165 g. of a solid, b. p. 162–200° at atmospheric pressure. Recrystallization from a benzene–petroleum ether solution gave 130 g., or a 50% yield, of 2,2-dimethyl-1,3-propanediol, m. p. 126–128°.

Preparation of 2,2-Dimethyl-1,3-dibromopropane.—Into a 1-liter flask was placed 208 g. (2 moles) of 2,2-dimethyl-1,3-propanediol, and to this was slowly added 542 g. (2 moles) of redistilled phosphorus tribromide, the flask being cooled in an ice-bath. A reflux condenser and thermometer were then attached, and the reaction mixture allowed to come to room temperature. It was heated to gentle refluxing for eighteen hours, and the temperature then raised to cause vigorous boiling. In six hours a red precipitate had formed. The temperature of the reaction mixture was increased to 140° and held there for eighteen hours. After cooling, it was poured onto ice and the resultant mixture steam distilled. The gummy orange residue in the flask was also steam distilled. The combined organic layers were dried over potassium carbonate, and the resulting 200 g. of material was distilled through a small packed column. From 8 moles of 2,2-dimethyl-1,3-propanediol was obtained 635 g., or a 34.6% yield of 2,2-dimethyl-1,3-dibromopropane, b. p. 84° at 28 mm., n^{20}_{D} 1.5050.

Preparation of 1,1-Dimethylcyclopropane.—The method of cyclization was that of Hass and McBee.[14] Into a 1-liter three-necked flask fitted with a dropping funnel, reflux condenser and mercury-sealed stirrer were placed 130 g. (2 moles) of zinc dust, 14 g. of sodium iodide, 43 g. of sodium carbonate, and 250 g. of dry recrystallized acetamide. The reflux condenser was connected to a dry-ice–acetone trap. The flask was kept between 150–165°, and 380 g. (1.65 moles) of 2,2-dimethyl-1,3-dibromopropane in the funnel was added dropwise to the reaction mixture in five hours. The 1,1-dimethylcyclopropane collected in the dry-ice–acetone trap was dried by passage over potassium hydroxide followed by phosphorus pentoxide. This product decolorized neither a dilute solution of bromine in carbon tetrachloride nor an alkaline potassium permanganate solution. It was distilled through the low temperature column in the Cryogenic Laboratory at 605 mm. to give fractions: 1, 12 cc., b. p. 14.4°; 2, 52 cc., 14.7°; 3, 45 cc., 14.8°; 4, 25 cc., 14.9°; residue, 30 cc., n^{20}_{D} 1.3873. Assuming dP/dT to be 30 mm./deg., the b. p. of fraction 2 at 760 mm. would be 19.9°. The m. p. was −108.4 to −107.3°.

Thanks are due to Dr. J. G. Aston for the use of the facilities of the Cryogenic Laboratory, and to Mrs. R. June Pfister, Mr. R. M. Kennedy, and Dr. Richard Greenberg for their invaluable assistance.

Summary

1. The products of the reaction of one mole of neopentyl chloride and one mole of sodium were 13% 2,2,5,5-tetramethylhexane, 36% neopentane, 25% 1,1-dimethylcyclopropane, and a trace of isobutylene.

2. The products of the reaction of five moles of neopentyl chloride and one mole of sodium were a trace of 2,2,5,5-tetramethylhexane, 41% neopentane, 51% 1,1-dimethylcyclopropane, and no isobutylene.

3. The bearing of these results on the mechanism of molecular rearrangements and of the Wurtz reaction has been discussed.

STATE COLLEGE, PENNA. RECEIVED JULY 15, 1940

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[14] McBee, Hass and Tarrant, Abstracts of the 97th Meeting, 1939, Am. Chem. Soc., Organic Section, p. 29, 1939.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY]

Scianthrene and the Synthesis of 1-Isopropyl-7-methylphenanthrene[1]

BY RUBY MURRAY ORCUTT AND MARSTON TAYLOR BOGERT

In a recent article,[2] Hidetaka Uota described an essential oil which he obtained by steam distillation of the finely divided twigs and leaves of the *Sciadopitys verticillata*, S. and Z., known as the "shade pine of South Japan." By distillation of this oil, in an atmosphere of carbon dioxide, at a pressure of 1 mm., he separated a fraction, b. p. 139–163° at 1 mm., from which there crystallized a new diterpene, sciadopitene, $C_{20}H_{32}$, m. p. 95–96°. Fusion of this solid with selenium, resulted in the production of a new hydrocarbon, $C_{18}H_{18}$, m. p. 86–87°, to which the author gave the name "scianthrene." A number of derivatives were prepared, and a series of reactions carried out which led him to the conclusion that this hydrocarbon was probably 1-isopropyl-7-methylphenanthrene, *i. e.*, an isomer of retene with the position of the two alkyl groups reversed.

Our laboratories being considerably interested in retene and related compounds, we have synthesized by two different methods what we believe to be the 1-isopropyl-7-methylphenanthrene, and the product so obtained does not agree in its properties with Uota's description of "scianthrene," as can be seen from the following comparison of melting points:

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[1] Presented in abstract before the Division of Organic Chemistry, at the Cincinnati Meeting of the Am. Chem. Soc., April 9, 1940.

[2] Uota, *J. Dept. Agr. Kyushu Imp. Univ.* **5**, 117–193 (1937); *C. A.*, **31**, 7416 (1937).

Compound	Scianthrene	1-Isopropyl-7-methyl-phenanthrene
Hydrocarbon	86–87	82–83
Picrate	123–124	119–120
Styphnate	138–139	148–149
Quinone	185–186	188–190
Quinoxaline	146	119–120

Uota reported also a trinitro*benzoate*, m. p. 146–147°. The product we obtained with trinitrobenzoic acid was, however, a trinitro*benzenate* and melted at 163–164°.

The steps in the syntheses of 1-isopropyl-7-methylphenanthrene appear in the Flow Sheet and require but little comment, since they follow well-known trails.

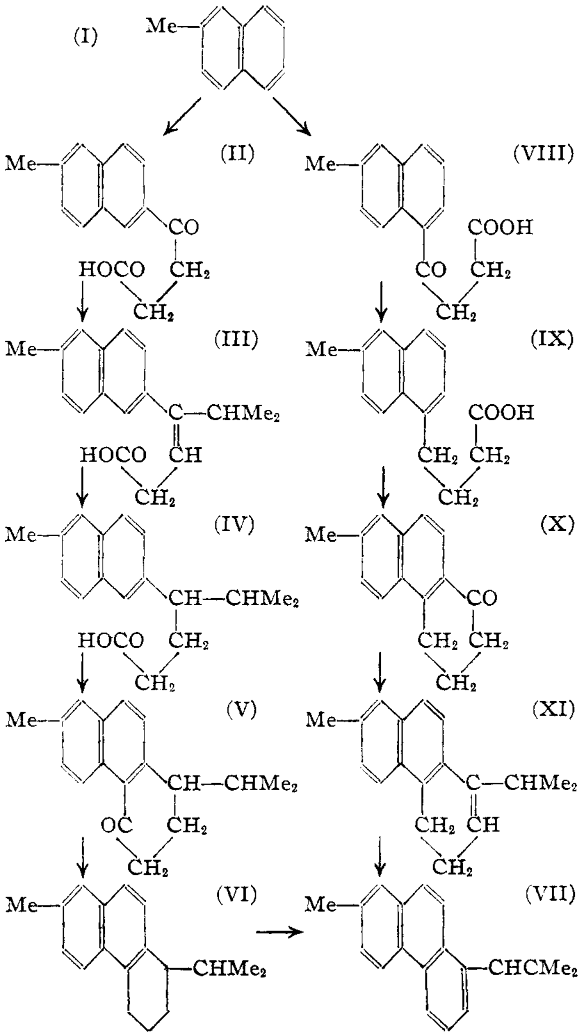
β-Methylnaphthalene (I), condensed with succinic anhydride, in nitrobenzene solution, by the action of aluminum chloride, gives β-(6-methyl-2-naphthoyl)-propionic acid (II), as shown by Haworth, Letsky and Mavin.[3] They observed that other acids are formed at the same time, but did not investigate them. We have now succeeded in isolating from these by-products a good yield (38%) of the isomeric β-(6-methyl-1-naphthoyl)-propionic acid (VIII).

In the first series of reactions, the methyl ester of the 2-naphthoyl acid (II) was the point of departure. This was subjected to the action of isopropylmagnesium iodide, in ether–benzene solution, followed by distillation of the intermediate hydroxy acid, and yielded the unsaturated isopropyl acid (III), which was in turn reduced by sodium amalgam to the corresponding saturated acid (IV). The latter was cyclized in benzene solution by the action of phosphorus pentachloride, followed by aluminum chloride, and the ketonic product (V) subjected to a Clemmensen reduction to form the tetrahydrophenanthrene (VI), whose dehydrogenation by selenium yielded the compound sought (VII).

In the second synthesis, the isomeric 1-naphthoylpropionic acid (VIII) served as the initial material, and the sequence of steps differed slightly from that of the first series, in that the naphthoyl derivative (VIII) was reduced first, by the Clemmensen method, to the methylnaphthylbutyric acid (IX), which was cyclized by phosphorus pentachloride, followed by aluminum chloride, to the ketophenanthrene (X). By the action of isopropylmagnesium iodide, and dehydration of the alcohol so formed, the dihydrophenanthrene (XI) was obtained. By digestion of the latter with selenium, the same product (VII) was obtained as in the first series; and this is evidence that in the first series the cyclization product (V) had the constitution assigned to it and was not the isomeric ketoanthracene.

Acknowledgment.—We are indebted to Mr. Saul Gottlieb of these laboratories for the analytical results reported in this paper.

FLOW SHEET



Experimental

A. Synthesis from β-(6-Methyl-2-naphthoyl)-propionic Acid

β-(6-Methyl-2-naphthoyl)-propionic Acid (II), and its methyl ester, were prepared from β-methylnaphthalene and succinic anhydride, as described by Haworth, Letsky and Mavin,[3] and our products agreed in their properties with the properties recorded by these investigators. The total yield of the acid was approximately 56%.

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[3] Haworth, Letsky and Mavin, *J. Chem. Soc.*, 1784 (1932).

γ-(6-Methyl-2-naphthyl)-δ-methylhydrosorbic Acid (III).—A solution of 26 g. of the methyl ester of (II) in 75 cc. of dry benzene, was treated at laboratory temperature with a solution of isopropylmagnesium iodide prepared from 35 g. of freshly distilled isopropyl iodide, 4 g. of magnesium turnings, and 50 cc. of anhydrous ether. As no reaction was evident, the mixture was warmed gradually and the ether vapor removed until a solution remained which boiled at about 70°. After four hours of refluxing at that temperature, the cooled solution was poured into acidulated ice water, the solvents eliminated by steam distillation, and the residue taken up in ether. The ether solution was washed twice with cold normal sodium hydroxide, to free the acid from unchanged initial ester (8 g. recovered, m. p. 82–83°). The yellow alkaline extract was acidified, the heavy oily precipitate collected in ether, the ether solution dried and the solvent removed. The residual viscous mass, presumably consisting of the hydroxy acid, proved so difficult to crystallize that it was subjected to distillation at a pressure of 2 mm. and a fraction obtained at 205°, accompanied by some decomposition. As this attempted purification by distillation was unsatisfactory, in subsequent experiments the entire crude acid product was converted into its methyl ester, whose ether solution was washed with a 10% sodium bicarbonate solution, dried over anhydrous sodium carbonate and distilled under a pressure of 2 mm. The fraction boiling at 185° (2 mm.) was a pale yellow oil and amounted to 12 g., or a yield of 60% based on the weight of ester used. Purified by a further rectification, it gave the following figures on analysis and was highly unsaturated toward both bromine and potassium permanganate.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.8; H, 7.9. Found: C, 80.6; H, 8.0.

Methyl γ-(6-Methyl-2-naphthyl)-δ-methylcaproic Acid (IV).—A mixture of 9.5 g. of the unsaturated acid (III), obtained by alkaline saponification of the above methyl ester and not further purified, with 380 g. of 2% sodium amalgam, 3 g. of sodium hydroxide, and 162 cc. of absolute methyl alcohol, was refluxed for six hours, left overnight, filtered, most of the methyl alcohol allowed to evaporate from the filtrate, and 400 cc. of water added. Acidification of this aqueous solution separated an oily precipitate, which was taken up in ether, the ether solution dried over sodium sulfate and the ether removed. The oily acid remaining (9 g.) was converted into its methyl ester and the crude ester (9 g.) distilled. A pale yellow clear oil was collected at 175°, under a pressure of 2 mm., which exhibited no unsaturation when treated in the cold with bromine in carbon tetrachloride, or potassium permanganate in acetone solution; yield, 74%, based on the initial unsaturated ester.

Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.2; H, 8.5. Found: C, 80.2; H, 8.5.

1-Isopropyl-7-methyl-4-keto-1,2,3,4-tetrahydrophenanthrene (V).—A mixture of 8.5 g. of the saturated acid, obtained by hydrolysis of the above ester (IV), with 6 g. of phosphorus pentachloride and 40 cc. of dry benzene, was refluxed for an hour, then cooled to 0° and treated gradually with 5.6 g. of aluminum chloride. After stirring for thirty minutes at room temperature and refluxing gently for a further two and one-half hours, the dark greenish mixture was poured into dilute acid containing ice and the benzene removed by steam distillation. The residue was taken up in ether, the ether solution washed with normal sodium hydroxide, and then with water, dried over sodium carbonate, and the ether removed. The dark-brown semisolid residue, amounting to 6.5 g., was dissolved in alcohol, the solution digested with Norit, and the filtered solution distilled. After the removal of the alcohol, the pressure was reduced to 2 mm. and a clear yellow oil came over at 175°. After two rectifications, the distillate solidified on standing and was crystallized from ethanol, giving white flaky crystals, m. p. 75–76° (cor.); yield, 74%.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.7; H, 8.0. Found: C, 85.9; H, 8.0.

Oxime.—Pale yellow leaflets, from alcohol, m. p. 205° (cor.), with deepening of color at 200° or above.

Anal. Calcd. for $C_{18}H_{21}ON$: N, 5.23. Found: N, 5.39.

1-Isopropyl-7-methyl-1,2,3,4-tetrahydrophenanthrene (VI).—A mixture of 6 g. of the above ketone (V), 20 cc. of toluene, 35 g. of amalgamated zinc, and 75 cc. of concentrated hydrochloric acid, was refluxed for twelve hours, followed by the addition of 25 cc. more hydrochloric acid and a further twelve hours of refluxing. The pale yellow oily layer was separated, washed once with a 5% sodium bicarbonate solution, then with water, dried over sodium carbonate, and the toluene distilled off. The residue was distilled over sodium, at a pressure of 2 mm., and 3 g. of colorless liquid collected at 175°. Purified by several rectifications, a colorless water-clear oil was obtained, of faint terpene-like odor; yield, 55%.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.7; H, 9.3. Found: C, 90.7; H, 9.4.

1-Isopropyl-7-methylphenanthrene (VII).—After heating 3.5 g. of the above hydrocarbon (VI) with 5 g. of selenium for twenty-four hours at 320–340°, the cold melt was extracted with petroleum ether and the solvent removed. The residual 3.2 g. partially solidified on standing. It was taken up in alcohol, decolorized by Norit, the solvent eliminated, and the residue distilled over sodium. A fraction, amounting to 2.5 g., was collected at 170°, under 1 mm. pressure, as a pale yellow oil which solidified as it cooled. Crystallized from alcohol, it formed white plates, m. p. 82–83° (cor.); yield, 70%.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.08; H, 8.02.

Picrate.—Orange needles, from alcohol, m. p. 119–120° (cor.).

Anal. Calcd. for $C_{24}H_{21}O_7N_3$: N, 9.07. Found: N, 9.09.

Styphnate.—Golden yellow silky needles, m. p. 148–149° (cor.), from alcohol.

Anal. Calcd. for $C_{24}H_{21}O_8N_3$: N, 8.77. Found: N, 8.71.

Trinitrobenzenate.—Prepared from an analytically pure sample of (VII) and trinitrobenzoic acid, in absolute ethanol solution, formed lemon-yellow needles, m. p. 163–164° (cor.).

Anal. Calcd. for $C_{24}H_{21}O_6N_3$: N, 9.40. Found: N, 9.55 and 9.58. The N calculated for the trinitrobenzoate is 8.55.

1-Isopropyl-7-methylphenanthraquinone.—Oxidation of the hydrocarbon (VII) in acetic acid solution with chromic oxide, yielded a quinone, which crystallized from alcohol in deep orange leaflets, m. p. 185–187° (cor.), darkening at 170°, and was still impure. It was therefore taken up in ether, the ethereal solution washed thoroughly with a 2% sodium bicarbonate solution, then with water, dried, the ether removed, and the residue purified by crystallization from alcohol. This product melted at 188–190° (cor.), with slight darkening at about 180°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.5; H, 6.2.

Quinoxaline.—Cream-colored fine needles, from alcohol, m. p. 119–120° (cor.).

Anal. Calcd. for $C_{24}H_{20}N_2$: N, 8.3. Found: N, 8.5.

B. Synthesis from β-(6-Methyl-1-naphthoyl)-propionic Acid

β-(6-Methyl-1-naphthoyl)-propionic Acid (VIII).—The acetic acid mother liquors from the preparation of the 2-naphthoyl isomer were concentrated, a large volume of water added, the precipitated solids collected, washed, and dissolved in normal sodium hydroxide. After digesting this alkaline solution with Norit, the clear pale brown solution was cooled and acidified with hydrochloric acid. The precipitated organic acid was somewhat oily, but tended to solidify on standing. It was collected in ether, the ethereal solution dried, the ether removed, and the residual acid esterified with absolute methanol and sulfuric acid. Fractionation of the crude ester, under 2 mm. pressure, yielded (a) 15 g., b. p. 200°, and (b) 8 g., b. p. 210–220°, from 28 g. of initial β-methylnaphthalene. Fraction (a) was analyzed, with the following results.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 75.0; H, 6.3. Found: C, 74.9; H, 6.3.

Hydrolyzed by boiling with 2 *N* sodium hydroxide, the free acid was obtained as a nearly colorless oily precipitate. It was collected in ether, the ether solution dried over anhydrous sodium sulfate, and the ether driven off. The oily residue (14 g.), on standing for several days, congealed to a mass of white needles. Recrystallized by chilling a saturated methanol solution, they melted at 141–143° (cor.).

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.31; H, 5.85.

Fraction (b) above (8 g.), b. p. 210–220° at 2 mm., when similarly hydrolyzed, gave an oily acid, from which there were obtained 4 g. of crystals, m. p. 140–144°, and 2 g., m. p. 160–163°, showing that this crude methyl ester (b) was evidently a mixture of the 1- and 2-naphthoyl isomers.

From the initial β-methylnaphthalene, the total yield of the 1-naphthoyl derivative was approximately 38%.

β-(6-Methyl-1-naphthyl)-butyric Acid (IX).—After boiling for nine hours a mixture of 9.5 g. of the above acid (VIII), 50 cc. of toluene, 12.5 g. of amalgamated zinc, and 40 cc. of concentrated hydrochloric acid, 10 cc. more of concentrated hydrochloric acid was added and the boiling continued for nine hours longer. The toluene was driven off with steam, the cooled oily residue extracted with ether, the ether solution dried and concentrated. There was thus obtained 8.5 g. of white crystals, m. p. 114–116°, which m. p. was raised to 116–118° (cor.) by further crystallizations from ether.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.1. Found: C, 78.9; H, 6.9.

Methyl Ester.—Colorless liquid, b. p. 160° at 2 mm.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5. Found: C, 79.2; H, 7.5.

7-Methyl-1-keto-1,2,3,4-tetrahydrophenanthrene (X) was prepared by cyclization of the above acid (IX), in practically the same way that (IV) was cyclized to (V). The ether solution of the crude product was washed twice with normal sodium hydroxide, to remove unchanged acid, then with water, dried, and the ether removed. The residue solidified as it cooled; yield, 7 g. from 10 g. of initial acid. Crystallized from petroleum ether, it formed yellow crystalline crusts which, when recrystallized from alcohol and decolorized by digestion with Norit, formed snow-white glistening leaflets, m. p. 92–94° (cor.).

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.7; H, 6.7. Found: C, 85.8; H, 7.0.

Semicarbazone.—Pale yellow needles, from alcohol, which began to sinter and darken at about 244°, and melted with decomposition at 258° (cor.).

Anal. Calcd. for $C_{16}H_{17}ON_3$: N, 15.7. Found: N, 15.8.

1-Isopropyl-7-methyl-3,4-dihydrophenanthrene (XI).—By the usual Grignard reaction, using isopropylmagnesium iodide upon the ketone (X), in an ether–benzene solution, followed by distillation of the crude intermediate tertiary alcohol, as described for the preparation of (III) from (II), this hydrocarbon was prepared. The crude product was obtained as a thick dark oil (14 g. from 14 g. of the ketone), which distilled at 175°, under a pressure of 15 mm., and was apparently a mixture of the tertiary alcohol and the unsaturated hydrocarbon, since it converted phenylisocyanate into carbanilide. It was therefore heated with potassium bisulfate (3 g.) until the water was removed, and the dry material was then distilled at 2 mm. pressure. Rectification of the distillate over sodium yielded a colorless oil, b. p. 150° at 2 mm., of terpenoid odor; yield, 6 g., or 38% (calculated to the ketone taken).

Anal. Calcd. for $C_{18}H_{20}$: C, 91.5; H, 8.5. Found: C, 91.7; H, 8.4.

1-Isopropyl-7-methylphenanthrene (VII).—A mixture of 2.5 g. of (XI) with 4 g. of selenium, was fused for twenty-four hours at 290–320°. The cooled product was extracted with petroleum ether, the solvent removed from the yellow fluorescent solution, the residue dissolved in alcohol, the solution decolorized (Norit), and the alcohol evaporated. The residue solidified on standing and amounted to 1.5 g., or about 60%. It was purified through the picrate, from which it was regenerated by the action of sodium carbonate solution, and then crystallized from alcohol, when it formed white plates, m. p. 82–83° (cor.), which m. p. remained practically unaltered when mixed with the 1-isopropyl-7-methylphenanthrene prepared by the first synthesis.

Anal. Calcd. for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.13; H, 7.94.

Picrate.—Orange needles, m. p. 119–120° (cor.), identical with the picrate of the first synthesis.

Anal. Calcd. for $C_{24}H_{21}O_7N_3$: N, 9.07. Found: N, 8.97.

Summary

The synthesis of 1-isopropyl-7-methylphenanthrene from β-methylnaphthalene by two different methods, gives a product that is not identical with the "scianthrene" obtained by Uota from the *Sciadopitys verticillata*, S. and Z., and to which he assigned that structure.

NEW YORK, N. Y. RECEIVED OCTOBER 10, 1940

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Studies of 1,3-Dienes. The Mercuration of 1,3-Butadiene and Synthesis of 2,3-Dialkoxy-1,3-butadienes

BY JOHN R. JOHNSON, WILLIAM H. JOBLING[1] AND GEORGE W. BODAMER

Under appropriate conditions typical ethylenic compounds undergo mercuration to give crystalline organomercury derivatives and the structure of these products has been definitely established. Although a few experiments on the mercuration of 1,3-dienes have been recorded, in no case has the constitution of the reaction products been determined with certainty. Thiele[2a] treated cyclopentadiene in ethyl alcohol with mercuric chloride and sodium acetate, and obtained an insoluble, intractable precipitate of unknown constitution, having the empirical formula $C_5H_4Hg_2Cl_2$. Recently Wright[2] succeeded in obtaining crystalline products by the mercuration of 1-phenyl-1,3-butadiene with mercuric acetate in methyl alcohol but encountered difficulties in attempting to establish their constitution. The present paper deals with the mercuration of 1,3-butadiene and with chemical transformations of the resulting organomercury compounds.

Pure 1,3-butadiene reacts rapidly with a solution of mercuric acetate in ethyl alcohol, giving rise to two isomeric crystalline diacetoxymercuridiethoxybutanes. The less soluble product (α-isomer, m. p. 162–163°) was isolated in 60% yield (average of five experiments) and the more soluble one (β-isomer, m. p. 111–112°) in 38% yield, indicating that the mercuration is essentially quantitative. Both isomers reacted immediately with cold dilute mineral acids to regenerate butadiene; both dissolved readily in aqueous alkali and were reprecipitated on neutralization with acetic acid. Treatment of the isomers with aqueous potassium iodide gave two different diiodomercuridiethoxybutanes, which in turn produced two isomeric diethoxydiiodobutanes when the iodomercuri groups were replaced by iodine (α-iodo derivative, m. p. 52–53°; β-iodo derivative, m. p. 46–47°). Either of the isomeric iodo derivatives gave the same diethoxybutadiene (m. p. 32°) when heated with sodium hydroxide. This indicates that the compounds of the α- and β-series are diastereoisomers and not structural isomers.

The constitution of the diethoxybutadiene was established conclusively by hydrolysis and by means of the Diels–Alder reaction. Cold dilute hydrochloric acid hydrolyzed the dialkoxydiene rapidly and quantitatively to biacetyl, which was identified as the dioxime and the phenylosazone. On heating with 1,4-naphthoquinone in benzene, the diene formed an adduct which readily was oxidized to 2,3-diethoxyanthraquinone (IV). On heating with sulfuric acid the latter was converted to 2,3-dihydroxyanthraquinone (hystazarin). The reaction of the diethoxybutadiene with toluquinone gave directly a small yield of 2-methyl-6,7-diethoxy-1,4-naphthoquinone. Evidently the intermediate adduct was dehydrogenated by the toluquinone, thereby reducing two-thirds of it to the hydroquinone.

The reactions of the diethoxydiene show conclusively that it is 2,3-diethoxybutadiene (III). From this it follows that the iodo derivatives are 2,3-diethoxy-1,4-diiodobutanes (II) and the original products of mercuration are the *meso* and racemic forms of 1,4-diacetoxymercuri-2,3-diethoxybutane (I).

$$CH_2{=}CH{-}CH{=}CH_2 + 2Hg(OAc)_2 + 2C_2H_5OH \longrightarrow$$

$$AcOHg{-}CH_2{-}CHOC_2H_5{-}CHOC_2H_5{-}CH_2{-}HgOAc \quad \text{(I)}$$

meso and racemic forms

$$\text{(I)} + KI + I_2 \longrightarrow$$

$$I{-}CH_2{-}CHOC_2H_5{-}CHOC_2H_5{-}CH_2I \quad \text{(II)}$$

meso and racemic forms

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(1) Du Pont Fellow in Chemistry, 1939–1940.

(2) (a) Thiele, *Ber.*, **34**, 71 (1901); (b) Wright, THIS JOURNAL, **57**, 1993 (1935).