

3-Bromomesitylacetyl chloride (0.38 g.) was obtained as alkali-insoluble residue. After crystallization from benzene-high-boiling petroleum ether, it formed white, fluffy needles melting at 231–232°.

Anal. Calcd. for $C_{11}H_{11}ONBr$: C, 51.58; H, 5.51. Found: C, 51.78; H, 5.49.

The acid was converted to the *acid chloride* (b. p. 146–148° (4 mm.)) in 85% yield by the action of thionyl chloride at room temperature.

3-Bromodesoxymesitoin.—A solution of 3-bromomesitylacetyl chloride (3.25 g.) in mesitylene (5 cc.) was added over fifteen minutes to a stirred mixture of mesitylene (15 cc.), aluminum chloride (2 g.), and carbon disulfide (40 cc.) at 0°. Over one hour, the mixture was gradually warmed to 50°, at which temperature it refluxed gently for fifteen minutes. It was decomposed with ice and hydrochloric acid; the organic layer was diluted with 100 cc. of ether and washed with dilute alkali and water. Steam distilla-

tion removed the solvents and excess mesitylene; the residue was dried and crystallized from absolute alcohol. The white solid product melted at 97–99°; a mixture with the product of the Friedel-Crafts reaction between mesitylacetyl chloride and bromomesitylene melted at 97–99°.

Summary

Isomeric bromo 1,2-dimesityl-1-propen-1-ols have been prepared; they are very unstable compared to similar vinyl alcohols containing no halogen substituent.

The Friedel-Crafts reaction of mesitylacetyl chloride and bromomesitylene has been shown to yield 3-bromodesoxymesitoin instead of the expected 3'-bromo compound.

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

Enediols. XI.¹ Vinylogs of Ethylene and Acetylene Glycols

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The production of a stable vinyl alcohol by the hydrogenation of mesityl α -mesitylvinyl ketone (I)³ suggested that the corresponding dienol (II) might be formed if the reduction could be caused to take place bimolecularly. Experiment has shown that this type of reduction can be accomplished readily and in high yield by use of the binary mixture, Mg-MgI₂.⁴

The structure of the dienol, 1,2,5,6-tetramesityl-1,5-hexadien-1,6-diol (II), was established by use of the cleavage described recently for enols of this type.⁵ Treatment with oxygen converted it to mesitol and 1,2-dimesitylolethane (III).

The dienol exhibited chemical properties similar to those of the mono-enol. It could be ketonized by long treatment with hot alcoholic hydrogen chloride to yield 1,2,5,6-tetramesityl-1,6-hexanedione (IV). The dienol was regenerated by use of ethylmagnesium bromide. Oxidation with permanganate brought about cleavage, giving the parent vinyl ketone (I). This remarkable reaction resembles the cleavage of 1,2-glycols by lead tetraacetate⁶; it was found that cleavage to the vinyl ketone could be effected with this reagent.

(1) For the tenth communication of this series see Fuson and Scott. *THIS JOURNAL*, **64**, 2152 (1942).

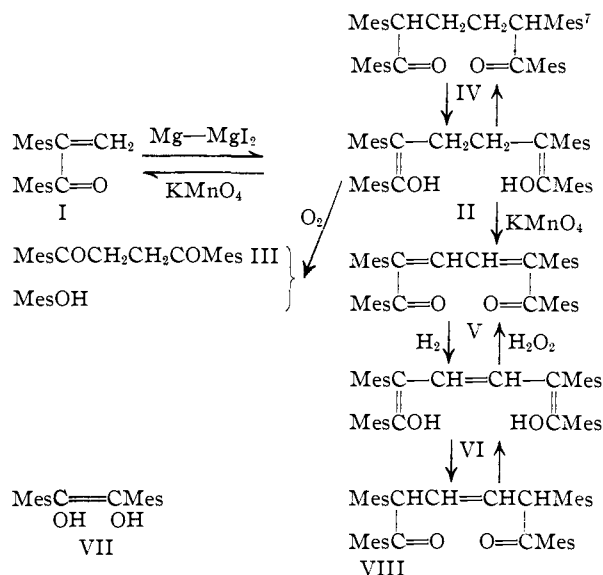
(2) DuPont Post-doctorate Fellow, 1940–1941.

(3) Fuson, Corse and McKeever, *THIS JOURNAL*, **62**, 3250 (1940).

(4) Gomberg and Bachmann, *ibid.*, **49**, 236 (1927).

(5) Fuson, Byers, Rachlin and Southwick, *ibid.*, **64**, 2886 (1942).

(6) Criegee, *Ber.*, **64B**, 200 (1931).



This scission of a 1,6-glycol with lead tetraacetate is in accord with the vinylogous relationship between this glycol and ethylene glycol. It is particularly interesting from a theoretical point of view, since the formation of a cyclic intermediate seems unlikely.⁸

The principal product of the oxidation, however, was not the vinyl ketone but the doubly unsaturated diketone, 1,2,5,6-tetramesityl-2,4-hexadien-

(7) Mes is used to represent the mesityl radical.

(8) Criegee, Kraft and Rank, *Ann.*, **507**, 159 (1933).

1,6-dione (V). This compound underwent 1,8 hydrogenation to yield what was perhaps the most remarkable compound of the entire series—the dienol, 1,2,5,6-tetramesityl-1,3,5-hexatriene-1,6-diol (VI). It is a vinylog of the enediol, 1,2-dimesitylacetylene glycol (VII). Like the acetylene glycol, it can be ketonized by treatment with alcoholic hydrogen chloride. From the resulting diketone (VIII) the dienol can be regenerated by the use of ethylmagnesium bromide.

Experimental^a

1,2,5,6-Tetramesityl-1,5-hexadiene-1,6-diol (II).—To a well-stirred mixture of 1.92 g. of magnesium, 40 cc. of dry ether and 80 cc. of dry benzene was added 9.8 g. of iodine. When the iodine color had disappeared, 11.68 g. of solid α -mesitylvinyl mesityl ketone was added within one minute. The solution was stirred and heated at the refluxing temperature for three hours. The reaction mixture was cooled, decomposed with iced hydrochloric acid and washed once with water. The aqueous layer was extracted with ether, and the combined organic solution was dried over calcium chloride. It was then concentrated to a volume of 25 cc. and cooled in an ice-bath. The product which precipitated weighed 11 g. (94%) and melted at 203–205°. The pure compound, recrystallized from benzene, melted at 207–208°.

Anal. Calcd. for $C_{42}H_{50}O_2$: C, 85.95; H, 8.60; mol. wt., 586. Found: C, 86.08; H, 8.69; mol. wt. (ebullioscopic in chloroform), 605.

1,2,5,6-Tetramesityl-1,5-hexadiene-1,6-diol Diacetate.—A solution of 2.0 g. of the diol (II) in 15 cc. of acetic anhydride was heated at the refluxing temperature for two hours. The reaction mixture was cooled and poured into water. The white diacetate, recrystallized from benzene, weighed 1.95 g. and melted at 217.5–218.5°.

Anal. Calcd. for $C_{46}H_{54}O_4$: C, 82.34; H, 8.11. Found: C, 82.72; H, 8.23.

Ketonization of 1,2,5,6-Tetramesityl-1,5-hexadiene-1,6-diol.—A solution of 2.0 g. of the diol in 200 cc. of absolute ethanol, which had previously been saturated with dry hydrogen chloride, was refluxed for twelve hours. The solid diketone started to separate from the hot solution. The mixture was cooled and filtered. The product weighed 1.5 g., and melted at 250–255°. A second crop of crystals weighing 0.4 g. was obtained. Recrystallized from benzene, the diketone (IV) melted at 259–261°.

Anal. Calcd. for $C_{42}H_{50}O_2$: C, 85.95; H, 8.60. Found: C, 86.04; H, 8.83.

Enolization of 1,2,5,6-Tetramesityl-1,6-hexanedione (IV).—To a Grignard solution made from 11 g. of ethyl bromide, 2.4 g. of magnesium and 50 cc. of ether was added a solution of 1 g. of the diketone (IV) in 50 cc. of dry benzene. The mixture was stirred and refluxed for twelve hours, cooled and decomposed with iced ammonium chloride solution. The aqueous layer was extracted with benzene, and the benzene solution was dried over calcium

chloride and concentrated to a volume of 10 cc. Cooling caused the separation of 0.8 g. of a solid, which, after recrystallization from benzene, melted at 207–208° alone or mixed with a sample of the diol obtained by the other method.

Reaction of 1,2,5,6-Tetramesityl-1,5-hexadiene-1,6-diol with Oxygen.—Oxygen was bubbled through a solution of 1 g. of the diol in 300 cc. of acetone for seventy-two hours. The solvent was removed by distillation and the residue was dissolved in ether. The ether solution was extracted three times with 10% potassium bicarbonate solution. Acidification of the combined bicarbonate solutions failed to cause the precipitation of an insoluble acid. The ether solution was then extracted with several portions of 10% sodium hydroxide solution. Acidification of the combined alkaline solutions caused the precipitation of 0.9 g. of mesitol. A sample, purified by sublimation, melted at 70° and did not depress the melting point of a known sample of mesitol.

The ether solution was washed with water and the residue, after removal of the ether, weighed 2.2 g. The crude solid was recrystallized from methanol. The first crop of crystals weighed 1.2 g. and melted at 136–137° alone or when mixed with an authentic sample of 1,2-dimesityloctane.

Reaction of 1,2,5,6-Tetramesityl-1,5-hexadiene-1,6-diol (II) with Potassium Permanganate.—A solution of 1.9 g. of potassium permanganate in 250 cc. of acetone was added over a period of one-half hour to a well-stirred solution of 5 g. of the diol in 160 cc. of acetone. The manganese dioxide was gathered on a filter and extracted in a Soxhlet apparatus with acetone until the solvent was no longer yellow. The solutions were combined and concentrated to a volume of 150 cc. The excess permanganate was removed by filtration as manganese dioxide and the clear yellow solution was concentrated to 25 cc. Cooling caused the separation of the canary yellow diketone (V) which weighed 2.2 g. and melted at 279–282°. After recrystallization from benzene, it melted at 282–284°.

Anal. Calcd. for $C_{42}H_{46}O_2$: C, 86.53; H, 7.97. Found: C, 86.73; H, 8.13.

The mother liquor was evaporated to dryness and subjected to fractional crystallization from methanol. In this manner there was isolated 0.2 g. of the diketone and 1.1 g. of a white compound identified as α -mesitylvinyl mesityl ketone; m. p. 131–132°.

Reaction of 1,2,5,6-Tetramesityl-1,5-hexadiene-1,6-diol (II) with Lead Tetraacetate.—To a hot well-agitated solution of 5 g. of the diol in 100 cc. of benzene was added 10.5 g. of lead tetraacetate. The mixture was stirred and refluxed for fourteen hours. It was filtered and the clear solution was concentrated to a volume of 20 cc. Cooling caused the separation of 2.5 g. of the yellow diketone (V), m. p. 279–282°. Further investigation of the mother liquor resulted in the isolation of 0.3 g. of α -mesitylvinyl mesityl ketone, m. p. 129–131°. The residue was a dark tar.

When the reaction mixture was heated for five hours, there was produced 2.4 g. of the yellow diketone (V) and 0.8 g. of α -mesitylvinyl mesityl ketone.

1,2,5,6-Tetramesityl-1,3,5-hexatriene-1,6-diol (VI).—A. A solution of 0.2 g. of the diketone (V) in 150 cc. of

(9) Microanalyses by Miss Mary S. Kreger, Miss Margaret McCarthy, Miss Theta Spoor and Mr. L. G. Fauble

benzene (thiophene-free) was shaken with a platinum oxide catalyst and hydrogen at atmospheric pressure until the yellow color had disappeared. The catalyst was removed by filtration and the solution was concentrated to a small volume and cooled. The resulting white diol melted to a yellow liquid at 252–253°.

Anal. Calcd. for $C_{42}H_{48}O_2$: C, 86.24; H, 8.28. Found: C, 86.14; H, 8.22.

When it was exposed to the atmosphere, the pure diol gradually assumed a brownish color. After two days it was brownish-yellow and the melting point was 235–240°.

B. To a solution of 0.5 g. of the diketone in 75 cc. of hot glacial acetic acid was added 3 g. of zinc dust. The mixture was heated on a steam-bath for one hour, after which time the zinc was removed by filtration. Cooling caused the separation of 0.45 g. of a brownish crystalline solid which melted, after washing with water, at 235–240°. Recrystallized from ethanol, the diol was white and melted to a yellow liquid at 252–253° alone or mixed with a sample of the diol obtained by method A.

1,2,5,6-Tetramesityl-1,3,5-hexatriene-1,6-diol Diacetate.—**A.** A solution of 0.5 g. of the diol (VI) in 25 cc. of acetic anhydride was heated at the refluxing temperature for ninety minutes. Cooling caused the separation of 0.5 g. of white needles, m. p. 271–273°. Recrystallized from glacial acetic acid, the diacetate melted at 273–274°.

Anal. Calcd. for $C_{46}H_{52}O_4$: C, 82.59; H, 7.83. Found: C, 82.63; H, 8.03.

B. To a solution of 0.18 g. of the diketone (V) in acetic anhydride was added 0.3 g. of fused zinc chloride and 3 drops of concentrated hydrochloric acid.¹⁰ The mixture was shaken for twenty minutes with 10 mg. of platinum oxide catalyst and hydrogen at atmospheric pressure. At the end of this time the solution was colorless and the product separated as white needles. It weighed 0.15 g. Recrystallized from glacial acetic acid, it melted at 273–274° alone or mixed with the diacetate obtained by method A.

Oxidation of 1,2,5,6-Tetramesityl-1,3,5-hexatriene-1,6-diol with Hydrogen Peroxide.—A solution of 0.28 g. of the yellow diketone (V) in 60 cc. of benzene (thiophene-free) was shaken with hydrogen at atmospheric pressure over platinum until the color had disappeared. The catalyst was removed by filtration and the benzene solution was shaken for ten minutes with 5 cc. of 30% hydrogen peroxide and 25 cc. of water. The benzene solution turned yellow. After removal of the solvent the yellow residue weighed 0.19 g. Recrystallized from benzene, the product

melted at 282–284° alone or when mixed with another sample of the yellow diketone.

Ketonization of 1,2,5,6-Tetramesityl-1,3,5-hexatriene-1,6-diol.—Two grams of the yellow diketone (V) was reduced by the zinc and acetic acid method. The resulting trienediol (1.8 g.) was transferred to a flask containing 500 cc. of absolute ethanol which had previously been saturated with dry hydrogen chloride. The solution was refluxed on a steam-bath for twelve hours. After cooling, this product (1.25 g.) was separated by filtration; m. p. 170–185°. The pure diketone (VIII) obtained by fractional crystallization from methanol melted at 201° and weighed 0.8 g.

Anal. Calcd. for $C_{42}H_{48}O_2$: C, 86.24; H, 8.28. Found: C, 86.00; H, 8.38.

Enolization of 1,2,5,6-Tetramesityl-3-hexene-1,6-dione (VIII).—To a Grignard solution made from 11 g. of ethyl bromide, 2.5 g. of magnesium and 25 cc. of ether was added a solution of 1.5 g. of the diketone (VIII) in 10 cc. of ether and 25 cc. of benzene. The mixture was stirred and refluxed for five hours. It was cooled and poured into iced ammonium chloride solution. The aqueous layer was extracted with 50 cc. of ether. The ether solution was dried over calcium chloride and evaporated to dryness on a steam-bath. Treatment of the residue with cold ethanol caused the separation of 0.8 g. of the diol (VI), m. p. 235–240°. Recrystallized from ethanol, it melted to a yellow liquid at 252–253° alone or mixed with a sample of the compound obtained by another method.

Summary

Bimolecular reduction of mesityl α -mesityl-vinyl ketone yields 1,2,5,6-tetramesityl-1,5-hexadien-1,6-diol, a vinylog of ethylene glycol. Oxidation of the diol produces chain cleavage analogous to that of 1,2-glycols, regenerating the parent vinyl ketone.

A second product of oxidation is 1,2,5,6-tetramesityl-2,4-hexadien-1,6-dione. This ketone undergoes 1,8 addition of hydrogen to yield 1,2,5,6-tetramesityl-1,3,5-hexadien-1,6-diol, a vinylog of acetylene glycol.

The new dienols can be ketonized by long treatment with alcoholic hydrogen chloride. The dienols can be regained by treating the resulting diketones with the Grignard reagent.

(10) Thompson, *This Journal*, **61**, 1281 (1939).