

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

**Vinyl Alcohols. IV.<sup>1</sup> Oxidative Cleavage**BY REYNOLD C. FUSON, D. J. BYERS,<sup>2</sup> A. I. RACHLIN AND P. L. SOUTHWICK<sup>3</sup>

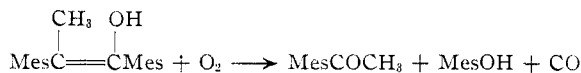
The vinyl alcohol, 1,2-dimesityl-1-propen-1-ol (I),<sup>4</sup> was observed to undergo slow deterioration in contact with the air.<sup>5</sup> In the absence of air, however, it has proved to be stable. Samples of this remarkable enol, kept in sealed tubes under nitrogen, show no change after eighteen months.

The oil produced by the action of oxygen on the enol was found to contain acetomesitylene and mesitoic acid, evidently produced by oxidative cleavage. Subsequent study of this cleavage has shown acetomesitylene to occur invariably as a principal product whereas mesitoic acid is generated only in small amounts or not at all. Another product, isolated in traces, proved to be



mesityl  $\alpha$ -mesitylvinyl ketone (II). Its formation is to be ascribed to 1,4-dehydrogenation of the enol, a reaction that had been brought about earlier by the use of permanganate, chromic anhydride<sup>6</sup> and chloranil.

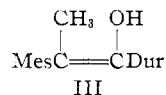
It remained to discover the moiety sheared off in the production of acetomesitylene. By suitable modification of the procedure it was an easy matter to isolate in quantity a low-melting, volatile solid, which proved to be *mesitol*. The amount corresponded roughly to that of acetomesitylene. Attempts to write an equation, however, revealed that a carbon atom was yet to be accounted for. Tests for formaldehyde and carbon dioxide showed that neither was produced in appreciable amounts. Analysis of the exit gas, however, provided the answer; carbon monoxide was present and in amounts proportional to those of acetomesitylene and mesitol. The production of a mole of carbon monoxide for every mole of oxygen absorbed explains the observation that there was no change in pressure during the reaction. The oxidative degradation can accordingly be represented by the following equation



Two additional products were detected in small amounts. One of these was hydrogen, which was found in the exit gases from the oxidation chamber. Its origin is not apparent. The other by-product was a phenolic compound melting at 169.5–171.5°. Its properties indicate that it may be made up of two mesitol residues but this surmise has not been verified.

It seems probable that a peroxide is formed which then breaks down to yield the three products shown in the equation. The peroxide could decompose in an alternative manner to yield mesitoic acid and acetomesitylene. The chief reaction, however, is that leading to the production of mesitol, carbon monoxide and acetomesitylene. It is a new type of oxidative cleavage. There is a possibility that it is related to the well-known Dakin cleavage of certain types of aromatic aldehydes and ketones to the corresponding phenols.<sup>7</sup>

The new reaction has been used to degrade several enols, structurally similar to I, and appears to be generally applicable to compounds of this type. For example, 1-duryl-2-mesityl-1-propen-1-ol (III)<sup>1</sup> yielded acetomesitylene, durenol, carbon monoxide and smaller amounts of 2,3,5,6-tetramethylbenzoic acid and duryl  $\alpha$ -mesitylvinyl ketone. It is interesting that in this cleavage no



high-melting phenol was detected. Results similar to the foregoing have been obtained in structure studies of other vinyl alcohols described elsewhere.<sup>8</sup>

**Experimental****Cleavage of 1,2-Dimesityl-1-propen-1-ol**

The cleavage is readily accomplished by bubbling oxygen through a solution of the enol in an organic solvent such as acetone, or a mixture of ether and petroleum ether. However, to facilitate collection of the gaseous products of the reaction it was found convenient to make use of a Parr

(1) For the preceding communication in this series, see Fuson and Sperati, *This Journal*, **63**, 2643 (1941).

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

(3) Abbott Fellow, 1942–1943.

(4) Mes and Dur denote mesityl and duryl, respectively.

(5) Fuson, Byers and Rabjohn, *ibid.*, **63**, 2639 (1941).

(6) Stodola, *Science*, **98**, 472 (1941).

(7) Dakin, *Am. Chem. J.*, **42**, 477 (1909).

(8) Fuson, Lindsey and Wellton, *This Journal*, **64**, 2888 (1942); Fuson, Byers and Rachlin, *ibid.*, **64**, 2891 (1942).

low-pressure hydrogenation machine of the Adams type.<sup>9</sup> The reaction was carried out by shaking acetone solutions of the enol with oxygen in this apparatus. Various procedures for separating and identifying the products of the cleavage were tried. The following is the description of a run in which the most satisfactory procedure was used.

**Treatment with Oxygen.**—A solution of 8.4 g. (0.029 mole) of the enol in 250 cc. of acetone was placed in the shaker bottle and treated with oxygen for three days at a gage pressure of 14.75 lb. per sq. in. The drop in pressure during this time was negligible.

**Analysis of Gases.**—Gas samples were taken from the shaker bottle by means of an exit tube provided in the stopper, and from the tank through the outlet valve. The gases were passed through sulfuric acid to remove acetone vapors and samples were collected by displacement of water from sample tubes of 300 cc. capacity.

The presence of carbon monoxide was detected by the palladium chloride test.<sup>10</sup> Quantitative analysis<sup>11</sup> of the gas samples was carried out with an apparatus of the Orsat type. Carbon dioxide was determined by absorption in 33% potassium hydroxide solution, and oxygen by absorption in a 10% solution of pyrogallol in 33% potassium hydroxide. After removal of carbon dioxide and oxygen, the gases were scrubbed with 90% sulfuric acid and then passed over cupric oxide at 250°. Hydrogen was then estimated from the decrease in the volume of the sample upon condensation of the water formed. Carbon monoxide was determined by absorption of the resulting carbon dioxide in 33% potassium hydroxide solution.

The sample from the shaker bottle contained 56.1 mole per cent. of carbon monoxide, and the sample from the tank 4.8 mole per cent. An estimate based on the capacity of the bottle and of the tank indicated the formation of approximately 0.028 mole of carbon monoxide in the reaction. No carbon dioxide was found in the gases produced in this run, although minute quantities were found in another run by passing the entire gaseous mixture through a saturated barium carbonate solution. Hydrogen was found to the extent of 2.6 mole per cent. in the sample from the bottle, and 0.6 per cent. in the sample from the tank.

The solution was taken from the shaker bottle, and the acetone removed by distillation from a steam-cone. The acetone distillate was refluxed for four hours while a slow stream of carbon dioxide was bubbled through it, and the exit gases were passed through 150 cc. of water kept at 0°. At the end of that time no formaldehyde could be detected in the water by the fuchsin test. In another run a fuchsin test which could not be decolorized by sulfuric acid was obtained from the acetone distillate, but the methone test was negative.

#### Acidic Components

The oil remaining after removal of the acetone was taken up in a very small amount of ether and extracted repeatedly with a 10% potassium hydroxide solution. Acidification

(9) Adams and Voorhees, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., second edition, 1941, p. 65.

(10) Fritz Bayer, "Gasanalyse," W. Böttger and F. Enke, Stuttgart, 1938, p. 52.

(11) The gas analyses were carried out by Mr. Robert S. Hanmer.

of the alkaline extracts yielded 4.2 g. of a solid precipitate. This material was dissolved in ether, and the solution was extracted twice with a 10% solution of potassium bicarbonate. Acidification of the extracts precipitated 0.2 g. of a white solid melting at 151–153°. No depression of the melting point was observed when this compound was mixed with an authentic sample of mesitoic acid.

The ether solution of the acidic components, which now contained only the phenolic fraction, was evaporated, and the residual solids were subjected to steam distillation. Two and four-tenths grams of a white solid melting at 67–69° was obtained by cooling and filtering the distillate. Crystallization from low-boiling petroleum ether gave white needles melting at 71–72° which did not depress the melting point of a known sample of mesitol.

The solid remaining in the steam-distillation flask was collected on a filter and dissolved in 10% potassium hydroxide solution. The solution was filtered free of a small amount of insoluble solid material, and acidified with hydrochloric acid. Five-tenths of a gram of a tan solid was precipitated. After repeated crystallization from glacial acetic acid, white crystals melting at 169.5–171.5° were obtained.

*Anal.*<sup>12</sup> Calcd. for C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>: C, 79.95; H, 8.28. Found: C, 79.60; H, 8.13.

Approximately 0.2 g. of the high-melting phenol was heated for a few minutes with 5 cc. of acetic anhydride and one drop of concentrated sulfuric acid. Excess acetic anhydride was decomposed by heating with water, and the resulting solid product was crystallized four times from high-boiling petroleum ether. White needles melting at 148–149° were obtained.

*Anal.* Calcd. for C<sub>22</sub>H<sub>26</sub>O<sub>4</sub>: C, 74.53; H, 7.40. Found: C, 74.71; H, 7.75.

**Neutral Components.**—After extraction with 10% potassium hydroxide, the ether solution containing the neutral components was washed with water, and the ether was removed by distillation. Distillation of the residual oil yielded 3.2 g. of a liquid boiling at 85–90° at 3 mm. A 0.5-g. portion of this oil was treated with 10 cc. of fuming nitric acid at 0°, and the nitration mixture was poured on ice. The precipitated white product melted at 135–137° after crystallization from ethanol, and did not depress the melting point of a known sample of dinitroacetomesitylene.

A small amount of methanol was added to the viscous red oil remaining in the distilling flask after removal of the acetomesitylene, and a crystalline precipitate formed immediately. About 0.3 g. of this material was obtained by cooling and filtering the solution. After crystallization from ethanol, it melted at 132–133° and was shown to be mesityl  $\alpha$ -mesitylvinyl ketone by the mixed melting point test.

#### Cleavage of 1-Duryl-2-mesityl-1-propen-1-ol

The cleavage was brought about by shaking a solution of 8.5 g. of the enol in 250 cc. of acetone with oxygen for three days at a gage pressure of 10 lb. per sq. in.

A gas sample from the bottle contained 39.4 mole per cent. of carbon monoxide, no appreciable carbon dioxide and 1.2 mole per cent. of hydrogen.

(12) Microanalyses by Miss Theta Spoor.

**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-tetra-methylbenzoic 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.

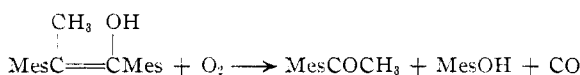
**Neutral Components.**—After extraction of the acidic components, the oil was washed with water and allowed to stand; a small amount of a crystalline product separated and was removed by filtration. Distillation of the filtrate yielded 1.5 g. of an oil boiling at 93–95° at 5 mm. Nitration of this oil 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  $\alpha$ -mesitylvinyl ketone. The solid mentioned above, which crystallized from the oily mixture, was crystallized from ethanol, and likewise proved to be duryl  $\alpha$ -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  $\alpha$ -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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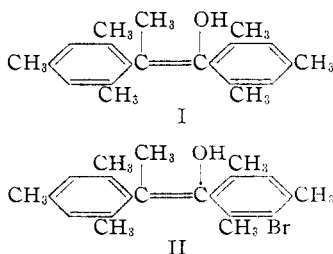
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Vinyl Alcohols. V.<sup>1</sup> Isomeric Bromo-1,2-dimesityl-1-propen-1-ols

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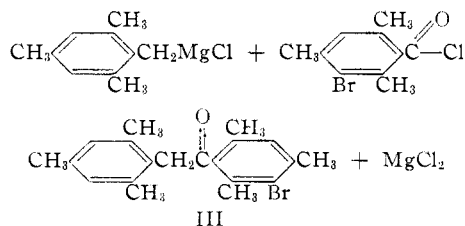
In an effort to relate the remarkable stability of 1,2-dimesityl-1-propen-1-ol<sup>2</sup> (I) to structural features, a number of similar enols were prepared. The method in every case involved the corresponding desoxybenzoin as a starting material. One of the most interesting of these syntheses was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



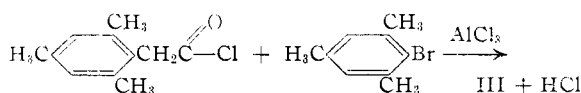
which in turn was prepared by condensing 3-bromomesityl chloride with  $\alpha^2$ -isodurylmagnesium chloride.

(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 Rahjohn, *ibid.*, **63**, 2630 (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.