mixture was refluxed one hour, cooled to 0°, and allowed to stand one hour. Separating in large cubical crystals, the amide—after filtering off and recrystallizing from petroleum ether—melted at 190–191° undecomposed; yield, 23% of theoretical.

Anal. Calcd. for $C_{10}H_{19}ON$: C, 70.96; H, 11.31. Found: C, 71.17; H, 11.10.

The carbon tetrachloride layer from the filtrate was dried over sodium sulfate and re-ozonized as above to give an additional 23% of the amide; total yield, 46% of the theoretical. The carbon tetrachloride layer from this first treatment was extracted with dilute hydrochloric acid to obtain 15% of the unchanged base. After evaporation of the solvent, there remained a small amount of neutral residue which gave qualitative reactions of an alcohol but was not further investigated.

Isolation of the $C_{10}H_{18}O_2$ Acid.—The sodium hydroxide layer from the ozonization of the base was acidified with dilute sulfuric acid and extracted with ether. The residual oil, after removal of the ether, was refluxed six hours with 2% methyl alcoholic hydrogen chloride. Following removal of alcohol, the residue was dissolved in ether and extracted with 10% sodium carbonate solution. Acidification of the alkaline solution gave an oil which was extracted with ether, dried over sodium sulfate and fractionated through a semi-micro column. All fractions solidified upon standing, and after recrystallization from dilute acetic acid, the product melted at 82–83° and by mixed melting point determination was shown to be identical with the $C_{10}H_{18}O_2$ acid obtained by degrading the benzoyl derivative of the $C_{16}H_{31}N$ base.

Hydrolysis of the $C_{10}H_{19}ON$ Amide.—A 20% solution of sodium hydroxide failed to completely hydrolyze the amide in a sealed tube at 140° for twelve hours. Refluxing with concentrated hydrochloric acid or dilute nitric acid gave an acid which was identical with that obtained from the ozonolysis products.

Degradation of the $C_{10}H_{19}ON$ Amide.—Six grams of the amide obtained by ozonolysis of the base was treated at 0° with an equal molecular quantity of bromine dissolved also at 0° in six times the molecular quantity of 10% potassium hydroxide. The mixture was stirred vigorously one hour, then gradually heated to 70° and maintained with stirring at this temperature one hour. Steam distillation of the mixture, extraction of the distillate with ether, drying over potassium hydroxide pellets and fractionation gave a $C_9H_{17}NH_2$ amine identical in physical properties with that obtained by the action of hydrazoic acid upon the naphthenic acid. The mixed melting point of the picrates of the amines obtained by both methods showed no depression.

Proof of the Identity of the Naphthenic Acid (*trans*-2,2,6-Trimethylcyclohexanecarboxylic Acid) from Petroleum and the $C_{10}H_{18}O_2$ Acid from Degradation of the $C_{16}H_{25}N$ Base.—A mixture of the naphthenic acid isolated from California petroleum by Shive, Horeczy, Wash and Lochte[12] and shown to be *trans*-2,2,6-trimethylcyclohexanecarboxylic acid, and the acid obtained by degradation of the naphthenic base gave no depression in melting point, 82–83°. The amide of the isolated acid prepared through the acid chloride did not depress the melting point, 190–191°, of the amide obtained by ozonolysis of the $C_{16}H_{25}N$ base.

Likewise the picrates (m. p. 226–227°) of the $C_9H_{17}NH_2$ amines obtained from the two sources by degradation of the acids with hydrazoic acid showed no depression in a mixed melting point determination.

Summary

1. The structure of the $C_{16}H_{25}N$ base isolated from California petroleum by Thompson and Bailey[8] has been shown to be 2-(2,2,6-trimethylcyclohexyl)-4,6-dimethylpyridine.

2. A structural correlation of a naphthenic acid and a naphthenic base from petroleum has been established for the first time.

AUSTIN, TEXAS RECEIVED DECEMBER 22, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF POLYTECHNIC INSTITUTE OF BROOKLYN]

The Preparation of Alpha and Beta Indanol and Some of Their Derivatives from Indene[1,2]

BY WILLET F. WHITMORE AND ARTHUR I. GEBHART

α-Indanol was first prepared by Wislicenus and König[3] and later by Weisgerber[4] in 50% yields by hydrolysis of chloroindane with aqueous potassium carbonate. It seemed likely that this alcohol might be obtained in better yield by the dehalogenation of indenebromohydrin by catalytic reduction with Raney nickel in the presence of potassium hydroxide. The bromohydrin, prepared by the method of Read and Hurst,[5] reduced rapidly to β-indanol instead of the anticipated α-indanol. Attempts to reduce indenebromohydrin in the presence of magnesium hydroxide, silver oxide or pyridine failed. Apparently potassium hydroxide reacted with the bromohydrin to produce indene oxide (indene epoxide) which

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(1) An abstract of a dissertation presented in 1941 to the Faculty of the Graduate School of the Polytechnic Institute of Brooklyn by Arthur I. Gebhart in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

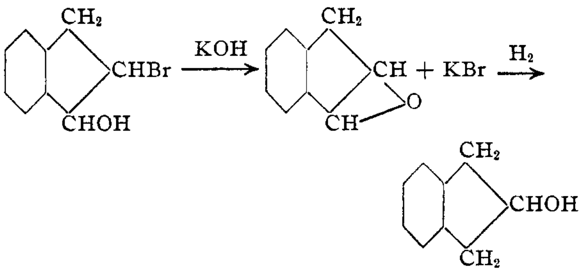
(2) The authors wish to thank the United Gas Improvement Company of Philadelphia who generously supplied the indene used in this study.

(3) Wislicenus and König, *Ann.*, **275**, 349 (1893).

(4) Weisgerber, *Ber.*, **44**, 1445 (1911).

(5) Read and Hurst, *J. Chem. Soc.*, **121**, 2552 (1922).

upon reduction opened the oxide ring to yield β-indanol.



This could be verified by the reduction of indene oxide. Our attempt to prepare the oxide in ether[6] was not entirely satisfactory. In dioxane indenebromohydrin was quantitatively converted to indene oxide, which was reduced to β-indanol, thus confirming the mechanism. This procedure furnishes a new and convenient method for preparing β-indanol. An investigation is now in progress to determine whether halohydrins or epoxides in general can be reduced to alcohols and, if so, whether any generalizations can be drawn concerning the direction in which the oxide ring opens in unsymmetrical molecules.

It was thought that acetylation of indenebromohydrin might prevent oxide formation and subsequent reduction would yield α-indanyl acetate. An attempt to acetylate with sodium acetate and acetic anhydride resulted in the formation of indeneglycol diacetate. By the method of Smith and Bryant,[7] indenebromohydrin acetate was obtained as an oil which, although stable at ordinary temperatures, decomposed when distilled at 4.5 mm. Since the acetate was so unstable, the benzoate was prepared. This, upon treatment with alcoholic potassium hydroxide, decomposed rapidly into ethyl benzoate, potassium bromide and indene glycol. This rather unusual reaction apparently involves the intermediate formation of indene oxide. The sensitivity of this ester to alkali precluded any attempt to reduce it to α-indanyl benzoate.

α-Chloroindane, prepared by slightly modifying the method of Pacaud and Allen,[8] reacted readily with sodium acetate in acetic acid to yield α-indanyl acetate containing some α-indanol, no doubt produced by the action of the sodium acetate. Saponification of this ester yielded α-indanol which, however, could not be crystallized from petroleum ether as claimed by Weisgerber.[4] From methyl alcohol the compound melted at 40.5°, which was in sharp disagreement with the melting point of 54° reported for α-indanol.[3,4] The alcohol regenerated from the purified benzoate still melted at 40.5°.

Despite earlier reports that α-indanone is reduced to hydrindene[9] and hydrindanols,[10] an attempt was made to reduce this ketone to α-indanol with Raney nickel but a mixture resulted. When the catalyst was "promoted" with platinic chloride[11] the reduction proceeded rapidly to α-indanol, in 87% yield, which crystallized from petroleum ether and melted at 52.5°. It was found that α-indanol exists in two forms, one melting at 40.5°, very soluble in petroleum ether and unstable, reverting, even in the solid phase, to a stable form melting at 52.5° which is practically insoluble in petroleum ether. By refluxing the stable form with ethyl alcohol, it reverts to the unstable form, which explains why the latter was always obtained by saponification of the esters with alcoholic potassium hydroxide.

Since catalytic reduction of indene oxide yielded β-indanol, it seemed that indene bromohydrin could be reduced to α-indanol providing some base was utilized which would not convert the bromohydrin to indene oxide. With magnesium hydroxide and "promoted" Raney nickel catalyst,[11] the reduction proceeded readily and α-indanol was obtained in 87% yield. This constitutes a new method for preparing this alcohol.

Since no characterizing derivatives of α-indanol have been reported, and for β-indanol only the phenylurethan and acid phthalate are known,[10] the benzoates, *p*-nitrobenzoates and α-naphthylurethans were prepared. α-Indanyl-α-naphthylurethan was found to exist in two interchangeable forms, one melting at 137° and the other at 145°.

Several saponifications of α-indanyl acetate, instead of α-indanol, yielded a product boiling about ninety degrees higher at 4.5 mm. The formation of this material was attributed to the action of alkali on the indanol or indanyl acetate during saponification, since it corresponded with a product obtained by Weisgerber[4] while preparing α-indanol by the action of aqueous potassium carbonate on chlorindane and which he reported as diindanyl ether. Investigation by the

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[6] Böeseken and van Loon, *Proc. Acad. Sci. Amsterdam*, **20**, 1186 (1918).

[7] Smith and Bryant, THIS JOURNAL, **57**, 61 (1935).

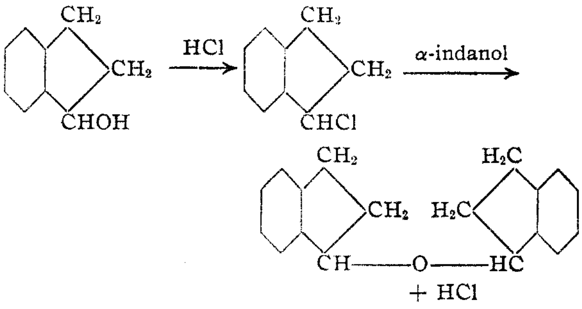
[8] Pacaud and Allen, "Organic Syntheses," **18**, 47 (1938).

[9] Zelinski and Packendorff, *Ber.*, **67B**, 300–302 (1934).

[10] Hückel, Sachs, Yantschulewitch and Nerdel, *Ann.*, **518**, 155–183 (1935).

[11] Reasenberg, Lieber and Smith, THIS JOURNAL, **61**, 384 (1939).

authors demonstrated that it resulted from the action on α-indanol of small amounts of hydrochloric acid used for washing, after saponification of the acetate. By refluxing α-indanol with hydrochloric acid in dioxane, evidence was obtained indicating that the acid acted on the indanol to produce chloroindane which in turn reacted with the excess alcohol present to yield diindanyl ether.



By repetition of the above procedure using 50% ethyl alcohol instead of dioxane, a colorless oil having a pine-like odor was obtained, corresponding with a compound obtained by Weisgerber,[4] which he considered to be indanyl ethyl ether but did not investigate further. Refluxing chloroindane with ethyl alcohol caused the liberation of hydrochloric acid and the same compound was obtained. Similarly, chloroindane when refluxed with α-indanol yielded diindanyl ether, thereby establishing the above mechanism. The corresponding reaction of α-indanol with other alcohols is being studied.

Crystallized slowly from methyl alcohol, diindanyl ether deposited a mixture of transparent rods and flat plates which, after separation, melted, respectively, at 68 and 74°. Analysis demonstrated that the compounds are isomeric, both are optically inactive and decompose into indene when refluxed with alcoholic hydrochloric acid, indicating that they are structurally similar. The mixture of isomers when heated with water under pressure decomposed into indene and α-indanol. When vacuum distilled both yielded indene, α-indanol and some undecomposed diindanyl ether. These transformations are more characteristic of secondary or tertiary alcohols than of ethers, but since no methane was evolved in a Zerewitinoff determination and practically the theoretical ethoxy value[12] was obtained for the indanyl ethyl ether, it was concluded that they are actually ethers. Up to the present it has not been possible to determine definitely the nature of these two isomers of diindanyl ether. Since both forms invariably crystallize together, it seems unlikely that they are dimorphous forms of the same substance. It is proposed to continue the investigation of these compounds with the purpose of establishing their structure.

Experimental

Catalytic Reduction of Indenebromohydrin to β-Indanol.—All reductions were made at room temperature and atmospheric pressure with the apparatus used by Lieber and Smith.[13] One-tenth mole (21.3 g.) of indenebromohydrin was placed in the reduction bottle and a solution of 7 g. of 85% potassium hydroxide in 130 cc. of 95% alcohol added followed by 3 g. of Raney nickel catalyst. Practically the theoretical hydrogen was absorbed, at a rate ranging from 200–250 cc. per 100 seconds. After filtration and acidification the solution was evaporated to a volume of 60 cc. and 150 cc. of water added, after which it was heated and shaken vigorously to dissolve any separated oil. The hot solution was treated with Norit, filtered, cooled to 32°, and any separated yellowish colored β-indanol removed as rapidly as possible by filtration. Subsequent standing at room temperature and then cooling to 5° caused brilliant colorless needles of β-indanol to separate; m. p. 69°;[14] yield, 60–67%.

Anal. Calcd. for $C_9H_{10}O$: C, 80.55; H, 7.52. Found: C, 80.15; H, 7.58.

Preparation of Indene Oxide (Indene Epoxide).—To a solution of 20 g. of indenebromohydrin in 100 cc. of dioxane, 12 cc. of 13 *N* aqueous potassium hydroxide and 16 cc. of absolute methyl alcohol were added. After standing at room temperature for fifteen minutes the mixture was poured into 400 cc. of water and the separated oil extracted with ether and washed with water. Evaporation of the ether yielded a colorless oil which solidified at room temperature. The entire product distilled at 97° (5 mm.); m. p. 31°; yield, 12.4 g. (theoretical). A mixed melting point with indene oxide prepared by a modified method[6] showed no depression.

Reduction of Indene Oxide to β-Indanol.—Three grams of Raney nickel was added to a solution of 6.6 g. (0.05 mole) of indene oxide in 100 cc. of ethyl alcohol. A total of 1233 cc. of hydrogen was consumed, at a rate ranging from 140–110 cc. per 100 seconds. The resulting β-indanol was crystallized as described above; yield, 65%; m. p. 69°. A mixed melting point with β-indanol obtained by reduction of indenebromohydrin showed no depression.

Action of Acetic Anhydride and Sodium Acetate on Indenebromohydrin.—Five grams of indenebromohydrin was refluxed for one hour with 2.5 g. of anhydrous sodium acetate and 25 cc. of acetic anhydride. The mixture was poured into water and extracted with ether. After washing free of acid and evaporating, 4 g. of an oil was obtained which contained only traces of bromine. Saponification yielded potassium acetate and colorless needle-like crystals

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[12] Clark, *J. Assoc. Off. Agr. Chem.*, **15**, no. 1, 136 (1932).

[13] Lieber and Smith, THIS JOURNAL, **57**, 2479 (1935).

[14] All melting points were taken on a Dennis–Shelton melting point bar; Dennis and Shelton, *ibid.*, **52**, 3128 (1930).

from hot water; m. p. 158°; a mixed melting point with indene glycol, 159°, gave no depression, showing the ester to have been indeneglycol diacetate. The saponification equivalent calcd. for indeneglycol diacetate is 235; found, 241.

Preparation of Indenebromohydrin Benzoate.—A solution of 10 g. of indenebromohydrin in 40 cc. of dioxane and 15 cc. of pyridine was cooled in ice and 10 g. of benzoyl chloride added. After cooling for ten minutes the mixture was allowed to stand at room temperature for two hours, then diluted with 200 cc. of water and extracted with ether. The ether was washed free of pyridine, dried over sodium sulfate and evaporated. The pasty residue, filtered on a fritted glass funnel, yielded 14.8 g. of solid. Recrystallized from isopropyl alcohol, elongated prisms, m. p. 104°, were obtained.

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.56; H, 4.13; Br, 25.21; saponification equivalent, 317. Found: C, 60.68; H, 4.31; Br, 25.29; saponification equivalent, 315.

Action of Alcoholic Potassium Hydroxide on Indenebromohydrin Benzoate.—By treating 1.000 g. of indenebromohydrin benzoate with 15.0 cc. of 0.5 *N* alcoholic potassium hydroxide at room temperature for forty-five minutes, potassium bromide separated and one equivalent of alkali was consumed. Steam distillation of the solution yielded 0.49 g. of ethyl benzoate. Evaporation of the solution remaining in the still to a small volume (3 cc.) yielded colorless crystals of indene glycol, m. p. 158°, which gave no depression with indene glycol.

Preparation of α-Indanyl Acetate.—A solution of 120 g. of anhydrous sodium acetate in 480 cc. of glacial acetic acid and 72 cc. of water was heated to 98°, under reflux in a boiling water-bath, and 120 g. of crude chloroindane[15] added all at once, stirring vigorously. Stirring and heating were continued for one hour, after which the mixture was allowed to stand overnight, diluted with a liter of water and extracted with ether. After washing free of acid with water and 5% sodium bicarbonate solution and removing the solvent, the residue was distilled at 3.5 mm. A fraction of 28 g. was collected from 53–58°, consisting chiefly of indene, after which 70 g. of a colorless oil, possessing an odor recalling benzyl acetate, distilled from 104–106.5°. This latter fraction contained 86% of α-indanyl acetate and 14% of α-indanol.

Saponification of α-Indanyl Acetate to α-Indanol.—Distilled α-indanyl acetate (158 g.) containing 86% ester was refluxed one hour with one liter of 1.0 *N* alcoholic potassium hydroxide. Three-fourths of the ethyl alcohol was distilled off, the excess alkali neutralized with acetic acid, four volumes of water added, and the separated oil extracted with ether and washed free of acid with water. After removing the ether and distilling the residue at 8 mm. a 9-g. fraction was obtained, from 55–60°, which was chiefly indene. The balance, 90 g., distilled from 115–116° as a colorless, somewhat viscous liquid which later solidified and melted at 38–40°. Acetylation[7] showed it contained 95.9% α-indanol.

Crystallization of the Two Forms of α-Indanol

Low Melting, Unstable Form.—The crude α-indanol resulting from the saponification of α-indanyl acetate was very soluble in warm petroleum ether (b. p. 28–38°) and could not be crystallized from it. By cooling a 20% solution in 50% methyl alcohol to −10° and seeding, colorless crystals separated which had to be filtered rapidly on a fritted glass funnel and sucked as dry as possible to prevent redissolving. The compound melted sharply at 40.5°.

Anal. Calcd. for $C_9H_{10}O$: C, 80.55; H, 7.52. Found: C, 80.15; H, 7.58.

Purification by benzoate formation and subsequent hydrolysis, and crystallization as described above, yielded the same product melting at 40.5°. Upon standing for several weeks these crystals melted sharply at 52.5°.

High Melting, Stable Form.—A solution of 20 g. of the crude indanol in 150 cc. of petroleum ether (b. p. 28–38°) when seeded with a crystal melting at 52.5° yielded a large crop of long, colorless prisms, m. p. 52.5°, no longer soluble in the mother liquor, even on boiling. When fused, it became soluble in petroleum ether but when crystallized it was again insoluble and melted at 52.5°.

Anal. Calcd. for $C_9H_{10}O$: C, 80.55; H, 7.52. Found: C, 80.28; H, 7.69.

The molecular weight by the Rast camphor method was 133.8. This form of α-indanol when refluxed for one hour with ethyl alcohol reverted to the unstable modification, m. p. 40.5°. A mixture of both forms melted slowly from 43–52.5°. After solidification it remelted at 52.5°.

Catalytic Reduction of α-Indanone to α-Indanol.—To an alcohol solution of 14.2 g. of α-indanone, 0.5 g. of sodium hydroxide, 3 g. of Raney nickel and 0.5 cc. of chloroplatinic acid (1 cc. = 0.084 g. Pt) were added. In seventy-two minutes 2612 cc. of hydrogen was consumed (calcd. 2640 cc.). After removing the catalyst, three volumes of saturated sodium chloride solution was added and the separated oil extracted with ether and washed with water. Evaporation of the ether yielded 12.2 g. of an oil, all of which distilled at 119° (10 mm.) and solidified on cooling. From petroleum ether, colorless crystals were obtained melting at 52.5°. A mixed melting point with α-indanol gave the same value.

Catalytic Reduction of Indenebromohydrin to α-Indanol.—To a solution of 5.6 g. of magnesium chloride hexahydrate in 120 cc. of alcohol, 4.2 cc. of 13.2 *N* potassium hydroxide, 10 g. of indenebromohydrin, 3 g. of Raney nickel and 0.5 cc. of chloroplatinic acid (1 cc. = 0.084 g. Pt) were added. A total of 1199 cc. of hydrogen was consumed (calcd. 1157 cc.). After evaporation of most of the ethyl alcohol, dilution with water and extraction with ether, an oil was obtained which yielded 4.5 g. of colorless crystals from petroleum ether; m. p. 52.5°. A mixed melting point with α-indanol showed no depression. Evaporation of the mother liquor yielded an additional 1.5 g. of the indanol.

Derivatives of Alpha and Beta Indanol

α-Indanyl benzoate prepared in pyridine–toluene solution was obtained in 76% yield. It crystallized from methanol in colorless rectangular plates; m. p. 63°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.63; H, 5.93; saponi-

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[15] The chloroindane was used without distillation, after removal of excess hydrochloric acid as described by the authors.[8] It was found that by using a fritted glass "gasifier" for introducing hydrochloric acid gas into indene the time of preparation of chloroindane could be greatly reduced.

fication equivalent, 238.1. Found: C, 80.39; H, 6.05; saponification equivalent, 238.2.

β-Indanyl benzoate was obtained in the theoretical yield. It crystallized from ethyl alcohol as glistening elongated prisms with angular ends; m. p. 63°; mixed melting point with α-indanyl benzoate, 41–44°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.63; H, 5.93. Found: C, 80.45; H, 6.01.

α-Indanyl *p*-nitrobenzoate was obtained in 85% yield. It crystallized from ethyl alcohol as cream colored, elongated prisms; m. p. 75°.

Anal. Calcd. for $C_{16}H_{13}O_4N$: C, 67.82; H, 4.63; N, 4.95. Found: C, 67.36; H, 4.80; N, 4.80.

β-Indanyl *p*-nitrobenzoate was obtained in theoretical yield. It crystallized from ethyl alcohol as glistening cream colored rectangular plates; m. p. 139°.

Anal. Calcd. for $C_{16}H_{13}O_4N$: C, 67.82; H, 4.63; N, 4.95. Found: C, 67.50; H, 4.80; N, 4.85.

α-Indanyl α-naphthylurethan crystallized from ligroin (b. p. 100°), in about an hour deposited needle crystals; m. p. 137°. If the crystals were allowed to remain in the solvent overnight, they melted at 145°. The same change occurred in ethyl alcohol. A mixture of both forms melted at 145°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: C, 79.17; H, 5.65; N, 4.62. Found: C, 79.57; H, 5.76; N, 4.35.

β-Indanyl α-naphthylurethan crystallized from ethyl alcohol as colorless, needle-shaped crystals; m. p. 191°.

Anal. Calcd. for $C_{20}H_{17}O_2N$: C, 79.17; H, 5.65; N, 4.62. Found: C, 79.04; H, 5.82; N, 4.40.

Preparation of α-Indanyl Ethyl Ether by the Condensation of α-Indanol with Ethyl Alcohol.—To a solution of 7 g. of α-indanol in 25 cc. of ethyl alcohol, 25 cc. of water and 0.4 cc. of concentrated hydrochloric acid were added, and the mixture refluxed for ten minutes. A heavy oil separated which, after diluting the alcohol with water, was extracted with ether and washed free of acid. Evaporation of the ether yielded a yellowish oil containing an appreciable amount of chloroindane which was removed by refluxing for one hour with 100 cc. of 0.5 *N* alcoholic potassium hydroxide and the product isolated as before. Practically the entire material, 6 g., distilled from 78–80° at 2 mm. as a colorless oil having an aromatic pine-like odor.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.43; H, 8.70. Found: C, 81.00; H, 8.80; sp. gr. 20/4° 0.9938; n^{20}_D 1.5170. Molecular refraction using Lorentz–Lorenz formula, 49.35; molecular refraction theoretical (Brühl values), 49.03. Calcd. for indanyl ethyl ether: $-OC_2H_5$, 27.80. Found: $-OC_2H_5$, 28.05. Upon heating this compound with 57% hydriodic acid, ethyl iodide volatilized and was identified by conversion to ethyl 3,5-dinitrobenzoate; m. p. 92°.

Preparation of α-Indanyl Ethyl Ether by Condensing Chloroindane with Ethyl Alcohol.—To demonstrate that the condensation of α-indanol with ethyl alcohol in the presence of hydrochloric acid proceeds through the intermediate formation of chloroindane, a mixture of 8 g. of precipitated calcium carbonate and 100 cc. of ethyl alcohol was heated to boiling under reflux, and 20 g. of freshly distilled chloroindane added over a fifteen-minute period. The mixture was then refluxed for one hour, and allowed to stand at room temperature for forty-eight hours, after which the product was isolated and purified as described in the previous experiment. At 5.6 mm. a fraction of 2 g., chiefly indene, distilled from 53–58°, after which 14.5 g. distilled from 88–93°. This latter fraction from its characteristic odor and physical constants, was indanyl ethyl ether.

Condensation of α-Indanol to Diindanyl Ether.—A solution of 40 g. of α-indanol and 1.2 cc. of concentrated hydrochloric acid in 100 cc. of dioxane was refluxed for two hours, cooled, diluted with 200 cc. of water and the separated oil extracted with ether and washed with water. After removing the ether, the residual oil was distilled at 6.2 mm. A fraction of 4.7 g. of indene was obtained from 53–56°, after which 6 g. distilled from 93–112° consisting chiefly of chloroindane and α-indanol. The temperature then rose rapidly and 18 g. distilled from 193–195° as a pale yellow oil which solidified on standing and crystallized from methyl alcohol in colorless crystals; m. p. 50–55°. Microscopic examination of these showed two crystal forms, one elongated prisms and the other dendritic structures of flat plates. A warm 10% solution of this mixture in methyl alcohol, slowly cooled to room temperature in a closed flask, deposited long transparent prisms, mixed with flat plate-like crystals. The prisms were removed from the mixture by hand picking and melted at 68°. By redissolving the residual crystals in the mother liquor, the process was repeated. After a certain amount of the prisms had been removed, a crop consisting almost entirely of flat plates separated, m. p. 72°, which, when recrystallized from methyl alcohol, melted at 74°. It appears that both forms are present in the mixture in about equal amounts.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.35; H, 7.25. Found: mixture of both forms, C, 85.85; H, 7.58; compound, m. p. 68°, C, 85.83; H, 7.38; compound, m. p. 74°, C, 85.86; H, 7.49.

The mixture of isomers would not acetylate, formed no derivative with naphthyl isocyanate and evolved no methane in a Zerewitinoff determination. Neither of the isomers was optically active. When refluxed for two hours with 0.5 *N* alcoholic hydrochloric acid both yielded indene exclusively. The mixture when heated with water for two hours at 265° (500 lb. pressure) decomposed into indene and α-indanol. Similarly, when the mixture was vacuum distilled at 3 mm. approximately equal amounts of indene, α-indanol and undecomposed diindanyl ether were obtained.

Preparation of Diindanyl Ether by Condensing Chloroindane with α-Indanol.—By refluxing 16 g. of α-indanol in dioxane with 7.2 g. of calcium carbonate and 18 g. of chloroindane for two hours, following in general the procedure used for condensing chloroindane with ethyl alcohol, a product was obtained which, when distilled at 5 mm., yielded a fraction of 11.7 g. from 195–201°. When this was crystallized from methyl alcohol, it was found to consist of the mixture of isomers of diindanyl ether and was identical in all respects with the product resulting from the action of hydrochloric acid on α-indanol in dioxane.

Summary

New methods for preparing alpha and beta

indanol have been described, and several derivatives of these alcohols have been made.

It has been demonstrated that α-indanol exists in two distinct polymorphs.

This alcohol condenses readily with itself and with ethyl alcohol to yield indanyl ethers. Two isomeric forms of diindanyl ether have been separated, one melting at 68° and the other at 74°.

BROOKLYN, N. Y. RECEIVED OCTOBER 15, 1941

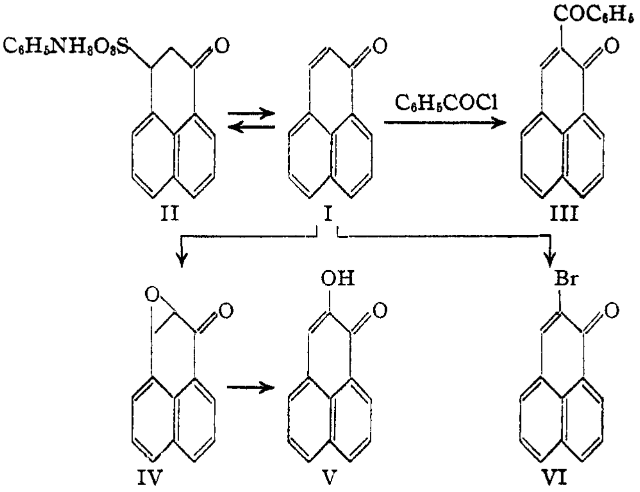
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Reactions of Perinaphthane Derivatives

BY LOUIS F. FIESER AND LAWRENCE W. NEWTON

Interest in the utilization of perinaphthenone and perinaphthanone derivatives as starting materials for the synthesis of polynuclear aromatic compounds[1] prompted the present exploratory study of other reactions of available members of the series.

Perinaphthenone (I), which is obtainable in quantity from β-naphthol and glycerol,[2,1a] resembles benzanthrone, of which it may be considered the parent substance, in giving a red vat with alcoholic alkali and hydrosulfite. Like an unsubstituted quinone, the bright yellow α,β-unsaturated ketone reacts with sodium bisulfite to give a colorless addition product, which was isolated in the form of an aniline salt presumably having the structure II; treatment of the salt with dilute hydrochloric acid at the boiling point results in the reversal of the reaction and precipitation of the ketone I. Although Zil'berman and Barkov[3] state that perinaphthenone reacts with hydroxylamine to give a nitrogen-free product, we found that the expected oxime can be obtained by refluxing the ketone with hydroxylamine hydrochloride in alcohol. Attempts to utilize perinaphthenone as a component in the Michael reaction, the Diels–Alder reaction, or the Friedel and Crafts condensation with benzene in the presence of aluminum chloride were unsuccessful and usually resulted in the recovery of unchanged starting material. A Friedel and Crafts condensation with benzoyl chloride was realized under forcing conditions which consisted in heating the components to 140° in the presence of aluminum chloride and zinc chloride. The chief product of the reaction proved to be 8-benzoylperinaphthenone-7 (III), for an identical orange-yellow substance was obtained by the condensation of the acid chloride of perinaphthenone-8-carboxylic acid (IX, below) with benzene in the presence of aluminum chloride. The reaction mixture from the benzoylation afforded also a second benzoylperinaphthenone which is less soluble and higher melting (304–307°) than the isomer III, and more highly colored (brownish red). The substance resembles 3,8 pyrenequinone[4] in color and melting point (309°) and may be the 3-benzoyl derivative of I.



In the reaction with hydrogen peroxide in aqueous alcohol in the presence of sodium carbonate, perinaphthenone was found to be attacked much less readily than 2-methyl-1,4-naphthoquinone,[5] but after somewhat prolonged heating the substance was converted into the oxide IV. The isomerization of this substance was effected, as in the naphthoquinone series,[5b] by dissolving the oxide in concentrated sulfuric

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[1] (a) Fieser and Hershberg, THIS JOURNAL, **60**, 1658 (1938); (b) Fieser and Hershberg, *ibid.*, **62**, 49 (1940); (c) Fieser and Novello, *ibid.*, **62**, 1855 (1940); (d) Fieser and Gates, *ibid.*, **62**, 2335 (1940).

[2] I. G. Farbenindustrie, German Patent 614,940 (1935) [*C. A.*, **29**, 8009 (1935)].

[3] Zil'berman and Barkov, *J. Gen. Chem., U. S. S. R.*, **7**, 1733 (1937) [*C. A.*, **32**, 538 (1938)].

[4] Vollman, Becker, Corell and Streeck, *Ann.*, **531**, 1 (1937).

[5] (a) Fieser, Campbell, Fry and Gates, THIS JOURNAL, **61**, 321 (1939); (b) Fieser, *J. Biol. Chem.*, **133**, 391 (1940).