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The Condensation of Paraformaldehyde with Acetomesitylene

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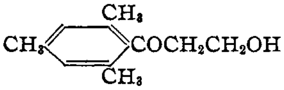
When acetomesitylene is condensed with paraformaldehyde in the presence of potassium carbonate and methanol the principal product is a liquid which was identified as the monomethylol derivative (I). Treatment with hydrochloric acid converted this compound into a substance which was thought to be the corresponding chloride (II).[2] However, subsequent work showed that these structures were open to question. The methylol derivative, made later by the action of formaldehyde on the bromomagnesium derivative of acetomesitylene,[3] proved to be different from that reported previously. The chloride was synthesized by adding hydrogen chloride to vinyl mesityl ketone (III).[4] The compound produced in this manner was entirely different from that first reported. These observations made it necessary to reëxamine the product from acetomesitylene and paraformaldehyde.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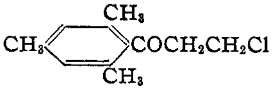
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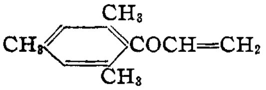
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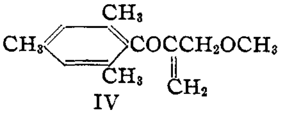
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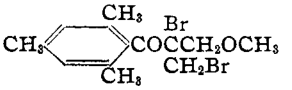

V

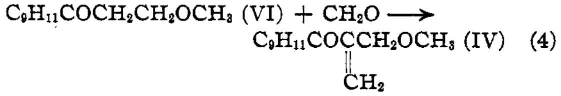
By careful refractionation of this oil it was found that the main portion was a compound somewhat richer in carbon than the liquid which was described earlier. It proved to be *an unsaturated ether* having the structure represented by formula IV. The evidence for this structure is conclusive. The compound reacts with bromine to give a stable dibromide (V) from which it is regenerated by treatment with sodium iodide. Catalytic hydrogenation converts the unsaturated ether to isobutyromesitylene. Zeisel determinations show that one methoxyl group is present. Structure IV is the only one which will explain all of these facts.

The formation of the unsaturated ether (IV) by the action of paraformaldehyde on acetomesitylene might be explained by the following steps[5]

$$C_9H_{11}COCH_3 + CH_2O \longrightarrow C_9H_{11}COCH_2CH_2OH \qquad (1)$$

$$C_9H_{11}COCH_2CH_2OH \longrightarrow C_9H_{11}COCH{=}CH_2 + H_2O \qquad (2)$$

$$C_9H_{11}COCH{=}CH_2 + CH_3OH \longrightarrow C_9H_{11}COCH_2CH_2OCH_3 \qquad (3)$$



$$C_9H_{11}COCH_2CH_2OCH_3\ (VI) + CH_2O \longrightarrow C_9H_{11}CO\underset{\overset{\|}{CH_2}}{C}CH_2OCH_3\ (IV) \qquad (4)$$

Experiments designed to test this mechanism have shown that it is possible. Distillation of the methylol derivative of acetomesitylene was ac-

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[1] Röhm and Haas Research Assistant.

[2] Fuson, Ross and McKeever, THIS JOURNAL, **61**, 414 (1939).

[3] *Cf.* Fuson, Fugate and Fisher, *ibid.*, **61**, 2362 (1939).

[4] A description of this new ketone will be published in connection with other work.

[5] Steps 3 and 4 are somewhat similar to those proposed by Gilbert and Donleavy for the polycondensation of acrolein and methylacrolein (THIS JOURNAL, **60**, 1737, 1911 (1938)).

companied by dehydration to the corresponding vinyl ketone (step 2). The addition of methanol to vinyl mesityl ketone (step 3) was found to take place in the presence of potassium carbonate. From the methoxypropiomesitylene (VI) so formed the unsaturated ether (IV) was obtained readily by treatment with paraformaldehyde (step 4). The unsaturated ether was made also by combining the last two steps, *i. e.*, by treating vinyl mesityl ketone with paraformaldehyde in the presence of methanol and potassium carbonate.

Experimental

Preparation of β-Mesitoylethyl Alcohol (I).—To 0.15 mole of the bromomagnesium enolate of acetomesitylene[3] in 300 cc. of absolute ether was added with stirring at 0° 0.3 mole of gaseous formaldehyde. The formaldehyde was produced by heating paraformaldehyde to 170–200° and was introduced into the reaction mixture through a large inlet tube. The mixture was stirred for ten hours at room temperature, then poured into 600 cc. of water which had been acidified with 30 cc. of concentrated hydrochloric acid. The ether layer was separated, washed three times with very dilute hydrochloric acid, twice with water and dried over calcium chloride. The ether was removed and the residue distilled *in vacuo*. There were obtained 6 g. of acetomesitylene, 14 g. of an almost colorless liquid boiling at 135–138° (4 mm.) and 3 g. of residue.

Ten grams of the liquid when redistilled yielded 5 g. of vinyl mesityl ketone, b. p. 95–96.5° (3 mm.), and 5 g. of β-mesitoylethyl alcohol, b. p. 121–123° (2 mm.); n^{20}_{D} 1.5340. The pure compound could not be distilled without appreciable loss, presumably due to dehydration.

Anal.[6] Calcd. for $C_{12}H_{16}O_2$: C, 74.94; H, 8.41. Found: C, 75.20; H, 8.37.

The low-boiling compound was proved to be vinyl mesityl ketone by a mixed melting point of the dibromo derivative with α,β-dibromopropiomesitylene. In one experiment, the crude β-mesitoylethyl alcohol decomposed completely when redistillation was attempted. Vinyl mesityl ketone was obtained in a yield of more than 90%.

Action of Concentrated Hydrochloric Acid on Mesitoylethyl Alcohol.—A mixture of 3 g. of the crude alcohol and 100 cc. of concentrated hydrochloric acid was stirred for forty-eight hours. The reaction mixture was poured into 500 cc. of water and extracted with ether. The ether extracts were washed several times with water, dried and the ether was removed by an air blast. The viscous yellow residue was cooled and induced to solidify by scratching the sides of the container. The chloride separated from low-boiling petroleum ether as colorless plates, m. p. 46–46.5°. The yield was 2.5 g. A mixed melting point with β-mesitoylethyl chloride (II)[4] showed no depression.

Preparation of 3-Methoxyisopropenyl Mesityl Ketone (IV).[2]—A mixture of 81 g. of acetomesitylene, 45 g. of paraformaldehyde, 5 g. of potassium carbonate and 200 cc. of methyl alcohol was shaken at room temperature for four days. The solution was poured into water, acidified with dilute hydrochloric acid and extracted with several small portions of benzene. The benzene extracts were washed thoroughly, the benzene was removed and the residue fractionally distilled at diminished pressure. The following fractions were obtained: (1) 16 g., b. p. 95–122° (4 mm.); (2) 56 g., b. p. 123–129° (4 mm.); (3) 6 g., b. p. 130–136° (4 mm.); (4) 20 g., residue. Fraction 2 was redistilled three times. The 3-methoxyisopropenyl mesityl ketone was a colorless oil, b. p. 110.5–111° (1.5 mm.); n^{20}_{D} 1.5208; d^{20}_{20} 1.0101.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.02; H, 8.31; $-OCH_3$, 14.22. Found: C, 76.86, 76.76; H, 8.58, 8.50; $-OCH_3$, 13.85, 14.12.

Preparation of the Dibromo Derivative (V).—A solution of 5.8 g. of bromine in 15 cc. of carbon tetrachloride was added dropwise with stirring to a mixture of 7.8 g. of the ketone and 50 cc. of carbon tetrachloride. The reaction mixture was washed thoroughly with water, dried for one hour over calcium chloride, filtered and the carbon tetrachloride removed by an air blast. A small amount of low-boiling petroleum ether was added to the oil, the solution cooled to 0° and the walls of the vessel were scratched. The mixture solidified almost completely. The dibromide was recrystallized from low-boiling petroleum ether, then methyl alcohol, m. p. 50.5–51.2°; yield 11.5 g.

Anal. Calcd. for $C_{14}H_{18}O_2Br_2$: C, 44.47; H, 4.80. Found: C, 44.49; H, 4.84.

Reaction of Sodium Iodide with the Dibromide.—To 11 g. of the dibromide dissolved in 150 cc. of acetone was added a water solution of 13.5 g. of sodium iodide. The solution darkened immediately. It was allowed to stand overnight at room temperature, poured into 500 cc. of water to which had been added 10 g. of sodium thiosulfate, and extracted with ether. The ether extracts were washed with dilute sodium thiosulfate, then with water, the ether was removed and the residue distilled. There was obtained 4 g. (62% of the theoretical amount) of a liquid boiling at 118° (3 mm.). To remove a trace of iodine this liquid was dissolved in ether and the solution washed with dilute sodium thiosulfate solution. After the solvent was removed the residue was twice distilled, b. p. 114° (2 mm.); n^{20}_{D} 1.5211.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.02; H, 8.31. Found: C, 76.76; H, 8.42.

It could be reconverted to the dibromide.

Catalytic Reduction of 3-Methoxyisopropenyl Mesityl Ketone.—A mixture of 10.2 g. (0.046 mole) of the ketone, 150 cc. of methyl alcohol and 0.5 g. of Raney nickel was reduced under a pressure of two atmospheres. About 0.085 mole of hydrogen was absorbed. The mixture was filtered, poured into water and extracted with ether. The ether extracts were washed with water, dried and distilled. After the ether had been removed, there was obtained a very small amount of low-boiling material, 5 g. of colorless oil, b. p. 120–123° (10 mm.), 3 g. of light yellow oil, b. p. 116–125° (6 mm.) and a small amount of residue. The large fraction was redistilled, b. p. 120–121° (10 mm.);

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(6) The analyses reported in this paper are microanalyses and were carried out by Mr. L. G. Fauble and Mr. W. H. Taylor.

n^{20}_{D} 1.5098. A second redistillation produced no change in the boiling point or refractive index. Isobutyromesitylene prepared from isobutyryl chloride and mesitylene by the Friedel–Crafts method boils at 120–121° (10 mm.) and has a refractive index n^{20}_{D} 1.5095. Nitration of this reduction product yielded a compound melting at 125–132°. After several recrystallizations from ethyl alcohol it crystallized in white plates, m. p. 135–138°. The mixed melting point with an authentic sample of dinitroisobutyromesitylene was 135–139°.

Preparation of β-Methoxypropiomesitylene (VI).—A solution of 10 g. of vinyl mesityl ketone, 100 cc. of methyl alcohol and 2 g. of potassium carbonate was shaken for thirty-six hours at room temperature. It was then poured into 300 cc. of water, acidified with dilute hydrochloric acid and extracted with ether. The ether extracts were washed and dried over calcium chloride. The ether was removed and the product distilled. There was obtained 7 g. (60% of the theoretical amount) of β-methoxypropiomesitylene, b. p. 117–117.5° (2.5 mm.); n^{20}_{D} 1.5110; d^{20}_{20} 1.0106, and 3.5 g. of residue.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.50; H, 8.86.

If fifteen drops of concentrated hydrochloric acid were used as the catalyst[7] and the reaction mixture refluxed for one hour, the yield of β-methoxypropiomesitylene was increased to 95%.

Bromination of β-Methoxypropiomesitylene.—To a solution of ten drops of the ketone and 3 cc. of carbon tetrachloride was added a 25% bromine–carbon tetrachloride solution until hydrogen bromide was evolved. The excess bromine and carbon tetrachloride were removed by an air blast. A small amount of low-boiling petroleum ether was added and the mixture cooled. It solidified almost completely. The solid recrystallized from methyl alcohol in the form of long white needles, m. p. 78–79.5°. A mixed melting point with α,β-dibromopropiomesitylene showed no depression.

Action of Paraformaldehyde on β-Methoxypropiomesitylene.—To 10 g. of the ketone was added 90 cc. of methyl alcohol, 3 g. of paraformaldehyde and 0.5 g. of potassium carbonate. The reaction mixture was shaken for four days. It was worked up as described above in the preparation of 3-methoxyisopropenyl mesityl ketone. There was obtained 7 g. of light yellow oil, b. p. 115–120° (2.5 mm.); n^{20}_{D} 1.5193, and 3 g. of residue. The oil was redistilled, b. p. 113.5–114° (2 mm.); n^{20}_{D} 1.5207. Bromination of this oil yielded a solid, m. p. 50–51°. The mixed melting point with the dibromo derivative of 3-methoxyisopropenyl mesityl ketone was 50–51°.

Reaction of Paraformaldehyde with Vinyl Mesityl Ketone.—A mixture of 17.4 g. of vinyl mesityl ketone, 6 g. of paraformaldehyde, 100 cc. of methyl alcohol and 2 g. of potassium carbonate was shaken at room temperature for four days. The reaction mixture was worked up as described in the preparation of 3-methoxyisopropenyl mesityl ketone. There was obtained by distillation 12.5 g. of liquid, b. p. 117.5–118.5 (2.5 mm.); n^{20}_{D} 1.5198, and from the residue 2.2 g. of white plates, m. p. 105–107°. A mixed melting point of this solid with a sample of 2,4-dimesitoyl-2,4-pentadiene[2] showed no depression.

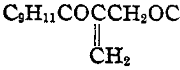
A small portion of the liquid was brominated. The solid isolated from the reaction melted at 50–51° and proved to be identical with the bromination product of 3-methoxyisopropenyl mesityl ketone.

Summary

The monomethylol derivative of acetomesitylene ($C_9H_{11}COCH_2CH_2OH$) has been synthesized by condensing the bromomagnesium derivative of acetomesitylene with formaldehyde.

The corresponding chloride ($C_9H_{11}COCH_2CH_2Cl$) has been prepared by the action of hydrochloric acid on either the monomethylol derivative or vinyl mesityl ketone.

Attempts to prepare the methylol derivative by treating acetomesitylene with paraformaldehyde in the presence of potassium carbonate and methanol have been found to yield a complex ether,



$C_9H_{11}CO\underset{\displaystyle CH_2}{\overset{}{\underset{\|}{C}}}CH_2OCH_3$.

A mechanism is presented for the formation of this ether.

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(7) Kohler, *Am. Chem. J.*, **42**, 375 (1909).