

Acidic Components.—The procedure was very similar to that described above for 1,2-dimesityl-1-propen-1-ol. Acidification of the bicarbonate extract yielded 0.5 g. of a white solid melting at 176.5–178.5° after crystallization from high-boiling petroleum ether. It did not depress the melting point of an authentic sample of 2,3,5,6-tetramethylbenzoic acid.

The remainder of the acidic fraction was dissolved in 10% potassium hydroxide solution, filtered free of insoluble material, and precipitated by acidification. One and four-tenths gram of a product melting at about 110° was obtained. Crystallized twice from low-boiling petroleum ether, it melted at 117–118° and did not depress the melting point of a known sample of durenol.

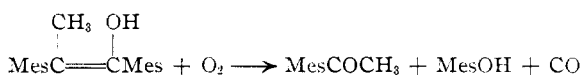
Neutral Components.—After extraction of the acidic components, the oil was washed with water and allowed to stand; a small amount of a crystalline product separated and was removed by filtration. Distillation of the filtrate yielded 1.5 g. of an oil boiling at 93–95° at 5 mm. Nitration of this oil as described above converted it to dinitroacetomesitylene.

Methanol was added to the viscous residue in the distilling flask, and the yellow solid which separated was filtered and crystallized from ethanol. It melted at 156.5–157.5° and did not depress the melting point of a sample of

duryl α -mesitylvinyl ketone. The solid mentioned above, which crystallized from the oily mixture, was crystallized from ethanol, and likewise proved to be duryl α -mesitylvinyl ketone. A total of 0.8 g. of this compound was isolated.

Summary

It has been found that treatment with oxygen causes the vinyl alcohol, 1,2-dimesityl-1-propen-1-ol, to undergo cleavage to acetomesitylene, mesitol and carbon monoxide according to the equation



Small amounts of mesityl α -mesitylvinyl ketone, mesitoic acid, hydrogen and an unidentified phenol were also detected among the reaction products.

Similar results were obtained with 1-duryl-2-mesityl-1-propen-1-ol.

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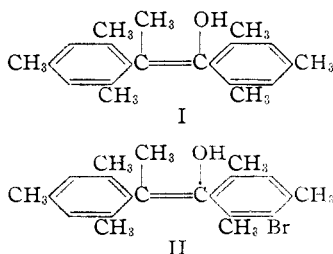
RECEIVED SEPTEMBER 8, 1942

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

Vinyl Alcohols. V.¹ Isomeric Bromo-1,2-dimesityl-1-propen-1-ols

BY REYNOLD C. FUSON, R. V. LINDSEY, JR., AND P. BURKE WELLDON

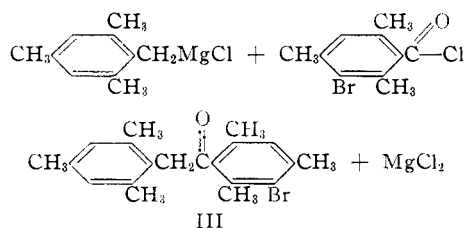
In an effort to relate the remarkable stability of 1,2-dimesityl-1-propen-1-ol² (I) to structural features, a number of similar enols were prepared. The method in every case involved the corresponding desoxybenzoin as a starting material. One of the most interesting of these syntheses was that of the bromo derivative (II) of the original enol. It was made from 3'-bromodesoxymesityoin (III),



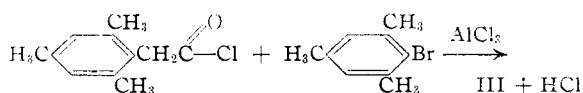
which in turn was prepared by condensing 3-bromomesityl chloride with α^2 -isodurylmagnesium chloride.

(1) For the preceding article in this series, see Fuson, Byers, Rachlin and Southwick, *THIS JOURNAL*, **64**, 2886 (1942).

(2) (a) Fuson, Corse and McKeever, *ibid.*, **62**, 3250 (1940); (b) Fuson, Byers and Rabjohn, *ibid.*, **63**, 2639 (1941).



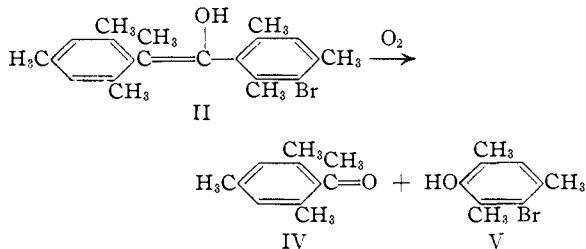
Because the yields of the bromodesoxymesityoin (III) were low, an effort was made to find a better method of synthesis. The most promising alternative appeared to be the Friedel-Crafts reaction between mesitylacetyl chloride and bromomesitylene.



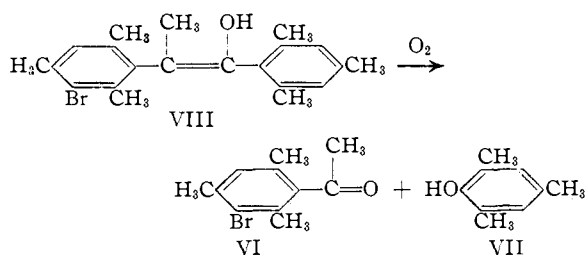
The result was, however, very surprising. The condensation proceeded smoothly to yield a compound of the expected composition and similar melting point. But a mixed melting point determination showed it to be different from the desired 3'-bromodesoxymesityoin.

That we were dealing with isomeric bromodesoxy-mesitoin became clear when it was found that each compound, when condensed with formaldehyde, yielded an unsaturated ketone that could be converted by hydrogenation to a vinyl alcohol. Both vinyl ketones melted at 150°, but a mixed melting point determination showed a 20° lowering. The new vinyl alcohols were considerably less permanent than the parent enol, 1,2-dimesityl-1-propen-1-ol (I); they were isolated only as unstable solids. Enol II was converted to the methyl ether.

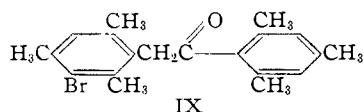
Fortunately, the newly discovered oxidative cleavage¹ of such enols offered a simple method of structure determination. The vinyl alcohol (II) derived from 3'-bromodesoxy-mesitoin (III) yielded acetomesitylene (IV) and 3-bromomesitol (V), as was expected.



The enol from the new desoxy compound was oxidized to 3-bromoacetomesitylene (VI) and mesitol (VII).



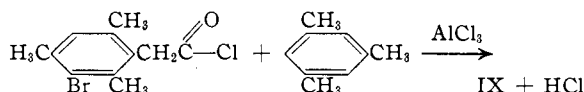
It must, therefore, have the structure, VIII. As a consequence, the desoxy compound from the Friedel-Crafts synthesis can be assigned the structure of 3-bromodesoxy-mesitoin (IX). Its



formation involves the transfer of the bromine atom from one ring to the other. This remarkable migration must occur at some intermediate point in the condensation, for the 3'-bromodesoxy-mesitoin did not undergo isomerization when treated with aluminum chloride. Although halogen mi-

grations during the Friedel-Crafts reaction are well-known,³ this one seems noteworthy for the selectivity with which it proceeds. The yields ranged from 40 to 90%.

The structure of 3-bromodesoxy-mesitoin was confirmed by an independent synthesis. This compound was obtained in satisfactory yields by condensing 3-bromomesitylacetyl chloride with mesitylene.



Experimental

3-Bromomesitoic Acid.—Mesitoic acid was brominated by the method of Shildneck and Adams⁴; omission of the iron catalyst gave consistently higher yields. There was obtained 288 g. (74% yield) of 3-bromomesitoic acid, m. p. 162–165°, from 260 g. of mesitoic acid.

The acid was converted to the *acid chloride* (b. p. 175–178° (28 mm.)) in 97% yield by the action of thionyl chloride at room temperature.

Condensation of 3-Bromomesityl Chloride with α^2 -Isodurylmagnesium Chloride.—A solution of 8.4 g. of α^2 -chloroisodurene in 350 cc. of dry ether was added over one and one-half hours to 10 g. of magnesium in 150 cc. of dry ether at 0°. The temperature of the mixture was allowed to rise to room temperature; stirring was continued for thirty minutes, after which a solution of 13 g. of 3-bromomesityl chloride in 25 cc. of dry ether was added dropwise. Stirring was continued for one hour; the reaction mixture was then decomposed with cold, dilute hydrochloric acid. The ether layer was extracted with dilute alkali, washed with water and evaporated. The residue was crystallized from absolute alcohol; 8 g. (45% yield) of 3'-bromodesoxy-mesitoin was obtained as white plates melting at 91–92°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{23}\text{OBr}$: C, 66.85; H, 6.40. Found: C, 67.00; H, 6.42.

Repetition of this preparation gave yields of less than 10%; the product was contaminated with large amounts of 1,2-dimesitylethane (m. p. 115–116°) from the coupling of the Grignard reagent and could be obtained pure only by repeated fractional crystallization from low-boiling petroleum ether.

Condensation of Mesitylacetyl Chloride with Bromomesitylene.—A solution of mesitylacetyl chloride (20 g.) and bromomesitylene (25 g.) in carbon disulfide (30 cc.) was added over forty-five minutes to a stirred mixture of bromomesitylene (20 g.), aluminum chloride (30 g.) and carbon disulfide (80 cc.) at 0°. Stirring was continued at 0° for three hours, and for an additional three hours at 0–17°. The reaction mixture was decomposed with ice and hydrochloric acid; the organic layer was diluted with 200 cc. of ether and washed thoroughly with 10% sodium hydroxide solution and water. Exhaustive steam distillation removed the solvents and excess bromomesitylene; the

(3) Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 692.

(4) Shildneck and Adams, *THIS JOURNAL*, **53**, 349 (1931).

last portion of the distillate yielded 1 g. of a white solid mixture from which was isolated tribromomesitylene.⁵ The viscous residue was crystallized from absolute alcohol; there was obtained 33.4 g. of white solid melting at 90–93°. A mixture of this solid and 3'-bromodesoxymesitylone melted at 71–75°. Recrystallization first from petroleum ether and then from methanol yielded white crystals melting at 98–99°. This compound was subsequently shown to be 3-bromodesoxymesitylone; yield, 90%.

Anal. Calcd. for $C_{20}H_{23}OBr$: C, 66.85; H, 6.40. Found: C, 66.91; H, 6.31.

3-Bromomesityl α -Mesitylvinyl Ketone.—The procedure was that described for the preparation of α -mesitylvinyl mesityl ketone.^{2b} From 8 g. of 3'-bromodesoxymesitylone there was obtained 6.84 g. of the vinyl ketone, melting at 150–151°; yield, 83%.

Anal. Calcd. for $C_{21}H_{23}OBr$: C, 67.92; H, 6.24. Found: C, 68.06; H, 6.32.

Mesityl α -(3-Bromomesityl)-vinyl Ketone.—The same procedure^{2b} was followed, except that the time of stirring was reduced to seventeen hours. Addition of a second portion of paraformaldehyde was unnecessary. From 12 g. of 3-bromodesoxy-mesitylone there was obtained 12.2 g. of mesityl α -(3-bromomesityl)-vinyl ketone, melting at 149–150°; yield, 98%.

Anal. Calcd. for $C_{21}H_{23}OBr$: C, 67.92; H, 6.24. Found: C, 67.82; H, 6.37.

A mixture of this compound and 3-bromomesityl α -mesitylvinyl ketone melted at 131–134°.

The Methyl Ether of 1-(3-Bromomesityl)-2-mesityl-1-propen-1-ol.—3-Bromomesityl α -mesitylvinyl ketone (15 g.) in glacial acetic acid (150 cc.) was subjected to one and one-half atmospheres pressure of hydrogen in the presence of platinum oxide catalyst. One mole of hydrogen was absorbed per mole of ketone. The solution was filtered into water; the enol was obtained as a white precipitate which became gummy after short exposure to air. It was dissolved in benzene; the solution was washed with dilute potassium bicarbonate solution and water. The benzene solution was partially distilled to dry it, and then was stirred and heated with 2.3 g. of finely divided sodium for one and one-half hours. Excess methyl sulfate was added, and the treatment continued for two hours. The benzene solution was warmed with dilute alkali, washed with water, and evaporated to dryness. Crystallization of the residue from ethanol yielded 12.5 g. of the enol ether, melting at 117.5–119°; yield, 80%.

Anal. Calcd. for $C_{22}H_{27}OBr$: C, 68.22; H, 6.98. Found: C, 68.22; H, 6.99.

Oxidative Cleavage of 1-(3-Bromomesityl)-2-mesityl-1-propen-1-ol.—3-Bromomesityl α -mesitylvinyl ketone (5.5 g.) in ether (50 cc.) was reduced to the enol. The solution was filtered, diluted with acetone and treated with oxygen for three days by the procedure of Fuson, Byers, Rachlin and Southwick.¹ Extraction of an ethereal solution of the residue with alkali followed by acidification yielded 2.24 g. of a solid which was sublimed *in vacuo* to give white needles, m. p. 81–82°. A mixture of this compound and an authentic sample of 3-bromomesitylone (prepared by the method of Jacobsen⁶) melted at 81–82°.

(5) Fittig and Storer, *Ann.*, **147**, 8 (1868).

(6) Jacobsen, *ibid.*, **195**, 270 (1879).

Distillation of the neutral residue yielded 1.4 g. of acetomesitylene, which was identified by conversion to the dinitro derivative as previously described.^{2b}

Oxidative Cleavage of 1-Mesityl-2-(3-bromomesityl)-1-propen-1-ol.—When mesityl α -(3-bromomesityl)-vinyl ketone was reduced in methanol by the usual procedure, the resulting enol was again a white solid which became gummy after short contact with air. Treatment of this unstable enol with cold potassium permanganate in acetone^{2b} dehydrogenated it to regenerate the vinyl ketone.

A solution of the enol (formed by reduction of 5.6 g. of mesityl α -(3-bromomesityl)-vinyl ketone) in an ether-acetone mixture was treated with molecular oxygen¹ for three days. The phenolic product obtained (1.4 g.) was shown to be mesitol by a mixed melting point determination. Distillation of the neutral residue gave 2.4 g. of 3-bromoacetomesitylene, b. p. 110–115° (3 mm.). The identity of this compound was established by use of the procedure of Adams and Miller.⁷ By treatment with phosphoric acid the ketone was cleaved to bromomesitylene, which was identified as the dinitro derivative.

Attempted Isomerization of 3'-Bromodesoxymesitylone.—Efforts to transform the 3'-bromo ketone to the isomeric 3-bromodesoxymesitylone by the influence of aluminum chloride were unsuccessful. Conditions of the original Friedel-Crafts reaction were duplicated. If excess bromomesitylene was added, the products were tribromomesitylene, starting material and some intractable oil.

3-Bromomesitylmethyl Chloride.—Gaseous hydrogen chloride was passed for eight hours into a violently agitated mixture of bromomesitylene (50 g.), paraformaldehyde (25 g.), zinc chloride (2 g.) and concentrated hydrochloric acid (250 cc.) at 65–70°. The cooled mixture was extracted with benzene; the benzene solution was washed with alkali and water, dried (calcium chloride) and distilled. Seven grams of unchanged bromomesitylene was recovered; the chloromethyl compound was obtained as white needles; m. p. 44–45°; b. p. 126–129° (2 mm.); weight, 45 g. (84% yield).

Anal. Calcd. for $C_{10}H_{12}BrCl$: C, 48.51; H, 4.80. Found: C, 48.72; H, 5.00.

3-Bromomesitylacetonitrile.—3-Bromomesitylmethyl chloride (24.75 g.) was added over five minutes to a mixture of sodium cyanide (8.4 g.), alcohol (28 cc.) and water (20 cc.) at 55–60°; stirring and heating were continued for three hours. The cooled mixture was extracted with benzene; the benzene solution was washed with water, dried (calcium chloride) and evaporated on the water-bath. The residue was crystallized from high-boiling petroleum ether, yielding white needles melting at 113–114°; weight, 19.6 g. (82% yield).

Anal. Calcd. for $C_{11}H_{12}NBr$: C, 55.48; H, 5.08. Found: C, 55.49; H, 4.94.

3-Bromomesitylacetic Acid.—3-Bromomesitylacetonitrile (11.9 g.) was hydrolyzed by refluxing and stirring with 104 cc. of 55% sulfuric acid for ten hours. The acid was obtained as white, fluffy needles after crystallization from benzene-high-boiling petroleum ether; m. p. 168.5–169.5°; weight, 10.06 g. (78% yield).

Anal. Calcd. for $C_{11}H_{13}O_2Br$: C, 51.36; H, 5.09. Found: C, 51.43; H, 5.23.

(7) Adams and Miller, *This Journal*, **62**, 53 (1940).

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 $C_{11}H_{14}ONBr$: 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.

URBANA, ILLINOIS

RECEIVED SEPTEMBER 8, 1942

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

Enediols. XI.¹ Vinylogs of Ethylene and Acetylene Glycols

BY REYNOLD C. FUSON, D. J. BYERS² AND A. I. RACHLIN

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 monoenol. 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).

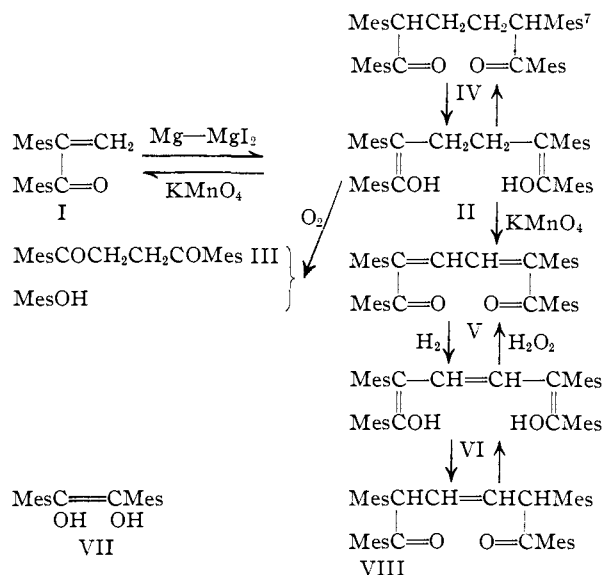
(2) DuPont Post-doctorate Fellow, 1940–1941.

(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).