acid separated and was purified by two recrystallizations from water accompanied by treatment with activated charcoal.

1,2,3,4-Tetrahydro-3-oxo-6-quinoxaline-phosphonic Acid.—When the monosodium salt of 3-nitro-4-α-carboxymethylaminophenylphosphonic acid was reduced with hydrogen and Raney nickel[4] catalyst the free base, 3-amino-4-α-carboxymethylaminophenylphosphonic acid, which was not isolated, lost water to form a quinoxaline derivative. 1,2,3,4-Tetrahydro-3-oxo-6-quinoxalinephosphonic acid which separated when the filtrate from the reduction was acidified to congo red paper, was filtered off, washed well with water and dried.

3-Nitro-4-phenoxyphenylphosphonic Acid.—3-Nitro-4-phenoxyphenylphosphonic acid was obtained by heating a mixture of 3-nitro-4-chlorophenylphosphonic acid (5 g.), anhydrous potassium carbonate (5 g.), phenol (10 g.), and a trace of copper powder, for nine hours at 125° with agitation. The excess phenol was removed by steam distillation. The phosphonic acid was precipitated with dilute hydrochloric acid and purified by two recrystallizations from dilute acetic acid accompanied by treatment with activated charcoal.

3-Nitro-4-(*o*-chlorophenoxy)-phenylphosphonic Acid and 3-Nitro-4-(*p*-chlorophenoxy)-phenylphosphonic Acid.—3-Nitro-4-(chlorophenylphosphonic acid (5 g.), anhydrous potassium carbonate (5 g.), isoamyl alcohol (15 ml.), copper powder (5 g.), and either *o*- or *p*-chlorophenol (2.5 g.) were heated at 145° for seven to nine hours in a flask fitted with a stirrer and a condenser. The isoamyl alcohol and excess phenol were removed by steam distillation. The phosphonic acid was precipitated with dilute hydrochloric acid and purified by two recrystallizations from dilute acetic acid accompanied by treatment with activated charcoal.

3-Amino-4-phenoxyphenylphosphonic Acid Derivatives.—The 3-nitro-4-phenoxyphenylphosphonic acid derivatives were reduced in the same manner as the 3-nitro-4-N-alkylaminophenylphosphonic acids to give 3-amino-4-phenoxyphenylphosphonic acid derivatives.

3-Nitro-4-hydroxyphenylphosphonic Acid.—3-Nitro-4-chlorophenylphosphonic acid was refluxed for four hours in 4 *N* sodium hydroxide solution. 3-Nitro-4-hydroxyphenylphosphonic acid separated slowly after the solution was made acid to congo red paper and was purified by recrystallization from water.

3-Amino-4-hydroxyphenylphosphonic Acid.—Catalytic reduction of 3-nitro-4-hydroxyphenylphosphonic acid in the same manner as the 3-nitro-4-N-alkylaminophenylphosphonic acids were reduced gave 3-amino-4-hydroxyphenylphosphonic acid which darkens quickly in air or in solution.

Summary

3-Nitro-4-chlorophenylphosphonic acid has been prepared and condensed with several aliphatic amines, namely, *n*-propyl, *n*-butyl, *i*-butyl, *n*-amyl, *i*-amyl and ethanolamines, morpholine and glycine. The corresponding amine derivatives of the condensation products were obtained by reduction except that of glycine which gave 1,2,3,4-tetrahydro-3-oxo-6-quinoxaline-phosphonic acid.

3-Nitro-4-chlorophenylphosphonic acid has been condensed with phenol, *o*-chlorophenol and *p*-chlorophenol to give phenyl ether derivatives. The aminophenyl ether derivatives have been prepared from the corresponding nitro compounds.

3-Nitro-4-hydroxyphenylphosphonic acid has been prepared and reduced to 3-amino-4-hydroxyphenylphosphonic acid.

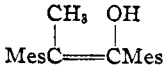
LINCOLN, NEBRASKA RECEIVED APRIL 15, 1941

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

Vinyl Alcohols. II. 1,2-Dimesityl-1-propen-1-ol

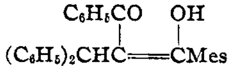
BY REYNOLD C. FUSON, D. J. BYERS[1] AND NORMAN RABJOHN[2]

The vinyl alcohol 1,2-dimesityl-1-propen-1-ol (I, Mes = mesityl), described in the preceding communication,[3] is remarkable because it contains only hydrocarbon substituents. Most enolic compounds have a carbonyl group and are probably chelated. The enol form (II) of benzohydrylbenzoylacetomesitylene described by Kohler, Tishler and Potter[4] is an example of this type. The stability of certain enols cannot be explained in this way, however. The enol form (III) of benzyl phenyl diketone[5] has been shown by Kohler and Barnes[6] to behave as an unchelated hydroxy ketone. The possibility of ascribing the sta-



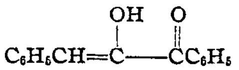
$\mathrm{MesC(CH_3){=}C(OH)Mes}$

I



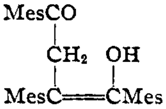
$\mathrm{(C_6H_5)_2CHC(COC_6H_5){=}C(OH)Mes}$

II



$\mathrm{C_6H_5CH{=}C(OH){-}C({=}O)C_6H_5}$

III



$\mathrm{MesC(CH_2COMes){=}C(OH)Mes}$

IV

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[1] Du Pont Post-doctorate Research Fellow, 1940–1941.

[2] Röhm and Haas Research Assistant.

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

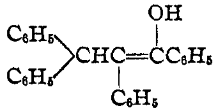
[4] Kohler, Tishler and Potter, *ibid.*, **57**, 2517 (1935).

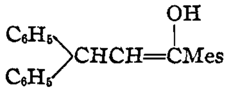
[5] Moureu, *Ann. chim.*, [10] **14**, 303 (1930).

[6] Kohler and Barnes, THIS JOURNAL, **56**, 211 (1934).

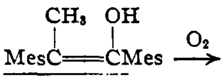
bility of this enol to its heteroconjugated system seems unlikely in view of the character of the monoenol (IV) of Lutz and Kibler.[7] This interesting enol cannot be chelated. It is very similar in structure to I.

Other enols[8] have been described which contain hydroxyl or alkoxyl groups in addition to the enol group. The stable enediols belong to this category.[9] Previous to the isolation of the propenol, I, enols that contain only hydrocarbon substituents had been studied in only a few instances. 9-Formylfluorene[10] and 9-benzoylfluorene[11] have been found to exist in enolic as well as ketonic forms. The enol form (V) of benzohydryldesoxybenzoin was isolated by Kohler in 1906.[12] The enol was, however, not characterized. More recently, Kohler, Tishler and Potter[4] showed that the enol form (VI) of benzohydrylacetomesitylene existed in solution.

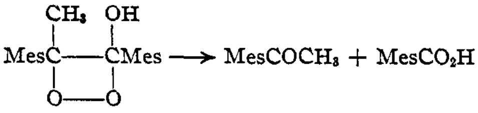

V


VI

Because of the unusual character of this type of substance, a further study has been made of the vinyl alcohol, I. Many of the chemical properties usually associated with enols seem to be lacking in the propenol. It is insoluble in strong aqueous sodium hydroxide and in Claisen's alkali. It gives no color with ferric chloride, and the test with Folin's reagent is inconclusive. The enol does not form an alkoxyacetic acid and fails to couple with diazonium compounds. It does, however, yield a methyl ether when heated with methyl sulfate and potassium hydroxide in methanol solution. Samples of this enol were observed to deteriorate slowly and, in the course of several weeks, to become liquid. In one instance it was possible to isolate a very small amount of solid of a composition approximately that of the enol peroxide, VII. In all other experiments the products were acetomesitylene and mesitoic acid. Apparently the following changes occurred.



$\mathrm{Mes}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{Mes} \xrightarrow{\mathrm{O_2}}$

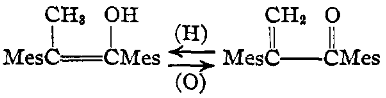


$\mathrm{Mes}\overset{\mathrm{CH_3}}{\underset{\mathrm{O}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{O}}{\mathrm{C}}}\mathrm{Mes} \longrightarrow \mathrm{MesCOCH_3} + \mathrm{MesCO_2H}$

VII

Deliberate attempts to make the peroxide were unsuccessful. When oxygen was bubbled through an ether–petroleum ether solution of the enol, according to Kohler's method,[12] the enol was slowly changed to acetomesitylene and mesitoic acid without the appearance of a peroxide. These cleavage products were obtained also by treatment of the enol or its acetate with ozone.

In view of the fission of the propenol by air and by ozone, it is remarkable that permanganate yielded no cleavage products whatever but brought about dehydrogenation. α-Mesitylvinyl mesityl ketone (VIII) was regenerated.

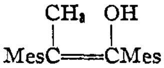


$\mathrm{Mes}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{Mes} \underset{(\mathrm{O})}{\overset{(\mathrm{H})}{\leftrightarrows}} \mathrm{Mes}\overset{\mathrm{CH_2}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Mes}$

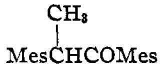
VIII

This curious change has also been effected by chromic anhydride[13] and by bromanil. The reaction is a 1,4-dehydrogenation[14] exactly analogous to the oxidation of an enediol to the corresponding diketone.

It is interesting that in no case has spontaneous ketonization been observed. The keto form (IX) was not detected in any of the mixtures resulting from long contact of the enol with air. Experiments are in progress designed to test the stability of the enol in the absence of air. It is possible that spontaneous ketonization might take place, but if so, the rate is exceedingly slow.



$\mathrm{Mes}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{Mes}$



$\mathrm{Mes}\overset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{HCOMes}$

IX

The keto form was finally obtained by prolonged heating of the enol in methanolic hydrogen chloride. It does not decolorize solutions of permanganate and is not acetylated under the conditions that cause acetylation of the enol. It was changed to the enol by the action of sodium ethoxide. When the ketone was heated with sirupy phosphoric acid it was cleaved to mesitylene and a new acid which has the properties to be expected of α-mesitylpropionic acid (X).

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(7) Lutz and Kibler, THIS JOURNAL, **62**, 365 (1940).

(8) Leading references are the following: Claisen, *Ber.*, **25**, 1781 (1892); Tiffeneau and Daufresne, *Compt. rend.*, **145**, 628 (1907); Crawford, THIS JOURNAL, **57**, 2000 (1935); **61**, 3310 (1939).

(9) See Fuson, Corse and Welldon, *ibid.*, **63**, 2645 (1941).

(10) Wislicenus and Waldmüller, *Ber.*, **42**, 785 (1909).

(11) Meyer and Gottlieb-Billroth, *ibid.*, **54**, 577 (1921).

(12) Kohler, *Am. Chem. J.*, **36**, 177 (1906). See also Ramart-Lucas, *Compt. rend.*, **154**, 1620 (1912); *Ann. Chim.*, [8] **30**, 412 (1913).

(13) Stodola, *Science*, **93**, 452 (1941).

(14) It seems probable that the observation of Kohler (ref. 12, p. 187) may have a similar explanation.

$$\mathrm{Mes\overset{CH_3}{\overset{|}{C}}HCOMes} \longrightarrow \mathrm{Mes\overset{CH_3}{\overset{|}{C}}HCO_2H + MesH}$$

X

Experimental

α-Mesitylvinyl Mesityl Ketone.—The original procedure[3] has been improved greatly by a number of changes. The modified procedure is illustrated by the following example. A solution of 30 g. of desoxymesitoin, 12 g. of paraformaldehyde, 5 g. of anhydrous potassium carbonate and 300 cc. of ethyl alcohol was vigorously stirred and heated at 65° (light bulb) for eighteen hours. At this time 6 g. of paraformaldehyde and 2.5 g. of anhydrous potassium carbonate were added and the heating and stirring continued for an additional thirty hours. The nearly colorless solution was poured into 1200 cc. of water and acidified with hydrochloric acid. After crystallization from ethanol the product weighed 27.1 g. (87%) and melted at 132–133°.

1,2-Dimesityl-1-methoxy-1-propene.—A solution of 7.35 g. of the propenol (I) in 50 cc. of methanol and 15.8 g. of redistilled methyl sulfate was heated to the point of reflux, and to this hot solution was added, with vigorous stirring, a solution of 15 g. of potassium hydroxide in 75 cc. of methanol. The alkali was added in small portions, and sufficient time was allowed to elapse between additions for the initial vigorous reaction to subside. After all the alkali had been added, the suspension was refluxed and stirred for thirty minutes and poured into water. After recrystallization from ethanol the product melted at 170–179° and weighed 3.2 g. (42%). When crystallized three times from benzene, it melted at 185–186°.

Anal.[15] Calcd. for $C_{22}H_{28}O$: C, 85.65; H, 9.16. Found: C, 85.73; H, 9.07.

Molecular Weight Determinations.—The molecular weights were determined by the boiling point method; chloroform was used as the solvent.[16] For the enol, the acetate and the methyl ether the calculated values are 294, 336 and 308, respectively. The observed values are 292, 338 and 310, respectively.

Dehydrogenation of 1,2-Dimesityl-1-propen-1-ol by Potassium Permanganate.—To a solution of 8 g. of the enol in 150 cc. of acetone was added, with stirring, a solution of 4.56 g. of potassium permanganate in 400 cc. of acetone. The reaction was carried out at room temperature and the permanganate added dropwise. After about half of the permanganate had been added, the pink color persisted; the remainder of the reagent was added in small portions at intervals sufficient to allow the color to fade. The original purpose of this experiment was to cleave the enolic double bond, which would require two atoms of oxygen per molecule of enol. The reaction which occurred requires only one atom of oxygen per molecule of enol, which explains the rapid decolorization of only one-half of the permanganate. The manganese dioxide was removed by filtration and the solvent evaporated. The residue was taken up in ether and extracted with 5% sodium hydroxide solution. Extraction of the acidified aqueous layer with ether and evaporation of the ether left a small amount of brown liquid and some white crystals. Crystallized from dilute methanol, the product melted at 130–132° and showed no depression when mixed with an authentic sample of α-mesitylvinyl mesityl ketone.

Removal of the ether from the bulk of the reaction product left a white solid contaminated with a small amount of yellow solid. Crystallized from ethanol, the white product weighed 5.6 g. and melted at 131.5–133.5°. A mixture with an authentic sample of α-mesitylvinyl mesityl ketone showed no depression of the melting point. An additional 0.4 g. was obtained from working up the mother liquor. The total yield was 75%.

Dehydrogenation of 1,2-Dimesityl-1-propen-1-ol by Bromanil.[17]—A solution of 1 g. of enol, 1.44 g. of bromanil and 5 cc. of xylene was refluxed for seven hours. The dark solution was cooled and the tetrabromohydroquinone removed by filtration. The filtrate was taken up in ether and washed with 5% sodium hydroxide solution. Removal of the solvent left a dark solid. Crystallized twice from ethanol (Norite), the product weighed 0.25 g. (25%) and melted at 130–131.5°. A mixed melting point test showed this to be α-mesitylvinyl mesityl ketone.

Ozonization of 1,2-Dimesityl-1-propen-1-ol.—A solution of 7 g. of the enol in 125 cc. of chloroform was treated with approximately 1% ozone for six and one-half hours. The solvent was removed on a steam-bath under reduced pressure, and the residue was heated with 100 cc. of water for two hours. The mixture was cooled, extracted with ether and the ether solution extracted repeatedly with dilute alkali. Acidification of the alkaline extract yielded about 0.5 g. of a white solid. Crystallized from low-boiling petroleum ether, the compound melted at 151–153°. A mixed melting point with an authentic sample of mesitoic acid showed no depression.

The ether extract was washed with water and dried over calcium chloride. Removal of the solvent left an oil which boiled at 120–122° (20 mm.), and weighed 2 g. Approximately 0.7 cc. of the oil was nitrated by 10 cc. of fuming nitric acid at 0°. After five minutes the nitration mixture was poured on ice, and the white solid crystallized from ethanol. The compound melted at 134–136° and did not depress the melting point of a known sample of dinitroacetomesitylene.

Ozonization of the enol acetate produced mesitoic acid and acetomesitylene which were identified as indicated above.[18]

Attempted Preparation of the Enol Peroxide of 1,2-Dimesityl-1-propen-1-ol.—Oxygen was bubbled through a solution of 8 g. of the enol in 200 cc. of low-boiling petroleum ether–ether mixture (3:1) for fifteen hours. No solid separated during this time, but most of the solvent had evaporated. The yellow oily residue was taken up in ether and extracted with 10% potassium bicarbonate solution. Acidification of the alkaline solution produced about 0.3 g. of a solid which melted at 151–152° after crystallization from low-boiling petroleum ether. A mixed melting point test proved this solid to be mesitoic acid.

Removal of the ether left 7.5 g. of an oil which was frac-

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(15) The analyses in this paper are microanalyses. They were carried out by Mr. L. G. Fauble and Miss Mary S. Kreger.

(16) Quantitative Analysis of Organic Compounds by Ralph L. Shriner, Edwards Brothers, Inc., Ann Arbor, Michigan, 1938, p. 61.

(17) Arnold and Collins, THIS JOURNAL, **61**, 1407 (1939).

(18) This experiment was carried out by Mr. L. J. Armstrong.

tionated at reduced pressure and yielded 4 g. of a liquid, b. p. 124–125° (23 mm.). A small portion of this oil was nitrated as described above. The resulting white solid was crystallized from ethanol and shown to be dinitroacetomesitylene by a mixed melting point test. The residue from the distillation boiled at 124–125° (2 mm.) and solidified in the side-arm of the distilling flask. The material weighed 1 g. and was identified as mesitoic acid by a mixed melting point test.

Air Oxidation of 1,2-Dimesityl-1-propen-1-ol.—A sample of the enol was allowed to stand exposed to the air for three months. During this time it changed to a liquid, and finally a solid separated. A small portion of this solid was removed mechanically, pressed on a porous plate and crystallized from dilute ethanol. The product melted at 151–152° and did not depress the melting point of an authentic sample of mesitoic acid.

A few drops of the oil were taken up in ether and extracted with 5% aqueous sodium hydroxide. Removal of the ether and nitration of the remaining oil as described earlier produced a white solid which melted at 135–136.5° after crystallization from ethanol. A mixed melting point with an authentic sample of dinitroacetomesitylene showed no depression.

In one experiment a product melting at 103–104° was isolated in very small amounts. It appeared to be an impure form of the enol peroxide.

Anal. Calcd. for $C_{21}H_{26}O_3$: C, 77.25; H, 7.97. Found: C, 76.88; H, 7.25.

Ketonization of 1,2-Dimesityl-1-propen-1-ol.—Dry hydrogen chloride was passed at a moderate rate into 50 cc. of methanol during one-half hour. After the addition of 5 g. of the enol the solution was refluxed for thirteen hours. The solvent was removed and the resulting oil crystallized twice from ethanol. The product weighed 3.3 g. and melted at 73.5–74.5°. An additional 0.9 g. of material which melted at 72–73.5° was recovered from the mother liquors. The compound did not decolorize permanganate and was returned unchanged after being heated with acetic anhydride.

Anal. Calcd. for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.38; H, 8.99.

Enolization of α-Mesitylpropiomesitylene.—A solution of 1 g. of the ketone in alcoholic sodium ethoxide (2 g. of sodium in 50 cc. absolute ethanol) was refluxed thirteen hours, cooled, poured into 300 cc. of water and acidified with hydrochloric acid. The mixture was extracted with ether and the extract dried with calcium chloride. Removal of the ether left an oily residue which was taken up in hot alcohol and cooled. A white solid was obtained which melted at 125–127°. A mixed melting point with 1,2-dimesityl-1-propen-1-ol showed no depression. The yield was nearly quantitative.

Hydrolytic Cleavage of α-Mesitylpropiomesitylene.—Fifty cubic centimeters of sirupy phosphoric acid and 4 g. of the ketone were stirred and refluxed for seven hours, poured into water and extracted with ether. The ether solution was extracted with 10% sodium hydroxide solution. The ether was separated from the alkali-insoluble material and the residue steam distilled until all the oily material was removed. The distillate was extracted with ether and dried with calcium chloride. After removal of the solvent, the residue was distilled at atmospheric pressure. The colorless product boiled at 162–165° and weighed 0.8 g. One-half cubic centimeter of the product was treated with yellow fuming nitric acid at 0° for five minutes and then poured into water. After crystallization twice from ethanol, the product melted at 83–85° and showed no depression in melting point when mixed with an authentic sample of dinitromesitylene.

The alkaline extract was acidified and extracted with ether. Removal of the ether left a dark solid which was triturated with three 10-cc. portions of hot low-boiling petroleum ether. The combined extracts were treated with Norite and concentrated to a small volume. The colorless product, obtained by cooling, weighed 0.5 g. and melted at 101–103°. Crystallized twice from high-boiling petroleum ether, the α-mesitylpropionic acid melted at 104–105°.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39; neut. eq., 192. Found: C, 74.86; H, 8.63; neut. eq., 190.

Summary

The vinyl alcohol, 1,2-dimesityl-1-propen-1-ol, and its acetate have been cleaved by ozone to yield mesitoic acid and acetomesitylene. The same products form when the enol is exposed to air for several weeks.

Oxidation with permanganate or bromanil reconverts the enol to α-mesitylvinyl mesityl ketone.

The enol has been ketonized by heating with methanolic hydrogen chloride. The ketone, α-mesitylpropiomesitylene, has been enolized by treatment with sodium ethoxide. Hot sirupy phosphoric acid cleaves the ketone to mesitylene and α-mesitylpropionic acid.

URBANA, ILLINOIS RECEIVED JUNE 19, 1941