[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

THE CONDENSATION PRODUCTS OF METHYLETHYL KETONE[1]

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Introduction

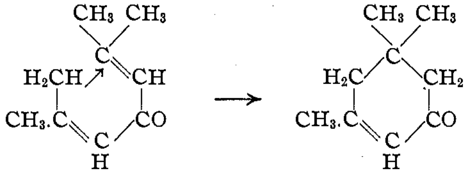
The action of various condensing agents upon acetone has been studied by numerous investigators.[2]

The most important of these condensation products of acetone are mesityl oxide, mesitylene, phorone, and isophorone. The following equations summarize the action of various reagents upon acetone.

$$(CH_3)_2CO + H_2CH.CO.CH_3 \longrightarrow (CH_3)_2C = CH.COCH_3. \text{ Mesityl oxide} \quad (1)$$

$$3(CH_3)_2CO \longrightarrow C_6H_3(CH_3)_3 \text{ 1,3,5. Mesitylene} \quad (2)$$

$$(CH_3)_2C_2 = CH.CO.CH_3 + OC(CH_3)_2 \longrightarrow (CH_3)_2C = CH.CO.CH = C(CH_3)_2. \text{ Phorone} \quad (3)$$



Isophorone (4)

$$4\ (CH_3)_2CO - 3\ H_2O = \text{Xylitone. (Constitution unknown.)} \quad (5)$$

In the light of the very interesting work that has been done on the condensation of acetone, it seemed important that corresponding investigations be made on methylethyl ketone, which is now available in large quantities.

A study of the literature shows that a compound assumed to be a homolog of mesityl oxide was first prepared by Pawlow[3] by the action of propionyl chloride upon zinc dimethyl and methylethyl ketone in the cold, and later by Schramm[4] by the action of sodium on methylethyl ketone in benzene solution. The substance Schramm obtained was a nearly colorless liquid of peppermint-like odor, boiling at 163–165° (729 mm.). The only derivative of this substance that Schramm attempted to obtain was a dark colored oil that easily decomposed, formed by the action of bromine. Schramm also obtained an impure ketone with a camphor-like odor, of the probable formula $C_{12}H_{20}O$, boiling at 248–253°, which he considered a trimethyl phorone. Descudé,[5] working with zinc chloride upon a mixture of acetyl chloride and methylethyl ketone, obtained a liquid of peppermint-like odor boiling at 167–168°, evidently the same as that obtained by Schramm, and a second liquid boiling at 248–253° which he considered to be a homolog of

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[1] From a thesis submitted to the Faculty of the Graduate School of the University of Colorado by W. Warren Howe in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] (a) Kane, *Pogg. Ann.*, **44**, 475 (1838). (b) Fittig, *ibid.*, 110, 35 (1859). (c) Von Baeyer, *ibid.*, **140**, 301 (1866). (d) Claisen, *ibid.*, **180**, 1 (1876). (e) Bredt and Rübel, *ibid.*, **289**, 10 (1895); **299**, 160 (1897). (f) Kerp and Müller, *ibid.*, **290**, 123 (1896); (g) **299**, 193 (1897). (h) Knoevenagel, *ibid.*, **297**, 185 (1897). (i) Crossley and Gilling, *J. Chem. Soc. Abs.*, **95**, 19 (1909). (j) Pinner, *Ber.*, **15**, 589 (1882).

[3] Pawlow, *Ann.*, **188**, 138 (1877).

[4] Schramm, *Ber.*, **16**, 1581 (1883).

[5] Descudé, *Ann. chim.*, [7] **29**, 494 (1903).

phorone. This second liquid was also studied by Braun and Kittel[6] who recorded a boiling point of 256° and found that, assuming a formula of $C_{12}H_{20}O$, it added 4 bromine atoms. They therefore concluded that the compound had two double bonds and arbitrarily assigned to it the formula $CH_3.CO.C(CH_3) = C(CH_3).C(CH_3) = C(CH_3).CH_2.CH_3$.

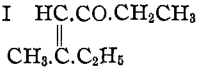
The present research was undertaken to study first, the action of hydrogen chloride and of sulfuric acid upon methylethyl ketone, and second, the action of sodium ethylate upon methylethyl ketone.

Theoretical Part

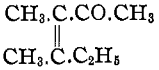
The theoretical possibilities are much greater for the formation of condensation products from methylethyl ketone than from acetone. From methylethyl ketone we derive for the homologs of mesityl oxide 2 different structural oxides, each of which may occur in a *cis* and a *trans* form.

Each of these 4 oxides in turn by condensing with a third molecule of methylethyl ketone may yield 2 different structural homologs of phorone. The *cis* and *trans* forms of these structural isomers are reciprocally identical. It is found, therefore, that there are 4 possible different isomers of the phorone thus obtained. The following tables show the structures of these isomes.

The Homomesityl oxides

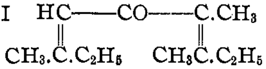
I


$$\begin{array}{l} HC.CO.CH_2CH_3 \\ \| \\ CH_3.C.C_2H_5 \end{array}$$

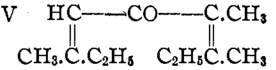
II


$$\begin{array}{l} CH_3.C.CO.CH_3 \\ \| \\ CH_3.C.C_2H_5 \end{array}$$

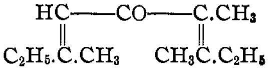
The Homophorones

III


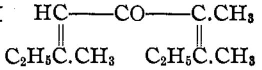
$$\begin{array}{lcl} HC & —CO— & C.CH_3 \\ \| & & \| \\ CH_3.C.C_2H_5 & & CH_3C.C_2H_5 \end{array}$$

IV


$$\begin{array}{lcl} HC & —CO— & C.CH_3 \\ \| & & \| \\ CH_3.C.C_2H_5 & & C_2H_5C.CH_3 \end{array}$$

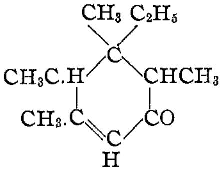
V


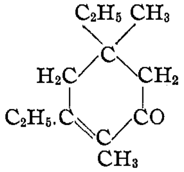
$$\begin{array}{lcl} HC & —CO— & C.CH_3 \\ \| & & \| \\ C_2H_5.C.CH_3 & & CH_3C.C_2H_5 \end{array}$$

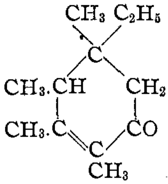
VI


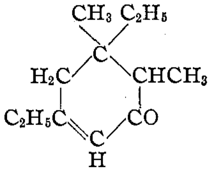
$$\begin{array}{lcl} HC & —CO— & C.CH_3 \\ \| & & \| \\ C_2H_5C.CH_3 & & C_2H_5C.CH_3 \end{array}$$

The isomeric homologs of phorone III, IV, V and VI may in turn suffer ring formation producing isomeric homologs of isophorone. A detailed study will show that 4 structurally different isomers, all homologs of isophorone, are possible. Their structures are indicated as follows.

(α)


(β)


(γ)


(δ)


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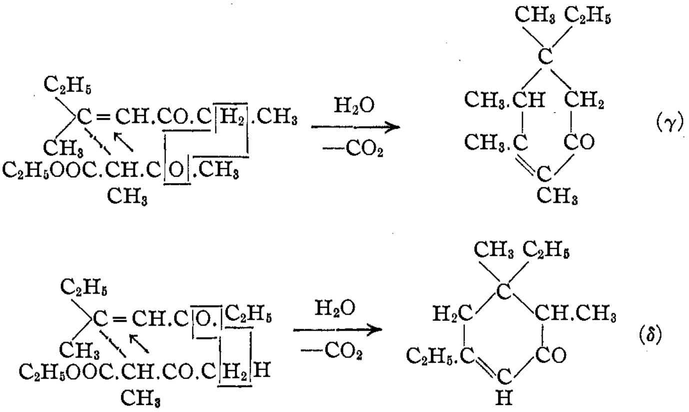
[6] Braun and Kittel, *Monatsh.*, 27, 804 (1906).

Similarly, a great number of isomeric homologs of xylitone could be worked out from a theoretical standpoint.

In this paper, for the convenience of nomenclature, we shall give the name "homomesityl oxide" to the homologs of mesityl oxide, the name "homophorone" to the homologs of phorone, and the name "homo-isophorone" to the homologs of isophorone. On oxidation homomesityl oxide I should yield propionic acid, and homomesityl oxide II should yield acetic acid, and a mixture of I and II should yield a mixture of acetic and propionic acids.

Syntheses carried out in the manner of Knoevenagel[2h] should throw light on the constitution of homo-isophorones, while molecular-refraction data should be valuable confirmatory evidence. If a homomesityl oxide has been shown to have the structure I, it should, when condensed with methyl aceto-acetic ester by Knoevenagel's method, yield homo-isophorones with structures corresponding to the isomers γ and δ, thus:



(6)

A study of the reactions, therefore, leads to the following.

(1) Homomesityl oxide I
+ methyl aceto-acetic ester ⟶ homo-isophorones γ and δ. (7)
(2) Homomesityl oxide II
+ methyl aceto-acetic ester ⟶ homo-isophorone α only. (8)
(3) Homomesityl oxide I
+ propionyl acetic ester ⟶ homo-isophorone β only. (9)
(4) Homomesityl oxide II
+ propionyl acetic ester ⟶ homo-isophorones γ and δ. (10)

It will be shown in the experimental part of this paper that only one compound corresponding to a homomesityl oxide occurs among the condensation products obtained by using sulfuric acid or sodium ethylate as condensing agent, and that the homomesityl oxide yields only propionic acid on oxidation with permanganate. It must, therefore, be homomesityl oxide I. It will also be shown that 3 other condensation products gave analytical results and molecular weights such that they must have the empirical formula $C_{12}H_{20}O$, and must, therefore, be either homophorones or homo-isophorones. Condensation of the experimentally obtained homomesityl oxide with methyl aceto-acetic ester after the method of Knoevenagel gave a mixture of 2 compounds which on fractionation under diminished pressure were found to be identical with two of the condensation products having the formula $C_{12}H_{20}O$. These two compounds boiling at 256–260° and 280–285°, respectively, at 630 mm., must therefore have the structures γ and δ, or δ and γ (according to Equation 7 given above).

The non-occurrence of homomesityl oxide II among the condensation products from either acid or alkaline condensing agents shows that this homomesityl oxide must have been used up during the reactions to form homophorones by condensing with another molecule of methylethyl ketone.

If we assume the exaltation of the molecular refraction of homo-isophorone to be the same as that for isophorone, this compound should show a molecular refraction, M, of 56.08. Similarly, homophorone should show a molecular refraction of 59.7. The actually observed molecular refraction of the third product of condensation showing an empirical formula $C_{12}H_{20}O$ and boiling point 206–210°, was 57.72. This value, while not as high as that calculated above, is altogether too high for a homo-isophorone. Also, the fact that this compound shows the next higher boiling point in the series to homomesityl oxide would point to its being a homophorone. The following table shows the boiling points of the two series (acetone and methylethyl ketone).

Mesityl oxide	127–130°	Homomesityl oxide	156–160°
Phorone	197	Compound in question	206–210
Isophorone	213–215	Homo-isophorone γ or δ	256–260
		Homo-isophorone δ or γ	280–285

Moreover, acetone with hydrochloric acid acting as a condensing agent yields only mesityl oxide and phorone. Similarly, hydrochloric acid acting on methylethyl ketone yields only homomesityl oxide and the compound in question, as will be shown by the experimental results. It is evident that further work must be done on this compound to settle definitely whether or not it is a homophorone or a homo-isophorone. What evidence we have points to its being a homophorone.

Experimental Part

The methylethyl ketone was a very pure, water-white product containing traces of acetone. On distillation, all but a small fraction of the product passed over at 70–73° (625 mm.).

Condensation of Methylethyl Ketone under the Influence of Dry Hydrogen Chloride

Into 160 g. of methylethyl ketone, packed in ice, dry hydrogen chloride was passed not too rapidly until the liquid was completely saturated. The cork of the container was tied down so as to leave the liquid under a slight pressure. The mixture was allowed to stand for 30 days. The ketone was then washed with water to remove the excess of acid, and poured into alcoholic potassium hydroxide; water was added, and an oily layer separated that was taken up with ether. The ether solution was dried over anhydrous sodium sulfate. After the ether was distilled an oily mixture remained that was fractionated, first at atmospheric pressure (625 mm.) up to 165°, and then under diminished pressure (15 mm.). Homomesityl oxide and homophorone only were obtained. The results are contained in Table I.

Condensation of Methylethyl Ketone under the Influence of Sulfuric Acid

Experiments were carried out with fuming C. P. sulfuric acid containing, 20% excess of sulfur trioxide, and with a C. P. concd. acid, d. 1.84. It was found that the action of fuming acid on methylethyl ketone for 10 to 12 days was the same as that of the concd. acid during 16 to 20 days. Since an observation of the final effect of sulfuric acid on the ketone was desired the action was allowed to proceed over a long period. A considerable amount of homomesityl oxide forms with the fuming acid in 2 hours or with the concd. acid in 24 hours. The fuming acid will give a fair yield of homophorones in 4 days and the concd. acid in 7 days. In any case, the acid mixture was poured into two 2-liter beakers half filled with snow or chipped ice, and a concd. solution of potassium hydroxide was added gradually until the black oil separated completely. The oil was not soluble in dil. sulfuric acid; therefore the dilute acid, colored with green to golden fluorescent sulfonic acids, was discarded. The black oil was dissolved in 5 times its volume of ether; the ether solution was then washed repeatedly with dil. sodium hydroxide solution and finally with water. This treatment changed the ether solution from a black to a beautiful golden-brown. After the ether had been dried with calcium chloride it was distilled and the oil fractionated, first at atmospheric pressure (625 mm.) and then under diminished pressure (15 mm.). Typical results are shown in Table I.

Many difficulties were encountered in using acid condensation agents with methylethyl ketone. In the experiments with both the hydrochloric and the sulfuric acids, addition products were formed that contaminated every fraction. After every precaution, traces of acid (hydrochloric or sulfurous) were found to come over during a distillation, and apparently pure fractions became dark colored on standing. The action of sodium ethylate, on the other hand, gave pure products.

Condensation of Methylethyl Ketone under the Influence of Sodium Ethylate

Pure sodium ethylate was prepared by the gradual addition of the calculated amount of absolute alcohol to sodium wire covered with a large volume of ether. Enough of the condensing agent was used to furnish sodium in the proportion 1 Na: 4 $C_2H_5.CO.CH_3$. The ethylate crystals were added in portions to the slightly cooled ketone. The mixture was then allowed to stand at ordinary temperatures protected from moisture for 3 or 4 weeks. When the sodium ethylate was not prepared pure, reddish, water-soluble waste products were obtained. The reaction mixture was then dissolved in 4 times its volume of ether and the ether solution washed 5 or 6 times with water until the wash water was neutral. The solution was dried over calcium chloride overnight, the ether distilled and the oil fractionated, first at atmospheric pressure until the homomesityl oxide was removed, and then at diminished pressure. Typical results are shown in Table I.

The results in this table are not "averages" but are from actual experiments selected from 20 to 30 such experiments.

Fractions 1, 2 and 3 were always obtained under normal pressure (625 mm. at Boulder).

Fractions 4 to 10, inclusive, were obtained at diminished pressure (15 mm.).

On repeated fractionation, Fraction 3 yielded pure homomesityl oxide; Fraction 4 yielded pure homophorone; Fractions 6 and 8 yielded the pure homo-isophorones.

Table I

Results

Fraction	Temperature ° C.	HCl gas G.	Fuming H_2SO_4 G.	H_2SO_4 G.	Sodium ethylate G.	Main constituent
1	60–90	56	12	40	60	methylethyl ketone
2	90–140	24	10	12	24	
3	140–165	60	49	35	27	homomesityl oxide
4	90–130	9	58	48	62	homophorone
5	130–145	..	16	40	50	
6	145–160	..	36	70	75	homo-isophorone
7	160–170	..	13	15	12	
8	170–180	..	37	45	34	homo-isophorone
9	180–200	..	24	45	38	
10	200–230 and above	..	50	50	58	
Character of agent		dry gas	450 20% ex. SO_3,	184 d. 1.84	250	
Weight of $CH_3COC_2H_5$ used		160	400	800	800	
Raw oil obtained		150	315	510	446	

It should be noted in connection with these tables of fractionation that the intermediate fractions, indicated in the table only by a temperature interval, many times represent nearly constant-boiling mixtures. These could be only partially separated even after repeated fractionation. The investigators[7] of the products of condensation of acetone encountered the same difficulty. That these fractions were truly "constant-boiling mixtures" was shown also by the fact that the refractive index varied, and that the combustion data on them varied.

Homomesityl Oxide

Physical Constants.—Homomesityl oxide, $C_8H_{14}O$, is a nearly colorless liquid with a peppermint-like odor and a camphor-like taste; b. p., 156–160°(625 mm.); d_4^{20}, 0.8628; n_D^{20}, 1.4453; $M_D \longrightarrow$ 38.94 (calc., 38.72); mol. wt. (from the vapor density), calc., 126.15; found, 132, 131.

Analysis. Calc. for $C_8H_{14}O$: C, 76.13; H, 11.18. Found: C, 76.35; H, 11.39.

Preparation of a Liquid Oxime.—The oxime was prepared by allowing the ketone to react with free hydroxylamine under the supposition that a crystalline oxime would in that way be formed as is the case with mesityl oxide; 20 g. of oil was dissolved in 70 cc. of alcohol and a saturated water solution of the calculated amount of hydroxylamine hydrochloride was added gradually. More alcohol was added to make the solution clear. The mixture was then refluxed for 2 hours, which caused a blackening of the product. A few drops were placed on a microscope slide and allowed to evaporate. No crystals appeared. The reaction mixture was, therefore, allowed to stand for 10 days. A saturated solution of potassium carbonate was then added gradually, causing the separation of an oily layer in which a few crystals were suspended. Since all attempts to cause further crystallization failed, the product was distilled at 17 mm. This

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[7] Ref. 2g, p. 212.

distillation gave 10 g. of the original oil and a fraction boiling at 120–140°. By repeated distillation a constant-boiling fraction was obtained of light greenish tinge, boiling at 132–137° (17 mm.).

Analysis. Calc. for $C_8H_{14}NOH$: N, 9.9. Found (Kjeldahl): 9.2.

An Attempt to Prepare a Semicarbazone.—Bodroux and Taboury[8] report a semicarbazone of homomesityl oxide melting at 114–115°. We wish to call attention to the fact that, although we also obtained a crystalline precipitate of melting point 114–115° by the action of 1 molecule of homomesityl oxide on 1 molecule of semicarbazide in alcoholic solution using potassium acetate to neutralize the semicarbazide hydrochloride, this precipitate proved to be a mixture. The precipitate was dissolved in alcohol and diluted with an equal volume of water. A fraction of melting point 140° precipitated almost immediately. The remaining fraction melted at 108°. The authors believe the reaction to be more complex than indicated by the work of Bodroux and Taboury, and hope by further work to isolate the normal semicarbazone of homomesityl oxide and a pyrazoline derivative which seems to be formed.

The Semicarbazide-semicarbazone.—One molecule of homomesityl oxide was allowed to react with 2 molecules of semicarbazide hydrochloride in alcoholic solution. In an acid solution of this kind the semicarbazide-semicarbazone precipitated almost immediately. The crystals were insoluble in alcohol and water and ordinary organic solvents. They were soluble in hot dil. hydrochloric acid and were reprecipitated by neutralizing the acid with sodium hydroxide. By recrystallizing in this way they were obtained pure, appearing as microscopic prisms; m. p., 265–266° (decomp.).

Analysis. Calc. for $C_{10}H_{22}N_6O_2$: N, 32.55. Found (Kjeldahl): 32.6.

Oxidation with Potassium Permanganate.—Twenty-five g. of homomesityl oxide was shaken with 600 cc. of water, in 50g. portions. A 5% solution of potassium permanganate was added in small quantities and the mixture frequently and vigorously shaken until it retained the color after standing for 24 hours. The slight excess of permanganate was destroyed by heat. A little over 2 molecules of permanganate were required to 1 of homomesityl oxide. The large volume of solution thus obtained was evaporated to 400 cc. and the residue was then acidified with dil. sulfuric acid. Carbon dioxide was evolved in this step. The acid solution was extracted several times with ether. After being dried over anhydrous sodium sulfate, the ether solution was evaporated, leaving a brown liquid. This liquid was distilled at 15 mm. A study of the analytical results of the distillate shows that the liquid was a mixture of propionic acid and some lower-boiling substance, not acetic acid. Three fractions were obtained. The highest one on titration was shown to be propionic acid; 0.2801 g. required for neutralization 0.1485 g. of sodium hydroxide solution, a quantity which neutralizes 0.2784 g. of propionic acid.

The next lower fraction could not have been acetic acid and it could not have contained acetic acid, since 0.4926 g. required for neutralization 0.2454 g. of alkali solution, a quantity that neutralizes 0.4601 g. of propionic acid, and only 0.3681 g. of acetic acid. Moreover, the highest fraction, b. p., 45–50° (15 mm.), gave a propionyl *p*-toluidine melting at 118° (the pure crystals should melt at 123°; not enough was obtained to be recrystallized); also, the boiling point of the fraction was 125–133° (622 mm.), identical with that of a known pure propionic acid at Boulder. A special effort was made to isolate acetic acid from these products; none was found. The presence of methylethyl ketone in the lowest distillate was indicated by the odor, but owing to the small yield of oxidation products, methylethyl ketone could not be isolated. The course of the reaction evidently is $(C_2H_5)(CH_3)C{=}CH.CO.C_2H_5 + 4O = (C_2H_5)(CH_3)C{=}O + C_2H_5$-

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[8] Bodroux and Taboury, *Compt. rend.*, 149, 422 (1909).

COOH + CO_2, and we must conclude that the homomesityl oxide here obtained has the constitution $(C_2H_5)(CH_3)C{=}CH.CO.C_2H_5$.

Homophorone

Physical Constants.—Homophorone, $C_{12}H_{20}O$, is a clear, slightly straw-colored liquid with a camphor-like odor and taste; b. p., 206–210° (625 mm.); d_4^{20}, 0.8857; n_D^{20}, 1.4792, M_D, calc. (without exaltation), 56.71; + exaltation for phorone (+3) = 59.71; found; 57.72; mol. wt. (from vapor density), calc., 180.22; found, 185, 172.

Analysis. Calc. for $C_{12}H_{20}O$: C, 79.93; H, 11.18. Found: C, 79.59; H, 10.97.

The composition of this compound must be determined by further work as indicated in the discussion. Moreover, the data given above are from a fraction prepared by condensing methylethyl ketone with sulfuric acid. It is believed to be present among the products obtained by the action of sodium ethylate. An unexpected difficulty, however, was encountered in getting a pure fraction and none has been obtained so far. The authors propose to continue the work on this point.

The Homo-isophorones, $C_{12}H_{20}O$

Homo-isophorone, b. p. 256–260° (630 mm.).—This homo-isophorone is a clear yellow liquid with a weak odor and taste of terpene; d_4^{20}, 0.9492; n_D^{20}, 1.5045; M_D, calc. (Eisenlohr), 54.98 + exaltation for isophorone, 54.98 + 1.1 = 56.08; found, 56.12; mol. wt. (from vapor density), calc., 180.22; found, 178,188.

Analysis. Calc. for $C_{12}H_{20}O$: C, 79.93; H, 11.18. Found: C, 80.08; H, 11.12.

An attempt was made to duplicate the work of Braun and Kittel[6] who reported that this homo-isophorone adds 4 atoms of bromine. We were unable to verify their results since our investigations showed that hydrogen bromide was generated in large volume long before an amount of bromine corresponding to 2 atoms was added. The addition of hydrogen chloride was then investigated; 5 g. of the oil was dissolved in 20 cc. of dry liquid carbon disulfide, and hydrogen chloride, dried over phosphorus pentoxide, was passed through the solution. A heavy, black oil separated. It was carefully removed with a pipet and the solvent allowed to evaporate. A weighed amount was then refluxed with a standard solution of sodium hydroxide, and the excess alkali was titrated with 0.1 *N* acid; 0.3898 g. of substance contained 0.0641 g. of hydrogen chloride. This result indicates that this homo-isophorone contains but one double bond and not two as reported by Braun and Kittel.

Homo-isophorone, b. p. 280–285° (630 mm.).—This homo-isophorone is a golden-brown, slightly viscous liquid. Its odor and taste are camphor-like; d_4^{20}, 0.9693; n_D^{20}, 1.5115; M_D, calc., 54.98 + exaltation for isophorone = 56.08; found, 55.74; mol. wt. from vapor density, calc., 180.22; found, 179, 168.

Analysis. Calc. for $C_{12}H_{20}O$: C, 79.93; H, 11.18. Found: C, 80.28; H, 10.81.

The Synthesis of the γ- and δ-Homo-isophorones

In this procedure the method of Knoevenagel[2h] was followed. First, methyl aceto-acetic ester was prepared by the usual method; a pure product was obtained; b. p., 176–178° (630 mm.). Fifty g. of the experimentally obtained homomesityl oxide was mixed with the calculated amount (57 g.) of methyl aceto-acetic ester, and the mixture well cooled. A 25% solution of sodium ethylate in absolute alcohol was prepared and enough of the reagent used to furnish sodium in the proportion 1 Na: 1 $CH_3COCHCH_3.COOC_2H_5$. The alcoholate solution was allowed to stand for 9 days at a temperature of 5–10°, then refluxed on the water-bath for 5 hours to complete the reaction, made acid with 20% sulfuric acid and refluxed for 6 hours to saponify the condensation product. The solution was then cooled and washed 5 times with ether. The ether solution was made slightly alkaline by washing with dil. sodium hydroxide solution, and dried with anhydrous sodium sulfate. After the ether had been distilled, there remained about 50 g. of an oil. Much of the original homomesityl oxide was recovered from this product. The following fractions were obtained from the oil which bore every resemblance to the 2 homo-isophorones described above, in color, odor, taste and physical constants.

FRACTION 1: b. p., 145–165° (15 mm.); n_D^{20}, 1.4970. The corresponding pure homo-isophorone: b. p., 256–260° (630 mm.); b. p., 150–157° (15 mm.); n_D^{20}, 1.5045.

FRACTION 2: b. p., 165–180° (15 mm.); n_D^{20}, 1.5053. The corresponding pure homo-isophorone: b. p., 280–285° (630 mm.); b. p., 170–178° (15 mm.); n_D^{20}, 1.5115.

It is evident, therefore, that the two higher-boiling compounds obtained by the condensation of methylethyl ketone have the constitutions γ and δ or δ and γ, as developed in the discussion.

Summary

1. The condensation products of methylethyl ketone under the influence of hydrogen chloride, of sulfuric acid, and of sodium ethylate have been studied. Hydrogen chloride yields 2 products, homomesityl oxide and homophorone. Both sulfuric acid and sodium ethylate yield homomesityl oxide, homophorone, and 2 homo-isophorones, besides other high-boiling products whose nature has not yet been determined.

2. Homomesityl oxide, prepared with the above reagents, has been shown to have the constitution $(C_2H_5)(CH_3)C{=}CH.CO.C_2H_5$.

3. A liquid oxime of homomesityl oxide has been prepared.

4. The semicarbazone of homomesityl oxide reported by Bodroux and Taboury has been shown to be a mixture. The semicarbazide-semicarbazone of mesityl oxide has been prepared.

5. The probable constitution of homophorone has been discussed.

6. Two homo-isophorones have been isolated, their important constants determined, and their structures shown to correspond to one of two possible constitutional formulas, γ and δ as shown above.

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