,766,344 (1930).

(5) Schroeter (*Ber.*, **57**, 1990 (1924)) reported that aluminum chloride converted tetralin into a variety of products including anthracene, hydrogenated phenanthrene and ditetralyl.

(6) Tsukervanik and Terent'eva, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 637 (1937).

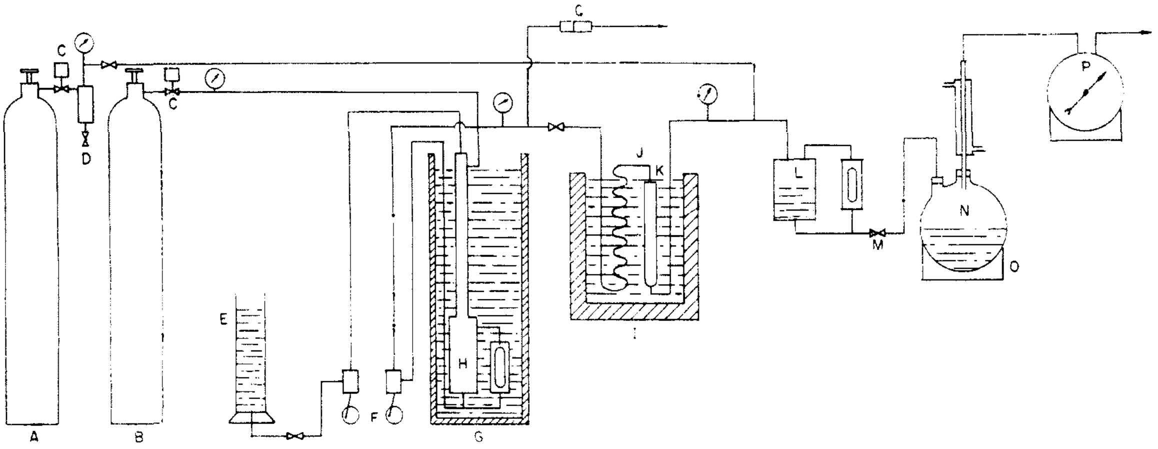

Fig. 1.—Pressure alkylation plant: A, nitrogen cylinder; B, olefin cylinder; C, Victor pressure regulator; D, Gas-O-Dome regulator; E, charge stock; F, Hills–McCanna double pump; G, thermostated bath; H, saturator; I, thermostated lead alloy bath; J, preheater line; K, catalyst tube; L, high pressure receiver; M, high pressure needle valve; N, stabilizer; O, Glas-Col heater; P, exit gas meter; Q, safety disc assembly.

readily isomerized by heating, *e. g.*, that 1-isopropylnaphthalene is quantitatively isomerized to the 2-isomer by simple distillation, is incorrect.

Experimental

Materials.—Indan was prepared by the hydrogenation of indene (m. p. −2 to −3°) at 100° and 70 atm. in the presence of 10% of nickel catalyst.[7] The filtered product was washed at 5° with 10% of its volume of concentrated sulfuric acid to remove unchanged indene (*ca.* 3%). If the hydrogenation was carried beyond this point, the yield of indan was low because of the formation of octahydroindene; if the crude product contained more than 3% of unreacted indene, troublesome emulsions were encountered during the washing with sulfuric acid. The washed, dried product was distilled at a reflux ratio of 5:1 through a 15-plate column. The major impurity (7% yield) distilled at 158–177° and contained octahydroindene. The constants of the indan fraction (87% yield) were: b. p. 177–178° (760 mm.), $n^{20}\mathrm{D}$ 1.5378, d^{20}_4 0.965.

Tetralin (b. p. 206.5–207.5° (760 mm.), $n^{20}\mathrm{D}$ 1.5410, d^{20}_4 0.971) was prepared by fractionating commercial tetralin through the above column. Ethylene and propylene were 99.5 and 75% pure, respectively, the contaminant of the latter being propane.

The alumina–silica catalysts used in the alkylation of indan were prepared as previously described.[8] The alumina–silica catalyst used in the alkylation of tetralin was a commercial product of the Phillips Petroleum Company containing approximately 1% of alumina and 99% of silica.

Apparatus and Procedure.—When alkylating with gaseous olefins at superatmospheric pressure over a fixed bed of solid catalyst (Fig. 1), the aromatic hydrocarbon was pumped by a double Hills–McCanna pump (type SA) into the top of a thermostated, packed saturator column which was connected to a cylinder of olefin through a reducing valve. The temperature-pressure conditions within the column were those experimentally shown to give the desired olefin concentration. The combined feed (olefin dissolved in aromatic) was pumped from the bottom of the column to the catalyst tube which was pressured by nitrogen. This equipment and operation simplified the otherwise difficult task of charging a gas-liquid feed of constant composition on a laboratory scale. When the alkylating agent was a liquid, it was mixed with the aromatic hydrocarbon and the mixture was pumped directly from a graduated charger to the catalyst tube. The combined feed was pumped either into the top or into the bottom of the reactor, both modes of entrance being equivalent with respect to catalyst performance and life.

The reactor (30.5 cm. long) was fabricated from 20.6 mm. i.d. stainless steel tubing. Catalyst was charged and discharged through the top of the reactor (Ipatieff knife-edge closure). The preheater line (60.7 cm. long, 4.7 mm. i.d. tubing) and reactor were immersed in an electrically heated, thermostated (±1°) lead alloy bath. The temperature contour of the longitudinal center of the catalyst bed (20.3 cm. long) was surveyed by means of a sliding thermocouple and found to be the same as that of the lead-bath. This method of heating a catalyst reactor is preferable to that previously described.[9]

Superatmospheric alkylation with hydrogen fluoride was made in a stainless steel Ipatieff autoclave, and atmospheric alkylation with sulfuric acid and aluminum chloride as catalysts was performed in a 3-neck glass flask equipped with reflux condenser, thermometer, mercury-sealed stirrer, and inlet and outlet tubes for the gaseous olefin.

The crude alkylates were distilled through a 15-plate Fenske column; when the amount was small, a 10-plate micro column was employed. The monoalkyl fractions of the alkylates, and the authentic alkylnaphthalenes employed in the proof of structure, were redistilled through a Heligrid packed Podbielniak column with 50:1 reflux ratio between plateaus and 10:1 on plateaus.

Alkylation Results

Alkylation of Indan Over Various Aluminum Oxide–Silicon Dioxide Catalysts.—The best aluminum oxide–silicon dioxide catalyst for the alkylation of indan at 400 p.s.i.g. by means of ethylene, propylene and isopropyl alcohol was 25% Al_2O_3–75% SiO_2; both catalyst components were inactive when used alone. The passage of 3 kg. (25.4 moles) of indan and 112 g. (4 moles) of ethylene (in sixteen hours) over 80 cc. (60 g.) of 25% Al_2O_3–75% SiO_2 ($^1/_8''$ × $^1/_8''$ pellets) at 250° and 300° gave a 75% yield of monoethylindan (based on ethylene) and high-boiling by-product of undetermined structure (230 g. of the latter at 250°, 640 g. at 300°). The amount of carbon deposited on the catalyst was about 0.9 g. in both cases.

Alkylation of Tetralin by Various Alkylating Agents over 1% Al_2O_3–99% SiO_2.—Tetralin was alkylated at 400 p.s.i.g. by ethylene, ethyl alcohol, diethyl ether, propylene, isopropyl alcohol, *t*-butyl alcohol and cyclohexene at temperatures ranging from 200 to 300°. For example, the passage of 5 kg. (37.8 moles) of tetralin and 186 g. (6.65 moles) of ethylene at 300° during twenty-four hours over 100 cc.

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(7) Ipatieff and Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

(8) Kutz and Corson, THIS JOURNAL, **67**, 1312 (1945).

(9) Kutz and Corson, *Ind. Eng. Chem.*, **38**, 761 (1946).

(83 g.) of Phillips Petroleum Co. catalyst (10-20 mesh) yielded 633 g. of monoethyltetralin (60% yield per pass) and 338 g. of higher boiling by-product (monoalkylate/by-product weight ratio 1.87). During a third consecutive 24-hour period at 300° and 400 p.s.i.g., the yields of monoethyltetralin and by-product were 424 g. and 189 g., respectively (weight ratio 2.24). At 200 and 250°, both at 400 p.s.i.g. and 900 p.s.i.g., the product weight ratio was 10.

Ethylation of tetralin by ethylene at 300° and 400 p.s.i.g. (5 kg. of tetralin, 186 g. of ethylene, twenty-four-hr. run) with "solid phosphoric acid" (Universal Oil Products no. 2 catalyst) produced 307 g. of monoalkylate (30% yield per pass) and 163 g. of higher boiling by-product.

Tetralin was more readily alkylated by ethylene than by ethyl alcohol, and diethyl ether was intermediate in activity. Propylene, isopropyl alcohol and cyclohexene at 250° were more active than ethylene at 300°; at 250° propylene was more active than isopropyl alcohol.

Sulfuric Acid, Aluminum Chloride and Hydrofluoric Acid as Isopropylation Catalysts for Indan and Tetralin.—Sulfuric acid (95%, 5°) yielded monoalkylate and higher boiling by-product in the weight ratio of about 3.5; aluminum chloride (15°) and hydrofluoric acid (25°, 130 p.s.i.g.) yielded the above products in the weight ratio of about 1 (the initial indan (or tetralin)/propylene ratio was 4 in all cases).

Constants and Isomeric Compositions of Indan and Tetralin Monoalkylates.—The data are presented in the following order: Compound, b. p. (760 mm.), n^{20}D, d^{20}_4, conditions of alkylation (catalyst, temperature, p.s.i.g.), isomer composition. Ethylindan, 220-221, 1.5297, 0.9434, 75% Al_2O_3-25% SiO_2, 300, 400, 26% of 4-, 74% of 5-; isopropylindan, 231-232, 1.5241, 0.9341, 75% Al_2O_3-25% SiO_2, 300, 400, 33% of 4-, 67% of 5-; ethyltetralin, 247-248, 1.5375, 0.9602, 1% Al_2O_3-99% SiO_2, 300, 400, 72% of 5-, 28% of 6-, isopropyltetralin, 256-257, 1.5310, 0.9547, 1% Al_2O_3-99% SiO_2, 250, 400, 6% of 5-, 94% of 6-; isopropyltetralin, 256-257, 1.5320, 0.9569, aluminum chloride, 20, 15, 1% of 5-, 99% of 6-; isopropyltetralin, 256-257, 1.5340, 0.9670, 95% H_2SO_4, 10, 15, 45% of 5-, 55% of 6-; *t*-butyltetralin, 147-148 (25 mm.), 1.5291, 0.9395, 1% Al_2O_3-99% SiO_2, 300, 400, 6% of 5-, 94% of 6-; cyclohexyltetralin, 115-120 (2 mm.), 1.5509, 0.9975, 1% Al_2O_3-99% SiO_2, 250, 400, 53% of 5-, 47% of 6-.

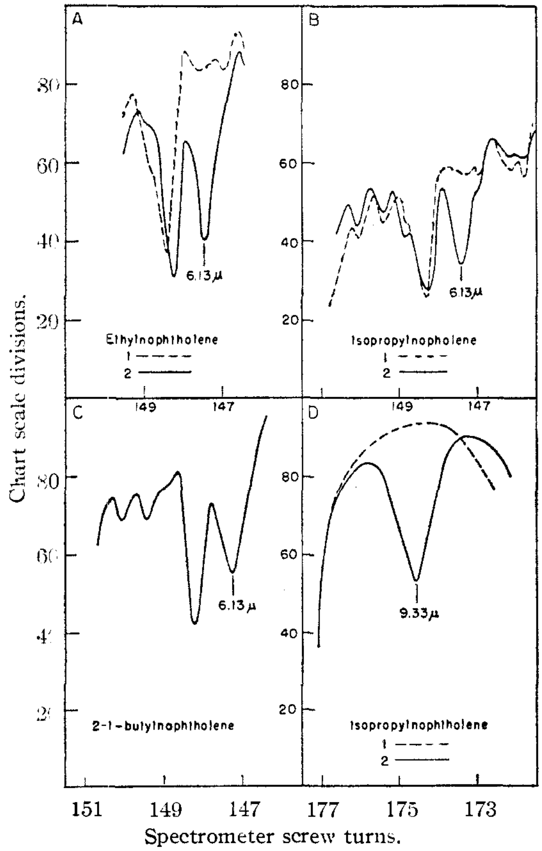

Fig. 2.—Spectra of ethyl-, isopropyl- and *t*-butylnaphthalenes (uncorrected).

Monoalkylindans, Isomer Determination

The monoalkylindans were oxidized by permanganate to mixtures of hemimellitic and trimellitic acids, and the relative amounts of these acids were determined by ultraviolet spectroscopy. The conventional method of analyzing these acid mixtures would involve the separation of the isomeric acids, which we were unable to accomplish. Also, the melting points of the acid mixtures had little quantitative significance. For example, the melting point of trimellitic acid itself ranged from 188 to 221°,[10] depending on the rate of heating.

Oxidation of Monoalkylindans.—For example, a mixture of 73 g. of monoethylindan and 1000 cc. of water was stirred at 70° for six hours, while 790 g. of potassium permanganate was added in small portions. Aliquots of the combined filtrate–wash water were concentrated, strongly acidified with sulfuric acid, and repeatedly extracted by methyl ethyl ketone. After removal of solvent by evacuation, the aqueous solution of the residue was boiled to expel traces of ketone, decolorized by charcoal, filtered, diluted to volume and titrated. This aqueous solution, of known titer, was analyzed by ultraviolet spectroscopy (see below) for isomer composition. The average acid yields from ethyl- and isopropylindans (5 expts. on each) were 85 and 75%, respectively.

Analysis of Hemimellitic–Trimellitic Acid Mixtures by Ultraviolet Spectroscopy.—The ultraviolet spectra of aqueous hemimellitic and trimellitic acids were dissimilar at 255 millimicrons (Fig. 5). Using this wave length, a straight line plot was obtained with isomer pairs of known composition. The validity of the plot was checked against known mixtures which had been treated in the same manner as the oxidation aliquots, *i.e.*, solution in water, acidification, extraction by methyl ethyl ketone, etc. The analytical values (trimellitic acid) of typical known mixtures were 23, 34 and 67%, as compared with the actual values of 21, 39 and 68%, respectively.

Validity of Isomer Determination of Monoalkylindan.—The determination involved the fairly well substantiated assumption that the oxidation of the monoalkylindans gave only hemimellitic and trimellitic acids. Qualitatively, hemimellitic acid (identified as trimethyl ester) and trimellitic acid (identified as anhydride) were isolated. Quantitatively, the acids extracted by methyl ethyl ketone titrated within 5% as benzenetricarboxylic acids. It was shown above that the isomer composition was preserved in the methyl ethyl ketone extract; the extraction efficiency was 90%.

Monoalkyltetralins, Isomer Determination

The monoalkyltetralins were dehydrogenated by means of sulfur to monoalkylnaphthalenes, and the amounts of 5- and 6-isomers in the latter were determined by infrared and ultraviolet spectroscopy.

Dehydrogenation of Monoalkyltetralins.—Each tetralin monoalkylate fraction was heated with the theoretical amount of sulfur for six hours at 200-220°[11] and then vacuum-distilled to remove the monoalkyl fraction which was treated with alcoholic picric acid. The picrate was crystallized from ethyl alcohol, decomposed by hot aqueous ammonia, and the liberated monoalkylnaphthalene was ether-extracted and distilled. In the case of cyclohexyltetralin, purification by picrate was not employed, the un-

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[10] All melting points were corrected.

[11] Barbot, *Bull. soc. chim.*, [4] **47**, 1314 (1930).

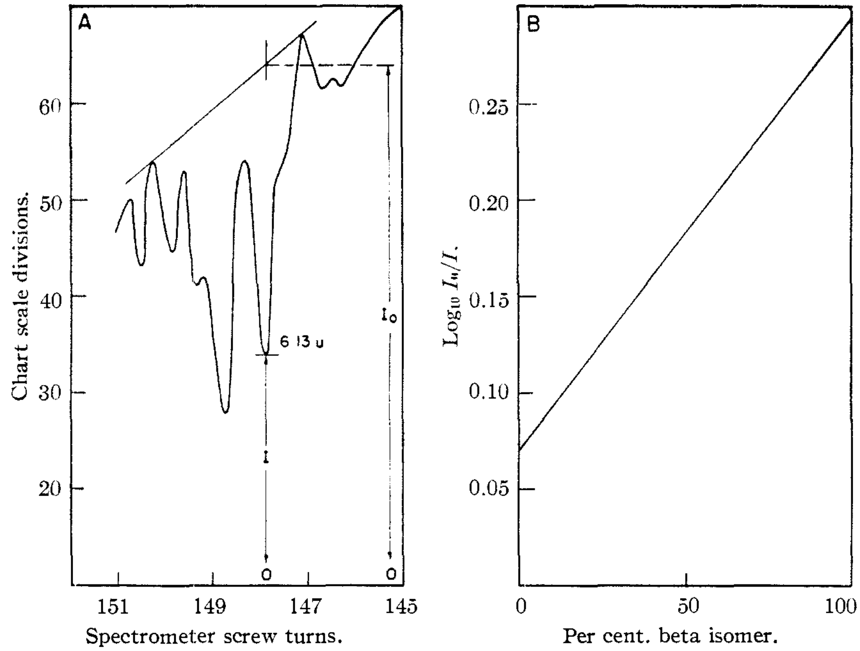

Fig. 3.—Spectra and optical density–composition plot for ethylnaphthalenes.

changed cyclohexyltetralin being separated from dehydrogenated product by vacuum distillation and recycled with more sulfur. The isomer compositions of the ethyl-, isopropyl- and *t*-butylnaphthalenes were determined by infrared spectroscopy, that of the phenylnaphthalene by ultraviolet spectroscopy.

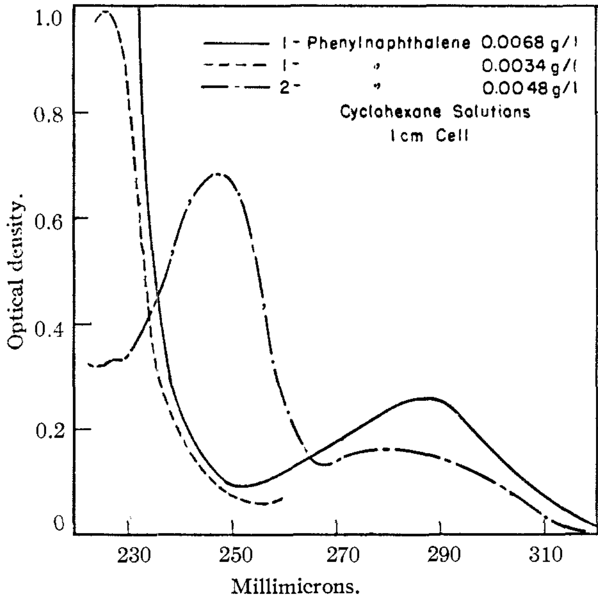

Fig. 4.—Spectra of phenylnaphthalenes.

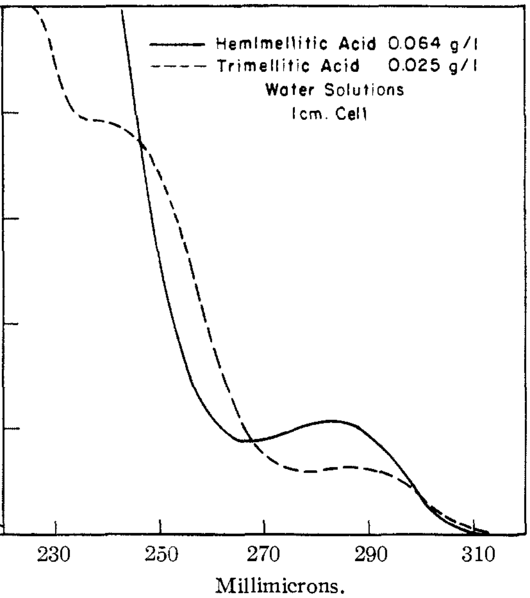

Fig. 5.—Spectra of hemimellitic and trimellitic acids.

Analysis of Ethyl-, Isopropyl- and *t*-Butylnaphthalenes by Infrared Spectroscopy.—The infrared spectra[12] of the 1- and 2-isomers of ethyl- and isopropylnaphthalenes disclosed numerous dissimilarities; *e.g.*, the 2-isomers possessed absorption bands in the vicinity of 6.13 microns, whereas the 1-isomers were practically transparent in this region (Figs. 2-A and 2-B). In the absence of an authentic sample of 1-*t*-butylnaphthalene, the *t*-butylnaphthalene mixtures were analyzed on the assumption that the 1-isomer was also transparent, and the value obtained spectroscopically agreed with that estimated from the melting point of the mixed picrates. Optical density–composition plots (Fig. 3) were constructed for known mixtures of isomers, using a conventional liquid cell (0.08 mm. thick). A wave length beyond the region of strong absorption of water vapor was employed for the determination of small amounts of 2-isopropylnaphthalene (Fig. 2-D).

Analysis of Phenylnaphthalene by Ultraviolet Spectroscopy.—The phenylnaphthalene mixture was analyzed in cyclohexane solution with a standard Beckmann spectrophotometer. At 250 millimicrons the intensity of absorption of the 2-isomer was fifteen times that of the 1-isomer (Fig. 4). The analytical curve was obtained by plotting the absorption coefficients (optical density × liter/g. × cm.) of known mixtures of isomers against their compositions.

Validity of Isomer Determination of Monoalkyltetralins.—Inasmuch as the dehydrogenation yield was poor (35% from isopropyl-, 55% from ethyl-tetralin), it was necessary to determine if the isomer composition of the original tetralin mixture was preserved in the dehydrogenated product. This was done by starting with known mixtures of monoalkylnaphthalenes, hydrogenating them to the tetralin stage, and then dehydrogenating and analyzing the dehydrogenated products. Known mixtures of 1- and 2-isopropylnaphthalenes and 1- and 2-ethylnaphthalenes were hydrogenated at 150° and 100 atmospheres with

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(12) Using research type recording spectrometer, Brady, *Ind. Eng. Chem., Anal. Ed.*, **16**, 422 (1944).

nickel to give tetralins with the alkyl group presumably in the non-hydrogenated ring.[13] The hydrogenated products were dehydrogenated with sulfur and the resulting alkylnaphthalenes were analyzed spectroscopically.

A 45–55 mixture of 1- and 2-isopropylnaphthalenes, after hydrogenation–dehydrogenation, analyzed as 42–58, whereas 43–57 and 73–27 mixtures of 1- and 2-ethylnaphthalenes, after hydrogenation–dehydrogenation, analyzed as 51–49 and 90–10, respectively. Evidently, the agreement was not good with the ethylnaphthalenes, especially with isomer mixtures rich in 1-isomer. On the other hand, isomerization did not take place when authentic samples of the 1- and 2-isomers of ethyl- and isopropylnaphthalenes were heated with sulfur, recovered as picrates, and regenerated therefrom.

Non-Isomerization of Monoalkylnaphthalenes by Simple Heating.—According to Tsukervanik and Terent'eva[6] 1-monoalkylnaphthalenes are readily isomerized by heating, *e.g.*, 1-isopropylnaphthalene is quantitatively isomerized to the 2-isomer by simple distillation. If this alleged isomerization were true, many proofs of structure would be invalidated. We refluxed 1-isopropylnaphthalene for five hours at atmospheric pressure and finally distilled it at atmospheric pressure. Spectroscopic examination of the distillate revealed no isomerization. Similar results were obtained with both isomers of monoethylnaphthalene. The purity of the isopropylnaphthalene of Tsukervanik and Terent'eva is questionable; two fractions were reported, one boiling at 262°, the other at 268°, both allegedly 2-isopropylnaphthalene. This publication of Tsukervanik and Terent'eva has already been questioned by Bromby, Peters and Rowe[14] with regard to the synthesis and proof of structure of 1-butylnaphthalene.

Preparation of Authentic Isomers

The following isomers were used in constructing the calibration curves for the spectroscopic analyses.

Hemi- and Trimellitic Acids.—Hemimellitic acid[15] (m. p. of anhydrous acid 208–209°, m. p. of trimethyl ester 98–100°) was obtained in 65% yield by permanganate oxidation of naphthalic anhydride. Trimellitic acid was obtained in 57% yield by permanganate oxidation[16] of pseudocumene (b. p. 168.6–168.8° (744 mm.), $n^{20}{}_D$ 1.5048, $d^{20}{}_4$ 0.8762) which had been purified *via* its sulfonic acid.[17] Trimellitic acid was also obtained in 55% yield by permanganate oxidation of 1,2,3,4-tetrahydro-6-carboxylic naphthalene[18] (m. p. 150–151°) which was prepared in 95% yield by hypochlorite oxidation of 1,2,3,4-tetrahydro-6-acetylnaphthalene. The solubility of trimellitic acid in 10 cc. of water is 0.13 g. at 0°, 0.83 g. at 30° and 7.1 g. at 100°.

Monoalkylnaphthalenes (Table I).—The isomeric ethyl- and isopropylnaphthalenes were prepared by hydrogenating the following vinyl- and isopropenylnaphthalenes. Prior to hydrogenation the unsaturates were stored at 0° to prevent polymerization. 1-Vinylnaphthalene (97% pure by bromine number) was obtained in 85% yield by dehydrating 1-(2-hydroxyethyl)-naphthalene over solid potassium hydroxide at 165° and 30 mm.[19] The antecedent 1-(2-hydroxyethyl)-naphthalene (b. p. 154.5° at 3 mm.) was prepared in 83% yield by the reaction of 1-naphthylmagnesium bromide with ethylene oxide.[20] 2-Vinylnaphthalene (m. p. 66°, crystallized from methanol) was separated from catalyzate resulting from the dehydrogenation (at 650° and 100 mm. over chromia–magnesia)[21] of mixed isomeric ethylnaphthalenes. The antecedent ethylnaphthalenes were prepared by autoclaving three moles of naphthalene with one mole of ethylene for three hours at 250° in the presence of 10% of Filtrol X-143. 1-Isopropenylnaphthalene (b. p. 106.5° (5 mm.), $n^{20}{}_D$ 1.6085, $d^{20}{}_4$ 1.006) resulted in 97% yield by dehydrating 1-naphthyldimethylcarbinol with hydrochloric acid.[22] 2-Isopropenylnaphthalene (b. p. *ca.* 132° (5 mm.), m. p. 54.5–55.5 °C.) was obtained in 71% yield by dehydrating 2-naphthyldimethylcarbinol over solid potassium hydroxide at 165°.[23]

An unsuccessful attempt was made to prepare authentic 1-*t*-butylnaphthalene by treating 1-naphthylmagnesium bromide with *t*-butyl bromide according to Späth[24] whose only evidence of structure was that of the initial bromonaphthalene. Repeated distillation gave a 5% yield of material boiling at 265–271° at 730 mm. ($n^{20}{}_D$ 1.6113, $d^{20}{}_4$ 1.120). We were also unable to prepare the 1-isomer by treating *t*-butylmagnesium chloride with 1-tetralone followed by dehydration–dehydrogenation. 2-*t*-Butylnaphthalene was obtained in 51% yield from *t*-butyl chloride, naphthalene and aluminum chloride.[25] The structure of the product was established by Bromby, Peters and Rowe.[14]

Table I

Constants of Authentic Monoalkylnaphthalenes

Substituent	Boiling point °C.	Mm.	$n^{20}{}_D$	$d^{20}{}_4$
1-Ethyl[a]	258.3	760	1.6052	1.0076
2-Ethyl[a]	257.9	760	1.5995	0.9922
1-Isopropyl[a]	267.9	760	1.5950	0.9953
2-Isopropyl[a]	268.2	760	1.5861	0.9762
2-*t*-Butyl	131–131.5	7	1.5786	0.9684
1-Phenyl	184–185	11.5	1.6664	1.096
2-Phenyl	239–242	50	(M. p. 101.5–102°)	

[a] Vapor pressure data were obtained in a Cottrell boiling point apparatus according to Quiggle, Tongberg and Fenske, *Ind. Eng. Chem., Anal. Ed.*, 6, 466 (1934). The temperatures corresponding to 10, 15, 20, 30, 50, 70, 100, 150, 200, 300, 500 and 760 mm., were the following, respectively: 1-ethylnaphthalene, 120.0, 129.2, 136.0, 146.2, 160.0, 169.7, 180.7, 193.9, 204.0, 219.0, 239.7 and 258.3°; 2-ethylnaphthalene, 119.1, 138.4, 135.3, 145.5, 159.4, 169.1, 180.1, 193.4, 203.5, 218.6, 239.3 and 257.9°; 1-isopropylnaphthalene, 129.3, 138.4, 145.2, 155.3, 169.0, 178.7, 189.7, 203.0, 213.0, 228.1, 249.0 and 267.9°; 2-isopropylnaphthalene, 128.5, 137.5, 144.3, 154.4, 168.1, 177.8, 188.8, 202.2, 212.4, 227.7, 248.9 and 268.2°.

1-Phenylnaphthalene was prepared by treating 1-tetralone with phenylmagnesium bromide followed by dehydration–dehydrogenation.[26] 2-Phenylnaphthalene was prepared by autoclaving 3 moles of naphthalene with one mole of cyclohexene in the presence of 10% of Filtrol X-143 for three hours at 210° (60% yield, b. p. 220–245° at 50 mm.), dehydrogenating the product with sulfur at 200–210° for sixteen hours, distilling the product at 50 mm., and crystallizing the 239–242° fraction from 96% ethyl alcohol.

Acknowledgment.—The authors express their thanks to Patricia David, Elizabeth Depp and H. R. McGraw for assistance in the experimental work and to L. J. Brady for certain of the spectroscopic data.

Summary

Indan and tetralin were alkylated with ethylene, propylene, cyclohexene, ethyl alcohol, isopropyl alcohol, tertiary butyl alcohol and diethyl

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(13) Fieser and Jones, This Journal, **66**, 1940 (1938).

(14) Bromby, Peters and Rowe, *J. Chem. Soc.*, 144 (1943).

(15) Graebe and Leonhardt, *Ann.*, **290**, 217 (1896).

(16) Schultze, *ibid.*, **359**, 143 (1908).

(17) Smith and Cass, This Journal, **54**, 1603 (1932).

(18) Newman and Zahn, *ibid.*, **65**, 1097 (1943).

(19) Palfray, Sabetay and Sontag, *Compt. rend.*, **194**, 2065 (1932).

(20) Ruzicka, Ehmann, Goldberg and Hosli, *Helv. Chim. Acta*, **16**, 833 (1933).

(21) Zal'kind and Arbuzova, *Plasticheskie Massy, Sbornik Statei*, No. 3, 249 (1939).

(22) Cook, *J. Chem. Soc.*, 456 (1932).

(23) Bergmann and Weizmann, *J. Org. Chem.*, **9**, 352 (1944).

(24) Späth, *Monatsh.*, **34**, 1965 (1913).

(25) Fieser and Price, This Journal, **58**, 1841 (1936).

(26) Weiss, "Organic Syntheses," **24**, 84 (1944).

ether in the presence of alumina–silica combinations, "solid phosphoric acid," aluminum chloride, sulfuric acid and hydrogen fluoride.

The determination of the isomer distribution in the resulting monoalkylates was not amenable to conventional methods, but it was accomplished by infrared and ultraviolet spectroscopy. The isomer distribution was found to be dependent upon the catalyst and/or conditions employed.

1-Ethylnaphthalene and 1-isopropylnaphthalene do not isomerize on simple distillation as reported by Tsukervanik and Terent'eva.

A laboratory apparatus for continuous alkylation under superatmospheric pressure was described which facilitated the otherwise difficult laboratory operation with a mixed gas–liquid feed.

Indan yielded condensation products of undetermined nature in the presence of alumina–silica and aluminum chloride.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Kinetics of the Reaction between the Ethylene Halohydrins and Hydroxyl Ion in Water and Mixed Solvents[1a]

BY C. L. MCCABE[1b] AND J. C. WARNER

The kinetics and course of the reaction between ethylene chlorohydrin and hydroxyl ion has been studied extensively in this[2a,2b] and other laboratories.[3a,3b,3c] The purpose of this study was to extend the investigation to the other halohydrins.

Experimental Method

The reactions were carried out in thermostats which held the temperature constant to within ±0.005° as measured by Beckman thermometers, which were calibrated against a National Bureau of Standards resistance thermometer. The rate of the reaction of the bromohydrin as well as iodohydrin was followed by determining halogen by the Volhard method; the rate with fluorohydrin was determined by following the hydroxyl ion concentration. In all experiments carbonate-free base was used and precautions were taken to exclude carbon dioxide during the course of the reaction.

The bromohydrin was prepared from ethylene oxide by a well established method.[4] Ethylene iodohydrin was prepared by the reaction between ethylene chlorohydrin and sodium iodide[5] in acetone solutions. Ethylene fluorohydrin was kindly furnished by the Chemical Corps, U. S. Army. The bromohydrin fraction used distilled at 51.0–51.1° at 4 mm., the iodohydrin at 75.0–75.2° at 5 mm. These distillations were carried out in a Vigreux flask with a variable take-off so that one could change receivers without admitting air. The iodohydrin is unstable and during the distillation iodine must be continually removed. Powdered silver was used for this purpose. The fluorohydrin as received was about 80% pure. It was further purified by two fractionations in a five-foot spiral wire column. The fraction used for the kinetic measurements boiled at 103.2° at 750 mm. On all three compounds an indication of the purity was obtained by allowing a weighed amount of the halohydrin to react to completion with excess base and then analyzing for halide ion. With bromohydrin as well as with iodohydrin, the amount of halide ion obtained in the reaction with base agreed within 0.1% with the calculated amount for the pure compounds.

When the ethylene fluorohydrin used in the kinetic experiments was allowed to react to completion with base, the purity indicated by fluoride analysis was 93.0% and that indicated by base consumed was 92.3%. Therefore, in calculating the fluorohydrin concentration, the substance was assumed to be 93.0% pure.

1,4-Dioxane was purified by refluxing over metallic sodium, followed by a distillation, and the methanol employed was redistilled. Carbon dioxide was excluded in each distillation.

The analysis of the amount of ethylene oxide formed from the reaction between hydroxyl ion and the ethylene halohydrins were carried out by a modification of Lubatti's method[6] in an enclosed flask with two compartments. In one, the base and halohydrin were allowed to react at room temperature, and after reaction was complete standard acid was added to the methyl orange end-point. The other compartment contained sufficient magnesium chloride hexahydrate to saturate the reaction mixture and enough alcoholic hydrochloric acid to make the reaction mixture about tenth normal. The reagents from the second compartment were transferred to the reaction mixture which was then allowed to stand for about thirty minutes. The amount of acid consumed in the conversion of ethylene oxide into halohydrin was calculated from the amount of standard base necessary to bring the mixture back to the methyl orange end-point.

The velocity constants were determined from the best straight line plot of the appropriate function of the concentration *versus* time. The unit of time for all constants reported in this paper is the minute.

Experimental Results

In Table I are summarized the velocity constants, activation energies and log *B* of the Arrhenius equation for the reactions of the various halohydrins with hydroxyl ion in water as solvent.

The rates of the reaction of these halohydrins with pure water have been investigated and are clearly negligible compared to the above rates of reaction with hydroxyl ion.[7]

Table II presents a summary of the velocity constants in water–methanol and water–dioxane mixtures for the various halohydrins. In columns five and six, velocity constants for the bromohy-

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[1] (a) Abstracted from a thesis submitted by C. L. McCabe to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the D.Sc. degree; (b) American Chemical Society Pre-doctoral Fellow, 1946–1947.

[2] (a) Winstrom and Warner, THIS JOURNAL, **61**, 1205 (1939); (b) Stevens, McCabe and Warner, *ibid.*, **70**, 2449 (1948).

[3] (a) Smith, *Z. physik. Chem.*, **81**, 339 (1912); (b) Brönsted, Kilpatrick and Kilpatrick, THIS JOURNAL, **51**, 428 (1929); (c) D. Porret, *Helv. Chim. Acta*, **27**, 1321 (1944).

[4] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 117.

[5] Wieland and Sakellarios, *Ber.*, **53**, 208 (1920).

[6] Lubatti, *J. Soc. Chem. Ind.* (*London*), **51**, 361 (1932).

[7] Unpublished experiments from this Laboratory.