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.

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[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).

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

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

meso and racemic forms

$$(I) + KI + I_2 \longrightarrow$$

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

meso and racemic forms

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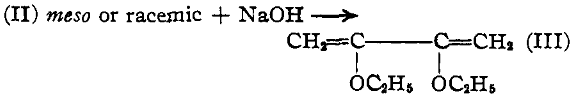
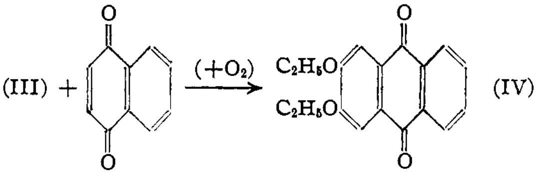
[1] Du Pont Fellow in Chemistry, 1939–1940.

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



$$\text{(II) } meso \text{ or racemic} + \mathrm{NaOH} \longrightarrow \underset{\mathrm{OC_2H_5}}{\mathrm{CH_2{=}C}}\!-\!\!-\!\!-\underset{\mathrm{OC_2H_5}}{\mathrm{C{=}CH_2}} \text{ (III)}$$

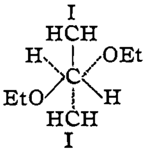
$$\text{(III)} + 2H_2O \longrightarrow CH_3{-}CO{-}CO{-}CH_3 + 2C_2H_5OH$$



Since the yield of 1,4-diacetoxymercuri-2,3-diethoxybutanes is almost quantitative, it is evident that the reaction of ethoxymercuric acetate with 1,3-butadiene involves independent contiguous addition and that no 1,4-addition takes place. If conjugate addition had occurred, one or more structural isomers of 1,4-diacetoxymercuri-2,3-diethoxybutane would necessarily have been formed.

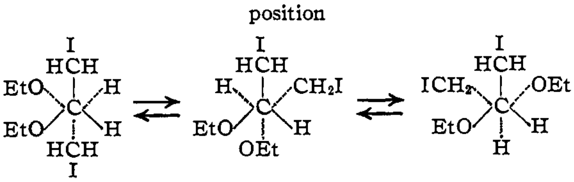
In an effort to establish the configurations of the compounds of the α- and β-series, attempts were made to convert the iodo compounds (II) in derivatives of *meso* and racemic tartaric acid. None of these was successful, owing to the inertness of the iodine atoms toward metathetical reagents—as has been observed in other β-halogenated ethers. Oxidation of the iodo compounds gave products that were of no value in establishing their configurations.

Considerations of the spatial distribution of the substituents in the stereoisomeric diiodides indicate that the *meso* form can assume a position in which both pairs of like substituents are *trans* to each other, whereas in the racemic form only one pair of identical substituents can be *trans* at any instant.



(Projection perpendicular to the central C—C axis, showing substituents on lower carbon atom in dotted lines.)

meso-Configuration—all pairs of substituents in *trans* position



d or *l* Configuration—only one pair of substituents in *trans* position

Electron diffraction studies of ethylene dihalides[3] and of the *meso* and racemic forms of 2,3-dibromobutane[4] have shown that in such molecules there is restricted rotation about the central C–C bond, and that the stable orientation is one in which the two halogens occupy a *trans* position. Assuming a similar restriction of rotation for the substituents $-OCH_3$ and $-CH_2I$ on the $C^2{-}C^3$ axis, one would expect the *meso* configuration to have a lower dipole moment than the racemic. This prediction is confirmed by the dipole moments of dimethyl α,β-dimethoxysuccinate and α,β-dichlorosuccinate, etc.,[5] which show the racemic form to have an appreciably higher dipole moment than the *meso* (3.16:2.79 and 3.00:2.40, respectively).

The dipole moments of the α- and β-forms of 1,4-diiodo-2,3-diethoxybutane were calculated from measurements of the dielectric constants in benzene solutions[6] and were found to differ appreciably ($\alpha = 1.70$, $\beta = 2.20$ Debye units). On the basis of these values the compounds of the α-series must be the *meso* forms and those of the β-series the racemic forms.

Butadiene reacts similarly with mercuric acetate in methyl alcohol but in this case the α-isomer of 1,4-diacetoxymercuri-2,3-dimethoxybutane (m. p. 148–149°) forms 80–85% of the product. By analogy with the ethoxy compounds, this is presumed to be the *meso* configuration. The β-isomer (racemic form) was isolated only in an impure state from the more soluble fractions. Treatment of the acetoxymercury compounds with potassium iodide followed by iodine gave the *meso* and racemic 1,4-diiodo-2,3-dimethoxybutanes (m. p. 99–100° and 37–38°). Either of the iodides gave 2,3-dimethoxy-1,3-butadiene on dehydrohalogenation with sodium hydroxide. Hydrolysis of the 2,3-dimethoxybutadiene gave biacetyl.

In the Diels–Alder reaction with 1,4-naphthoquinone, 2,3-dimethoxybutadiene gave an adduct that was converted by mild oxidation into 2,3-dimethoxyanthraquinone. Using maleic anhydride in a similar way, 4,5-dimethoxytetrahydrophthalic acid was obtained. Thus, the use of the 2,3-dialkoxybutadienes in Diels–Alder reactions makes possible the synthesis of a variety of di-

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[3] Beach and Palmer, *J. Chem. Phys.*, **6**, 639 (1938); Beach and Turkevich, THIS JOURNAL, **61**, 303 (1939).

[4] Stevenson and Schomaker, *ibid.*, **61**, 3173 (1939).

[5] Bodenheimer, cited in *Z. physik. Chem.*, Bodenstein-Festband, 620 (1931). For other examples, see Weissberger and Sängewald, *ibid.*, **9B**, 133 (1930), and **12B**, 399 (1931); Hassel and Naeshagen, *Tids. Kjemi Bergvesen*, **10**, 126 (1930), cited in *J. Org. Chem.*, **2**, 245 (1937).

[6] We are indebted to Mr. Leslie G. Joyner for these measurements.

alkoxy (and dihydroxy) systems which are relatively inaccessible by other methods.

Studies of the mercuration of substituted dienes in various hydroxylic media, and the use of the 2,3-dialkoxydienes in synthesis are in progress.

Experimental

1,3-Butadiene.—The crude butadiene prepared by the pyrolysis of cyclohexene[7] was purified by conversion to the monomeric sulfone,[8] which was recrystallized from water and reconverted into butadiene by heating. A weighed quantity of the dry sulfone was heated in an oil-bath at 160–165° and the evolved gases were passed through a tower filled with clay chips immersed in 25% sodium hydroxide solution (to remove the sulfur dioxide). The gaseous butadiene was either condensed in a freezing mixture or passed directly into a reaction mixture. The recovery of pure 1,3-butadiene from the sulfone was 93–95% of the theoretical amount.

In some of the latter experiments a high grade of butadiene (99%) from a commercial cylinder was used.

Mercuration in Ethyl Alcohol.—Forty grams (0.125 mole) of mercuric acetate and 225 cc. of absolute ethyl alcohol were placed in a 500-cc. filtering flask fitted with a large expansion bulb reaching nearly to the bottom of the flask. Gaseous butadiene (0.067 mole) from the sulfone, or from a measured quantity of liquid butadiene in a test-tube, was introduced through the side tube of the filtering flask. The reaction mixture was shaken to facilitate absorption of the gas. After the absorption started the flask was placed on a hot-plate and maintained just below the boiling point of the alcohol. The mercuration can be carried out with good results at room temperature but a longer time is required since the mercuric acetate dissolves quite slowly. When all of the butadiene had been absorbed a test portion of the solution was withdrawn and made alkaline with aqueous sodium hydroxide. If a yellow precipitate of mercuric oxide formed, a small additional quantity of butadiene was introduced and the absorption process continued until the sodium hydroxide test was negative.

meso - **1,4 - Diacetoxymercuri - 2,3 - diethoxybutane.**—The mercuration mixture was allowed to cool to 20° and the crystals of the less soluble product (α-isomer) were filtered with suction and washed twice with ether. The first crop of crystals weighed 20–23 g. The filtrate and washings were subjected to distillation on a steam-bath until most of the alcohol had been removed. The residue was filtered when cold and the filtrate was reserved for isolation of the more soluble product (β-isomer). The second crop of crystals of the α-isomer was washed with ether and combined with the first crop, giving a total of about 25 g. (60% yield, based on mercuric acetate) of the α-isomer. The product formed colorless crystals from ethyl alcohol; m. p. 162–163°.

Anal. Calcd. for $C_{12}H_{22}O_6Hg_2$: Hg, 60.5. Found: Hg, 60.8, 60.4.

The diacetoxymercury compound reacted immediately with cold dilute mineral acids to regenerate butadiene. It is sparingly soluble in water but dissolves readily in aqueous alkali, and is reprecipitated on neutralization with acetic acid. With alkali halides the insoluble dihalomercury derivatives are formed; treatment with bromine or iodine gives the corresponding 1,4-dihalo-2,3-diethoxybutane.

The α-isomer is assigned the *meso* configuration on the basis of comparison of the dipole moments of the α- and β-forms of the 2,3-diethoxy-1,4-diiodobutanes.

racemic - **1,4 - Diacetoxymercuri - 2,3 - diethoxybutane.**—The filtrate from the second crop of crystals of the α-isomer was diluted with 10 cc. of water and aspirated at 60–65°, adding more water as needed, until all of the acetic acid was removed. The weight of the final dry residue was 14–16 g. (33–38% yield). The crude β-isomer was recrystallized twice from warm water, and gave colorless crystals of the pure racemic form, m. p. 111–112°.

Anal. Calcd. for $C_{12}H_{22}O_6Hg_2$: Hg. 60.5. Found: Hg, 60.5, 59.9.

The chemical reactions of the β-isomer are similar to those of the α-isomer.

meso-**2,3-Diethoxy-1,4-diiodobutane.**—A solution of 25 g. (0.15 mole) of potassium iodide in 50 cc. of water was added with stirring to a suspension of 50 g. (0.075 mole) of the *meso* diacetoxymercury compound (m. p. 162–163°) in 200 cc. of water. After stirring for thirty minutes the precipitate of 2,3-diethoxy-1,4-diiodomercuributane was filtered with suction and allowed to dry in the air. The yield was practically quantitative.

The diiodomercury compound was refluxed with 200 cc. of carbon tetrachloride and 39 g. (0.153 mole) of iodine for two hours. Mercuric iodide appeared after the first few minutes of heating; the mixture was still colored due to excess iodine at the end of the heating period. The reaction mixture was filtered while hot and the residual mercuric iodide was washed with three portions of hot carbon tetrachloride. The filtrate and washings were evaporated until the solvent had been removed completely and then treated with hot water containing sodium bisulfite until the iodine color had disappeared. The product liquefied under hot water but crystallized on cooling. The crude material weighed 25–26 g. (85% yield). After three crystallizations from ethyl alcohol, and drying over calcium chloride, the product formed colorless crystals, m. p. 52–53°.

Anal. Calcd. for $C_8H_{16}O_2I_2$: I, 63.8. Found: I, 63.1, 62.9.

Attempts to convert the diiodide into 1,3-diethoxy-1,4-butanediol by heating with silver oxide and water were unsuccessful, and the diiodide was recovered unchanged. The same result was observed with silver acetate, and sodium cyanide. Oxidation of 10 g. of the diiodide with aqueous permanganate at 100° gave 1.1 g. of oxalic acid dihydrate; m. p. 100–101°, neut. equiv. 64. The identity of the oxalic acid dihydrate was confirmed by mixed m. p. with a known specimen.

The dipole moments of the α-diiodide (m. p. 52–53°) and β-diiodide (m. p. 46–47°) were found to be 1.70 and 2.20 Debye units, respectively, calculated by Onsager's formula from measurements of the dielectric constant in

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[7] Hershberg and Ruhoff, "Organic Syntheses," Vol. 17. 1937, p. 25.

[8] Staudinger and Ritzenthaler, *Ber.*, **68**, 455 (1935).

dilute benzene solution. The α-diiodide is therefore assigned the *meso* configuration, since this form should have a lower moment than the racemic modification.

***racemic*-2,3-Diethoxy-1,4-diiodobutane.**—The β-form of the diacetoxymercury compound (m. p. 111–112°) was converted to the diiodo derivative as described for the α-isomer. The racemic diiodomercury derivative separated as a white precipitate which changed rapidly to a greenish-yellow gum. The aqueous solution was poured off and the gummy product was refluxed with iodine in carbon tetrachloride for two hours. From 17 g. (0.25 mole) of the diacetoxymercury compound, 8.5 g. (0.51 mole) of potassium iodide, and 13 g. (0.51 mole) of iodine, there was obtained 8.1 g. of racemic-2,3-diethoxy-1,4-diiodobutane (80% yield). After three crystallizations from alcohol the product melted at 46–47°.

Anal. Calcd. for $C_8H_{16}O_2I_2$: I, 63.8. Found: I, 64.2, 63.9.

2,3-Diethoxy-1,3-butadiene.—A mixture of 25.7 g. (0.065 mole) of *meso*-2,3-diethoxy-1,4-diiodobutane (m. p. 52–53°) and 60 g. (1.5 moles) of pulverized sodium hydroxide was placed in a 125-cc. flask and heated in an oil-bath to 200–210°. The diethoxybutadiene distilled rapidly from the reaction mixture. The product weighed 4.3 g. (47% yield). Under similar conditions 9.0 g. (0.023 mole) of the racemic diiodide (m. p. 46–47°) and 20 g. (0.5 mole) of sodium hydroxide gave 1.4 g. of the same diene (44% yield).

Subsequent experiments showed that the dehydrohalogenation could be carried out more satisfactorily by using carbitol (diethylene glycol monoethyl ether) as a diluent, in the following manner: In a 500-cc. Claisen flask were placed 250 cc. of redistilled carbitol, 40 g. (0.1 mole) of *meso*-2,3-diethoxy-1,4-diiodobutane, and a solution of 12 g. (0.3 mole) of sodium hydroxide in 14 g. of water. On heating, water and the diene passed over and were caught in a receiver chilled in ice. The diene, which had solidified in the receiver, was warmed gently until it melted and then washed with warm water. The dry weight of the product was 9.5 g. (65% yield). On distillation the pure 2,3-diethoxy-1,3-butadiene boiled at 162–163° (740 mm.); the distilled product melted at 32°. The diene has a pleasant odor resembling anise. It is sparingly soluble in water but readily soluble in organic solvents.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.6; H, 9.92. Found: C, 66.16, 66.34; H, 9.64, 9.66.

Diethoxybutadiene is hydrolyzed rapidly by dilute mineral acids to give biacetyl. It reacts instantly with bromine, and takes part readily in Diels–Alder reactions.

A sample of the diene was shaken with dilute hydrochloric acid and hydroxylamine hydrochloride was added. The solution was made alkaline with sodium hydroxide and warmed for a few minutes on the steam-bath. Addition of a solution of nickel acetate gave immediately a pink precipitate of the characteristic nickel derivative of dimethylglyoxime.

In another experiment the hydrolyzed product was treated with phenylhydrazine hydrochloride and sodium acetate. The osazone of biacetyl precipitated on warming, and after washing with benzene melted at 241–242°. A mixed m. p. with authentic biacetyl osazone (m. p. 241–243°) was 241–243°.

Addition of 2,3-Diethoxy-1,3-butadiene to 1,4-Naphthoquinone: 2,3-Diethoxyanthraquinone.—A solution of 1.5 g. of the diene and 1.5 g. of 1,4-naphthoquinone in 3 cc. of benzene was refluxed for six hours. On cooling a purplish solid crystallized. The benzene and excess diene were evaporated from the reaction mixture, and the residue dissolved in alcohol. A small amount of sodium hydroxide was added, and air was blown through the solution. A yellow solid separated slowly. This was recrystallized twice from alcohol to give yellow needles melting at 167–168°. The reported melting point of 2,3-diethoxyanthraquinone is 160–163°, for a product obtained by ethylation of hystazarin.[9]

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 73.0; H, 5.45. Found: C, 72.44, 72.44; H, 5.3, 5.14.

A small amount of the product was dealkylated by heating with concd. sulfuric acid at 200–205° for fifteen minutes. When the resulting solution was poured over cracked ice an orange-yellow precipitate of hystazarin (2,3-dihydroxyanthraquinone) was obtained. Since the melting point of hystazarin is not recorded, the identity of the product was checked by the following color reactions: sodium hydroxide, blue solution; aqueous ammonia, violet solution; barium hydroxide, blue precipitate; calcium hydroxide, violet precipitate; concd. sulfuric acid, blood red solution; alcoholic ferric chloride, green coloration. The observed reactions were in agreement with those reported for hystazarin.[10]

2-Methyl-6,7-diethoxynaphthoquinone.[11]—A mixture of 0.4 g. (3.3 millimoles) of toluquinone and 0.54 g. (3.8 millimoles) of 2,3-diethoxybutadiene was heated under reflux on a steam-bath for thirty-six hours. The reaction mixture was taken up in 5 cc. of ethyl alcohol, from which the product separated in the course of several hours. Recrystallization from ethyl alcohol gave 0.1 g. of the quinone; orange needles, m. p. 132–133° (cor.).

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.20; H, 6.16. Found: C, 68.58; H, 6.28.

The yield in this reaction could undoubtedly be improved by using three molar equivalents of toluquinone to one of the diene, since the toluquinone acts as a dehydrogenating agent for the intermediate adduct.

1,4 - Diacetoxymercuri - 2,3 - dimethoxybutanes.—The apparatus and general procedure described for the mercuration in ethyl alcohol were used with slight modifications. A tube containing 10.6 cc. (6.8 g., 0.126 mole) of liquid butadiene was connected with the absorption flask which contained 250 cc. of boiling methyl alcohol and 80 g. (0.25 mole) of mercuric acetate, partly dissolved and partly in suspension. The contents of the flask were allowed to cool during the absorption of the diene, which was completed in thirty minutes. During this time the mercuric acetate dissolved completely and the diacetoxymercury compound began to separate.

The reaction mixture was cooled in a refrigerator at −10°, and the first crop of crystals of the α-isomer was filtered and washed with ether; weight 32 g., m. p. 145–146°. The filtrate and washings were distilled on the

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[9] Schoeller, *Ber.*, **22**, 684 (1889).

[10] Schoeller, *ibid.*, **21**, 2503 (1888).

[11] This experiment was carried out by Dr. B. R. Baker at the University of Illinois.

steam-bath until most of the methyl alcohol was removed, and on cooling a second crop was obtained; weight 13–14 g., m. p. 140–143°. The two crops were combined and recrystallized from ethyl alcohol to give the pure α-isomer of 1,4-diacetoxymercuri-2,3-dimethoxybutane, m. p. 148–149°. By analogy with the ethoxy series, this is presumed to be the *meso* form.

The filtrate from the second crop of the α-isomer was allowed to evaporate slowly in the air and the solid that separated spontaneously was filtered off at intervals of twelve hours. The first 10 g. of material collected in this way was preponderantly the α-isomer; although this material melted at 130–135° it gave a 60% yield of the α-diiodide when treated with potassium iodide and iodine (see below). The total yield of α-isomer in the mercuration is about 55–56 g. (70% of the theoretical).

The final crops of material, amounting to 8 g. (10% yield), consisted largely of the β-isomer since they gave the lower-melting, β-form of the diiodide. The crude β-diacetoxymercury compound could not be recrystallized satisfactorily and none of the pure compound was obtained.

1,4-Diiodo-2,3-dimethoxybutanes.—The pure α-diacetoxymercury compound was converted to the diiodomercury derivative and then to the diiodo compound as described for the ethoxy series. The purified α-isomer of 1,4-diiodo-2,3-dimethoxybutane was obtained in 80–85% yields; m. p. 99–100°. This is presumably the *meso* form.

Anal. Calcd. for $C_6H_{12}O_2I_2$: I, 68.6. Found: I, 68.4, 68.8.

The crude β-diacetoxymercury compound gave the β-isomer of 1,4-diiodo-2,3-dimethoxybutane, m. p. 37–38°, in 40–45% yield. The intermediate diiodomercury derivative discolored and became gummy in the same way as the corresponding β-ethoxy compound. The low-melting diiodide is presumably the racemic form.

Anal. Calcd. for $C_6H_{12}O_2I_2$: I, 68.6. Found: I, 68.3, 68.5, 68.8.

1,4-Dibromo-2,3-dimethoxybutane.[11]—In one experiment the total solid product of mercuration was converted by aqueous potassium bromide to the bromomercuridimethoxybutanes. The precipitate was dissolved in benzene, treated with bromine, and heated. Crystallization from ethyl alcohol gave the higher-melting α-dibromide, m. p. 83–84°, in about 30% yield. The β-dibromide was not isolated in a pure state.

Anal. Calcd. for $C_6H_{12}O_2Br_2$: C, 26.09; H, 4.35. Found: C, 26.23; H, 4.47.

2,3-Dimethoxy-1,3-butadiene.—The α-diiodide (m. p. 99–100°) was heated with aqueous sodium hydroxide and carbitol in the manner described for diethoxybutadiene. From 16 g. of the iodo compound there was obtained 4.0 g. (80%) yield of crude dimethoxybutadiene; b. p. 134–138°, m. p. 16–17°. In a larger scale preparation[11] the product was fractionated and the diene collected at 136–137°; $n^{28°}\mathrm{D}$ 1.4518, $n^{18°}\mathrm{D}$ 1.4563. This product was not analytically pure (C, 61.45, 61.64; calcd., 63.16). Another specimen which had been subjected to numerous manipulations in the air showed an even lower carbon content (51%). Evidently the diene undergoes alteration in the air, absorbing water or oxygen.

A purer sample of the diene was obtained by a slight modification of the dehydrohalogenation procedure. A solution of 158 g. of the α-diiodide in 500 cc. of warm carbitol (100°) was added dropwise to a solution of 43 g. of sodium hydroxide in 50 cc. of water and 100 cc. of carbitol, maintained at the boiling point (about 200°). The diene distilled from the reaction mixture during the addition of the diiodide and the reaction was stopped when the vapor temperature reached 135°. The diene was separated, washed with water, dried for twelve hours over magnesium sulfate, and redistilled. The fraction collected at 134.5–135.5° (745 mm.) was redistilled from metallic sodium under reduced pressure (nitrogen). This gave 23.5 g. (48% yield) of quite pure 2,3-dimethoxybutadiene; b. p. 51–52° (30 mm.), m. p. 19°.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.16; H, 8.77. Found: C, 62.49, 62.54; H, 8.90, 8.81.

Hydrolysis of the diene in the presence of a little hydrochloric acid, followed by addition of phenylhydrazine hydrochloride and sodium acetate, gave the osazone of biacetyl in 96% yield.

2,3-Dimethoxyanthraquinone.—A benzene solution of 1.5 g. of 2,3-dimethoxy-1,3-butadiene and 2.0 g. of 1,4-naphthoquinone was refluxed for eight hours. The benzene was evaporated and the residual purple-brown solid dissolved in alcohol. A preliminary test indicated that this adduct could not be oxidized merely by bubbling air through an alkaline solution. Upon treating the alcoholic solution of the adduct with aqueous sodium hypochlorite solution ("Clorox"), a solid separated at once. Two recrystallizations from ethyl alcohol gave yellow-brown crystals (1 g., 40% yield) of 2,3-dimethoxyanthraquinone, which melted at 231–233° (uncor.) and gave the characteristic blood red color with concd. sulfuric acid. The recorded melting points of this quinone are 235–236°, and 237°.[12]

Summary

Mercuration of 1,3-butadiene with mercuric acetate in methyl or ethyl alcohol gave the *meso* and racemic forms of 2,3-dialkoxy-1,4-diacetoxymercuributanes. Treatments of the acetoxymercury compounds with potassium iodide and iodine gave the corresponding crystalline *meso* and racemic forms of the 2,3-dialkoxy-1,4-diiodobutanes.

The configurations of the 2,3-diethoxy-1,4-diiodobutanes were established by comparisons of their dipole moments.

2,3-Dimethoxy- and 2,3-diethoxy-1,3-butadiene were synthesized by dehydrohalogenation of the 2,3-dialkoxy-1,4-diiodobutanes. These dienes undergo hydrolysis readily to give biacetyl and react with 1,4-naphthoquinone to give adducts that can be oxidized to 2,3-dialkoxyanthraquinones.

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[12] Perkin, *J. Chem. Soc.*, **91**, 2070 (1907); Lagodzinski, *Ber.*, **28**, 118 (1895); *Ann.*, **342**, 99 (1905).