

product. By moderating the conditions, an appreciable amount of monosulfonation took place.

2. In the sulfonation of propenylbenzene the sole product was 1-phenylpropene-2-sulfonic acid.

3. Allylbenzene gave about a 50% yield of 3-

phenyl-2-hydroxypropane-1-sulfonic acid, isolated as the barium salt from the hydrolyzed reaction mixture. An appreciable quantity of 3-phenyl-2-propene-1-sulfonic acid also was formed.

EVANSTON, ILLINOIS

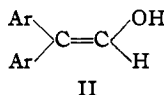
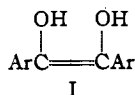
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Vinyl Alcohols. X.<sup>1</sup> 2,2-Diarylvinylic Alcohols

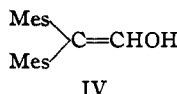
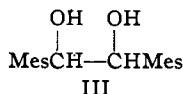
BY REYNOLD C. FUSON, PHILIP L. SOUTHWICK<sup>2</sup> AND STANLEY P. ROWLAND<sup>3</sup>

It has been demonstrated<sup>4</sup> that in stilbenediols (I) the tendency of a hydroxyl group to undergo ketonization is dependent on the radical in the 2 position to a greater extent than on that in the adjacent 1 position. It was conceivable that



crowding at the 1 carbon atom might be dispensed with altogether. This postulates the existence of a stable enol of type II. Reports have been made, in fact, of the isolation of certain diaryl-acetaldehydes in the corresponding enol forms. These claims, however, have not been substantiated.

In the search for such a vinyl alcohol it was assumed that its stability would increase with the size and complexity of the aryl radicals and attention was turned to the mesityl radical. As was reported earlier,<sup>5</sup> dehydration of hydromesitoin (III), isohydromesitoin<sup>6</sup> or a mixture of the two was found experimentally to yield the enol form (IV) of the normal rearrangement product, dimesitylacetaldehyde. The dehydration was accomplished with 55% sulfuric acid, a mixture of glacial acetic acid and hydrochloric acid or phosphorus pentoxide. In fact, the vinyl alcohol could be produced from isohydromesitoin simply by heating. The highest yields (80%) were obtained by the sulfuric acid method. Two high-melting by-products, apparently a dimer and a trimer of the vinyl alcohol, were isolated in small amounts.



2,2-Dimesitylvinylic alcohol (IV) yielded an acetate which proved to be unlike either of the

(1) For the preceding communication in this series see Fuson, Armstrong and Shenk, *THIS JOURNAL*, **66**, 964 (1944).

(2) Abbott Fellow, 1942-1943. Present address: Merck and Company, Rahway, New Jersey.

(3) du Pont Fellow in Chemistry, 1942-1943. Present address: Rohm and Haas Company, Philadelphia, Pennsylvania.

(4) Fuson and Soper, *THIS JOURNAL*, **65**, 915 (1943).

(5) Fuson and Rowland, *ibid.*, **65**, 992 (1943).

(6) Fuson, Horning, Ward and Marsh, *ibid.*, **64**, 30 (1942).

two 1,2-dimesitylvinylic acetates: 2,2-Dimesitylvinylic benzoate was also synthesized. It, likewise, was found to be different from the 1,2-dimesitylvinylic benzoates. These results confirm the conclusion that in the stable vinyl alcohol the two mesityl radicals are attached to the 2 carbon atom.

The new vinyl alcohol (IV) behaved in general as an alcohol rather than as an enol. For example, it was not acidic and gave no color with ferric chloride. Its stability was remarkable, as the methods of preparation attest. In contrast to typical enols, it was unaffected by oxygen even on long contact. Catalytic hydrogenation converted the vinyl alcohol to the corresponding saturated alcohol, 2,2-dimesitylethanol; m. p. 118-119°. The isomeric 1,2-dimesitylethanol melts at 128-129°.<sup>7</sup>

Attempts to bring about ketonization of the vinyl alcohol by heating with solutions of hydrogen chloride in methanol or ethanol produced solid derivatives which were identified as the corresponding methyl and ethyl ethers, respectively. In methanol under similar conditions isohydromesitoin also yielded the methyl ether. The aldehyde, 2,2-dimesitylacetaldehyde, which was to be expected is not known. There is, in particular, no evidence of the presence of the aldehyde in solutions of the enol.

Oxidation of the vinyl alcohol as well as of the corresponding saturated alcohol, 1,1-dimesitylethanol, generally produced abnormal changes. There was observed a pronounced tendency for rearrangement to a 1,2-dimesityl derivative. Thus when the vinyl alcohol was oxidized with ozone the product was mesitoin; chromic anhydride or selenium dioxide produced mesitil.

Oxidation with permanganate or hypochlorite produced a dimeric derivative, which had properties reminiscent of those of hexaarylethanes. Its solutions developed a red or purple color when heated. Cooling of the mixture discharged the color. The compound could be recovered unchanged. It contained one active hydrogen atom. No satisfactory formula has been written for this compound. Oxidation with chromic acid converted it to mesitil. There was evidence that

(7) Fuson, Denton and Best, *J. Org. Chem.*, **8**, 64 (1943).

in the oxidation of the vinyl alcohol the hydroxyl group was the point of attack for the acetate was not attacked by permanganate.

The only reagent which caused oxidation without rearrangement was alkaline hydrogen peroxide, which gave dimesityl ketone.

This tendency for rearrangement from the 2,2- to the 1,2-dimesityl structural type was encountered generally. Thus dehydration of 2,2-dimesitylethanol yielded 1,2-dimesitylethylene. 1,2-Dimesitylethylene was produced also by the action of concentrated sulfuric acid or hydriodic acid on isohydromesitoin. Reduction of isohydromesitoin with phosphorus and iodine yielded 1,2-dimesitylethane.<sup>8</sup> Treatment of the vinyl alcohol with a mixture of phosphorus pentachloride and phosphorus oxychloride converted it to 1,2-dichloro-1,2-dimesitylethane. Although this compound was not obtained in pure form, its structure can hardly be questioned. Dehydrochlorination transformed it into the hitherto unknown acetylenic compound, dimesitylacetylene.

High-pressure hydrogenation processes also led to curious results. Thus the vinyl alcohol was converted partially to dimesitylmethane by this method. The acetate also yielded this hydrocarbon.



It is to be expected that other 2,2-diarylvinyl alcohols in which the aryl radicals provide excessive crowding will prove to be stable also. This expectation has been confirmed in the case of 2,2-diisodurylvinyl alcohol (VI). This alcohol was made from hydroisoduroin (V) in a manner similar to that described for the synthesis of the dimesityl analog.

### Experimental

**2,2-Dimesitylvinyl Alcohol (from Hydromesitoin).**—A mixture of 5 g. of hydromesitoin and 90 cc. of 55% sulfuric acid was heated overnight on a steam-bath, cooled and filtered. The crude product was washed with water, dried and heated for a few minutes with methanol. The hot mixture was filtered to remove insoluble, solid material. This solid was heated under reflux with a large volume of ethanol and again collected by filtration of the hot mixture. After the insoluble solid had been recrystallized several times from ethyl acetate it melted at 290–292°. It formed fine, white platelets. Analysis and molecular weight determinations indicated that it was approximately a trimer of dimesitylvinyl alcohol.

*Anal.*<sup>9</sup> Calcd. for  $\text{C}_{60}\text{H}_{72}\text{O}_2$ : C, 85.67; H, 8.63; mol. wt., 841. Found: C, 86.73; H, 8.67; mol. wt. (ebullioscopic in chloroform), 875.

When the ethanol filtrate was cooled 0.5 g. of leaflets (m. p. 185–188°) was obtained. After recrystallization from ethanol the compound melted at 189–191°. Analysis and molecular weight determinations indicated that it was approximately a dimer of the vinyl alcohol.

(8) Wenzel, *Monatsh.*, **35**, 954 (1914).

(9) The microanalyses reported in this paper were carried out by Miss Margaret McCarthy, Miss Theta Spoor, Miss Dorothy Schneider, Miss Mary S. Kreger and Mr. L. G. Fauble.

*Anal.* Calcd. for  $\text{C}_{40}\text{H}_{48}\text{O}_2$ : C, 85.67; H, 8.63; mol. wt., 561. Found: C, 87.95; H, 8.54; mol. wt. (ebullioscopic in chloroform), 500.

The methanol filtrate mentioned earlier was evaporated to dryness and the 2,2-dimesitylvinyl alcohol, thus obtained, was recrystallized from high-boiling petroleum ether. At this point the vinyl alcohol weighed 3 g. and melted at 126–129°. The pure compound melted at 129–129.5°.<sup>5</sup>

**From Isohydromesitoin.**—Five grams of isohydromesitoin, treated with 55% sulfuric acid by the procedure used with the isomeric glycol, yielded 3.8 g. of 2,2-dimesitylvinyl alcohol along with traces of higher melting solids.

The vinyl alcohol was also produced from isohydromesitoin by heating with a mixture of acetic and hydrochloric acids. A mixture of 2 g. of isohydromesitoin, 24 cc. of hot glacial acetic acid and 6 cc. of hydrochloric acid was heated for one hour under reflux. Water was added to the hot solution in sufficient amount to cause a slight turbidity and, after the mixture had cooled to room temperature, the solid was removed by filtration. The 2,2-dimesitylvinyl alcohol was recrystallized from methanol; m. p. 128–129; yield 1.1 g.

The dimesitylvinyl alcohol could be obtained also by heating isohydromesitoin with phosphorus pentoxide. At 285° the glycol underwent dehydration without a catalyst to yield the vinyl alcohol.

Oxygen was bubbled through a solution of 2 g. of 2,2-dimesitylvinyl alcohol in 100 cc. of acetone for one hundred hours. Only unchanged vinyl alcohol was isolated.

The benzoate of the vinyl alcohol was also purified by recrystallization from methanol; m. p. 175.5–176°.

*Anal.* Calcd. for  $\text{C}_{27}\text{H}_{25}\text{O}_2$ : C, 84.34; H, 7.34. Found: C, 84.40; H, 7.60.

The acetate of 2,2-dimesitylvinyl alcohol crystallized from methanol; m. p. 132.5–133°.

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{26}\text{O}_2$ : C, 81.95; H, 8.13. Found: C, 82.14; H, 8.33.

Ozonization of 5.7 g. of 2,2-dimesitylvinyl acetate in 80 cc. of carbon tetrachloride yielded a solid product which, when recrystallized from high-boiling petroleum ether, melted at 198–199°. It was shown by the method of mixed melting points to be identical with a specimen of dimesitylacetic acid which was made from dimesitylketene.<sup>10</sup>

An attempt was made to oxidize the acetate with permanganate under the conditions described for the oxidation of the vinyl alcohol. The acetate was recovered unchanged.

Hydrogenation of 3 g. of the acetate of 2,2-dimesitylvinyl alcohol at 200° and 3000 pounds of hydrogen pressure yielded 1 g. of dimesitylmethane melting at 135–136°.<sup>11</sup>

**An Attempt to Ketone 2,2-Dimesitylvinyl Alcohol.**—A solution of 2 g. of the vinyl alcohol in 70 cc. of methanolic hydrogen chloride was heated for eighteen hours under reflux. The 2,2-dimesitylvinyl methyl ether crystallized from methanol in platelets; m. p. 129–130°; yield 1.8 g.

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{20}\text{O}$ : C, 85.67; H, 8.90. Found: C, 85.95; H, 9.19.

The same compound was formed when isohydromesitoin was treated with methanolic hydrogen chloride. To 40 cc. of methanol, previously saturated with dry hydrogen chloride, was added 1.2 g. of isohydromesitoin. The mixture was shaken until solution was complete and was allowed to stand at room temperature for seven hours. The product was removed by filtration and recrystallized from methanol; m. p. 129–130°.

Treatment with hydriodic acid in glacial acetic acid converted the ether to 1,2-dimesitylethylene.<sup>7</sup>

**2,2-Dimesitylvinyl Ethyl Ether.**—Treatment of the vinyl alcohol with ethanolic hydrogen chloride yielded the ethyl ether. It was crystallized from methanol; m. p. 96–97°.

(10) A report of this synthesis will be presented separately.

(11) Baeyer, *Ber.*, **5**, 1094 (1872); Kohler and Baltzly, *THIS JOURNAL*, **54**, 4015 (1932).

*Anal.* Calcd. for  $C_{22}H_{28}O$ : C, 85.64; H, 9.18. Found: C, 86.22; H, 9.12.

#### Reduction of 2,2-Dimesitylvinyl Alcohol

(A) **With Zinc Dust.**—When the vinyl alcohol was mixed with half its weight of zinc dust, heated at  $300^\circ$  for thirty minutes and distilled under diminished pressure, 1,2-dimesitylethylene was obtained.

(B) **By the Clemmensen Method.**—Amalgamated zinc in a hydrochloric-glacial acetic acid mixture (1:5) has no effect on the vinyl alcohol.

(C) **With Phosphorus and Iodine.**—A mixture of 1 g. of the vinyl alcohol, 0.6 g. of red phosphorus, 0.4 g. of iodine, five drops of water and 30 cc. of glacial acetic acid was heated under reflux for nineteen hours and poured into water. The product, 1,2-dimesitylethane (m. p.  $117-118^\circ$ ), was obtained in nearly quantitative yield.

(D) **With Hydriodic Acid.**—A mixture of 0.5 g. of the vinyl alcohol, 15 cc. of glacial acetic acid and 5 cc. of hydriodic acid (sp. gr. 1.50) was heated for one hour on a steam-bath and cooled. The long needles which separated were identified as 1,2-dimesitylethylene.

(E) **With Hydrogen.**—A solution of 10 g. of the vinyl alcohol in 100 cc. of ethanol was subjected for six hours to a hydrogen pressure of 2000 to 3000 pounds and a temperature of  $200^\circ$  in the presence of a Raney nickel catalyst. There was obtained 3 g. of dimesitylmethane.<sup>11</sup> The methanolic filtrates were evaporated, and the residue was crystallized from high-boiling petroleum ether. The product, 2,2-dimesitylethanol, melted at  $118-119^\circ$ .

*Anal.* Calcd. for  $C_{20}H_{26}O$ : C, 85.05; H, 9.28. Found: C, 84.78; H, 9.27.

A 5-g. sample of the vinyl alcohol was hydrogenated under similar conditions in the presence of a copper chromite catalyst. The products were the same as with Raney nickel.

2,2-Dimesitylethanol formed an acetate in good yield when treated with a 40% solution of acetic anhydride in pyridine. The acetate crystallized from methanol in fine, white needles; m. p.  $164.5-165^\circ$ .

*Anal.* Calcd. for  $C_{22}H_{28}O_2$ : C, 81.44; H, 8.70. Found: C, 81.34; H, 8.28.

The benzoate of 2,2-dimesitylethanol was formed by treatment with benzoyl chloride and pyridine. It crystallized from methanol in fine, white plates; m. p.  $151.5-152.5^\circ$ .

*Anal.* Calcd. for  $C_{27}H_{30}O_2$ : C, 83.90; H, 7.82. Found: C, 83.97; H, 7.95.

Oxidation of 2,2-dimesitylethanol with chromic anhydride yielded dimesityl ketone. A mixture of 1 g. of the ethanol, 2.5 g. of chromic anhydride and 80 cc. of glacial acetic acid was allowed to stand for thirty-six hours, with occasional shaking. The product melted at  $135-136^\circ$  and did not depress the melting point of a known sample of dimesityl ketone.

When 0.7 g. of 1,2-dimesitylethanol was heated overnight on a steam-bath with 20 cc. of water and 6 cc. of sulfuric acid it was converted to 1,2-dimesitylethylene.

A mixture of 0.4 g. of 2,2-dimesitylethanol, 0.4 g. of red phosphorus, 0.4 g. of iodine, 5 drops of water and 35 cc. of glacial acetic acid was heated under reflux overnight. There was obtained 0.4 g. of 1,2-dimesitylethane; m. p.  $117-118^\circ$ .

#### Oxidation of 2,2-Dimesitylvinyl Alcohol

(A) **With Ozone.**—A 5.5% stream of ozone was passed through a solution of 2 g. of 2,2-dimesitylvinyl alcohol in 50 cc. of carbon tetrachloride solution at room temperature for one hour. The mixture was poured into water containing a little hydrogen peroxide, and the resulting mixture was heated under reflux for one hour. The product, after being recrystallized repeatedly from high-boiling petroleum ether, melted at  $130-131^\circ$ . It did not depress the melting point of mesitol.

(B) **With Chromic Anhydride.**—Two and one-half grams of chromic anhydride was added to a cold solution

of 1 g. of 2,2-dimesitylvinyl alcohol in 80 cc. of glacial acetic acid. After the mixture had been allowed to stand overnight, it was poured into water. The product melted at  $122-123^\circ$  and proved to be mesitol.

Oxidation with selenium dioxide also produced mesitol.

(C) **Alkaline Potassium Permanganate.**—A solution of 0.5 g. of potassium permanganate in 12 cc. of water was added slowly to a solution of 0.9 g. of 2,2-dimesitylvinyl alcohol in 20 cc. of acetone. The solution was stirred for a few minutes and poured into water. The product, a pink solid, was recrystallized from high-boiling petroleum ether. It formed fine, white needles which melted to a red liquid, with evolution of a gas, at  $184.5-185^\circ$ .

*Anal.* Calcd. for  $C_{40}H_{46}O_2$ : C, 85.97; H, 8.30; mol. wt., 559. Found: C, 86.08, 85.89; H, 8.48, 8.30; mol. wt. (ebullioscopic in chloroform), 543.

This dimeric oxidation product of the vinyl alcohol developed a violet to red color when heated in solution to  $70^\circ$  or higher. When the solution was cooled the color disappeared and the original dimeric compound could be recovered.

(D) **With Ethanolic Potassium Hydroxide.**—A solution of 2 g. of the vinyl alcohol and 2 g. of potassium hydroxide was heated under reflux for eight hours and diluted with water. In addition to unchanged vinyl alcohol there was isolated 0.25 g. of white crystals melting at  $182-183^\circ$ . These proved to be identical with those produced by oxidation of the vinyl alcohol with potassium permanganate.

(E) **With Sodium Hypochlorite.**—To a solution of 2 g. of 2,2-dimesitylvinyl alcohol in 40 cc. of methanol was added 5 cc. of hypochlorite reagent, prepared by passing 3.3 g. of chlorine into a cooled solution of 3.5 g. of sodium hydroxide in 25 cc. of water. The mixture was allowed to stand for fifteen minutes and diluted with water. The solid product was removed and recrystallized from ethyl acetate. There was obtained 1.2 g. of white crystals melting at  $179-180^\circ$ . This product was identical with that obtained by the oxidation with potassium permanganate. It was not altered by further treatment with hypochlorite.

A mixture of 1.8 g. of the dimeric oxidation product, 3.5 g. of chromic anhydride and 80 cc. of glacial acetic acid was allowed to stand for thirty-six hours and poured into water. The yellow product, when purified by recrystallization from methanol, melted at  $122-123^\circ$  and did not depress the melting point of a known sample of mesitol. The yield was 0.7 g.

A solution of 1.8 g. of the dimeric oxidation product in 80 cc. of absolute methanol (or ethanol) was saturated with hydrogen chloride and heated overnight under reflux. The product separated from ethyl acetate in hard, white plates; m. p.  $180-181^\circ$ . This compound gave a  $10^\circ$  depression of the melting point when mixed with a sample of the dimeric oxidation product. The new substance exhibited none of the color phenomena of the parent compound.

*Anal.* Calcd. for  $C_{38}H_{44}O_2$ : C, 85.15; H, 8.37. Found: C, 85.19; H, 8.31.

The dimeric oxidation product was not reduced in the presence of a platinum oxide catalyst under atmospheric pressure of hydrogen. In the Grignard machine<sup>12</sup> it slowly liberated one mole of methane.

**Oxidation of Isohydromesitoin.**—A mixture of 1 g. of isohydromesitoin, 2.5 g. of chromic anhydride and 80 cc. of glacial acetic acid was allowed to stand overnight at room temperature. The product, melting at  $152-153^\circ$ , was shown to be mesitoic acid.

#### Reduction of Isohydromesitoin

(A) **With Phosphorus and Iodine.**—A mixture of 1 g. of isohydromesitoin, 0.6 g. of iodine, 0.4 g. of red phosphorus, a few drops of water and 30 cc. of glacial acetic acid was heated overnight under reflux and poured into water. The product, melting at  $117-118^\circ$ , proved to be 1,2-dimesitylethane.<sup>8</sup>

(B) **With Hydriodic Acid.**—A mixture of 1 g. of isohydromesitoin, 10 cc. of hydriodic acid and 30 cc. of glacial

(12) Kohler and Richtmyer, *This Journal*, **52**, 3736 (1930).

acetic acid was heated for three hours on a steam-bath. The product was 1,2-dimesitylethylene; m. p. 128–131°; yield 0.8 g.

(C) **With Sulfuric Acid.**—In an attempt to dehydrate isohydromesitoin treatment with concentrated sulfuric acid was tried. The glycol (4.5 g.) was dissolved slowly in 30 cc. of concentrated sulfuric acid which had been cooled to 0°. The deep brown solution was kept cool for five minutes and then poured on 600 g. of ice. The solid was collected, dried and dissolved in methanol. From this solution a small amount of sandy solid separated. After two crystallizations from methanol it formed white crystals; m. p. 128–130°. A mixture with 1,2-dimesitylethylene showed no depression in melting point.

**1,2-Dichloro-1,2-dimesitylethane.**—A mixture of 1 g. of isohydromesitoin, 2 g. of phosphorus pentachloride and 10 cc. of phosphorus oxychloride was allowed to stand overnight. This mixture was poured into water and the dichloride was extracted with ether; m. p. 176–179°; yield 0.7 g.

*Anal.* Calcd. for  $C_{20}H_{24}Cl_2$ : C, 71.64; H, 7.21. Found: C, 71.43; H, 7.33.

The dichloride was formed also from 2,2-dimesitylvinyl alcohol by a procedure similar to the above; m. p. 173–176°. The same compound was produced when a chloroform solution of 1,2-dimesitylethylene was treated with phosphorus pentachloride; m. p. 170–175°. Recrystallization of this product from high-boiling petroleum ether or methanol failed to change the melting point. It is presumed that the substance is a mixture of the two possible diastereoisomers.

From the methanol mother liquor was isolated a compound melting at 127–128° which was shown by the method of mixed melting points to be 2,2-dimesitylvinyl methyl ether. The final step in the formation of the ether may be similar to that involved in the conversion of 2,2-diphenyl-1-chloroethylene into 2,2-diphenylvinyl ethyl ether by the action of sodium ethoxide.<sup>14</sup>

**Dimesitylacetylene.**—A solution of 0.7 g. of the dichloride, 1.8 g. of potassium hydroxide and 25 cc. of ethanol was heated under reflux for four hours. The dimesitylacetylene was recrystallized from methanol; m. p. 127.5–128.5°.

*Anal.* Calcd. for  $C_{20}H_{22}$ : C, 91.55; H, 8.45. Found: C, 91.61; H, 8.61.

**Cleavage of Isohydromesitoin.**—A solution of 3 g. of isohydromesitoin in 40 cc. of ethanol was subjected for two hours to a nitrogen pressure of 1500 pounds and a temperature of 200° in the presence of a copper chromite catalyst. The product melted at 88–89° and did not depress the melting point of a known sample of mesitylcarbinol. Ethyl acetate was also detected. The experiment was repeated with petroleum ether as solvent instead of ethanol. The product was mesitaldehyde, which was oxidized in the air to mesitoic acid; m. p. 152–153°; yield 1.8 g.

(13) This experiment was carried out by Dr. Chris E. Best.

(14) Buttenberg, *Ann.*, **279**, 324 (1894).

**Isoduraldehyde.**—This aldehyde was made by the Adams and Montgomery<sup>15</sup> modification of the Gattermann method. It was purified by fractional distillation; b. p. 112–114° (3 mm.);  $n_D^{20}$  1.5560. It solidified to colorless crystals; m. p. 22–25°.

*Anal.* Calcd. for  $C_{11}H_{14}O$ : C, 81.44; H, 8.70. Found: C, 81.55; H, 8.90.

Exposure to air caused oxidation to 2,3,4,6-trimethylbenzoic acid which was purified by recrystallization from high-boiling petroleum ether; m. p. 166–167°. The melting point given by Gattermann<sup>16</sup> was 164–165°.

**Hydroisoduroin.**—Treatment of isoduraldehyde with the binary mixture Mg–MgI<sub>2</sub><sup>17</sup> converted it to a mixture from which one form of the expected hydrosodurion was isolated, along with its dehydration product, 2,2-diisodurylvinyl (m. p. 149.5–151.5°).

The glassy solid obtained by the reduction of 20 g. of the aldehyde was treated with 100 cc. of low-boiling petroleum ether. The hydroisoduroin was insoluble. It was removed by filtration and recrystallized from methanol from which it separated in white needles; m. p. 225.5–226.5°.

*Anal.* Calcd. for  $C_{22}H_{30}O_2$ : C, 80.94; H, 9.26. Found: C, 81.18; H, 9.09.

**2,2-Diisodurylvinyl Alcohol.**—A mixture of 0.3 g. of hydroisoduroin, 24 cc. of glacial acetic acid and 6 cc. of concentrated sulfuric acid was heated under reflux for three hours and allowed to stand overnight. Dilution of the mixture with water precipitated the vinyl alcohol. It crystallized from methanol in large, clear prisms; m. p. 149.5–151.5°. A mixed melting point determination showed it to be identical with the sample of the vinyl alcohol obtained from the reduction mixture.

*Anal.* Calcd. for  $C_{22}H_{28}O$ : C, 85.64; H, 9.18. Found: C, 85.13; H, 9.17.

Samples of this vinyl alcohol showed no change after two years of standing in the air.

When the vinyl alcohol was treated with benzoyl chloride in the presence of pyridine, a benzoate was formed. It was recrystallized from absolute alcohol; m. p. 156.5–158°.

*Anal.* Calcd. for  $C_{23}H_{32}O_2$ : C, 84.42; H, 7.82. Found: C, 84.59; H, 7.70.

### Summary

Hydromesitoin and isohydromesitoin have been found to undergo dehydration to yield 2,2-dimesitylvinyl alcohol.

Numerous reactions of the new vinyl alcohol have been reported.

2,2-Diisodurylvinyl alcohol has also been described.

URBANA, ILLINOIS

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(15) Adams and Montgomery, *THIS JOURNAL*, **46**, 1518 (1924).

(16) Gattermann, *Ber.*, **32**, 1118 (1899).

(17) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236 (1927); **52**, 4967 (1930).