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

THE CONDENSATION PRODUCTS OF DIETHYL KETONE

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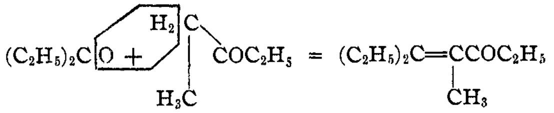
The condensation products of methylethyl ketone under the influence of hydrogen chloride, concd. sulfuric acid, and sodium ethylate have been studied by Ekeley and Howe.[1] Hydrogen chloride yielded homologs of mesityl oxide and phorone, while sulfuric acid and sodium ethylate each yielded homologs of mesityl oxide, phorone, and two isomeric homologs of isophorone. Sodium ethylate was found to be the most satisfactory condensing agent, since it gives purer products than the acid reagents. Where concd. or fuming sulfuric acid is used, the products are nearly always contaminated with sulfonic acids which are exceedingly difficult to eliminate, while hydrogen chloride has a tendency to form addition products due to the unsaturated nature of the compounds.

This paper deals with the condensation products formed by the action of sodium ethylate upon diethyl ketone.

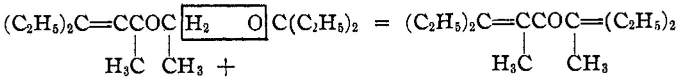
Theoretical Part

The theoretical condensation products of diethyl ketone may be shown by the following reactions.



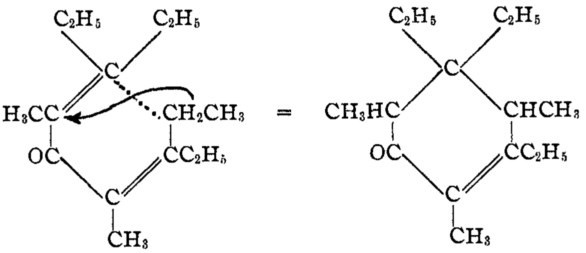
$$(C_2H_5)_2CO + H_2C(CH_3)COC_2H_5 = (C_2H_5)_2C{=}C(CH_3)COC_2H_5 \qquad (1)$$

Homolog of mesityl oxide



$$(C_2H_5)_2C{=}C(CH_3)COCH_2(CH_3) + OC(C_2H_5)_2 = (C_2H_5)_2C{=}C(CH_3)COC(CH_3){=}C(C_2H_5)_2 \qquad (2)$$

Homolog of phorone



(3)

Homolog of isophorone

$$4(C_2H_5)_2CO - 3H_2O = C_{20}H_{34}O, \quad \text{Homolog of xylitone} \qquad (4)$$

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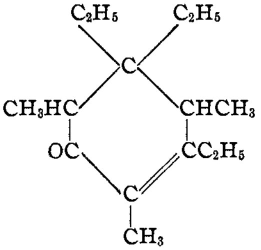
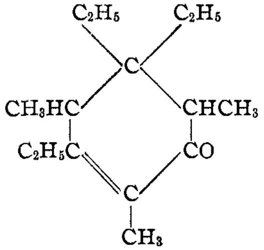
[1] Ekeley and Howe, THIS JOURNAL, **45**, 1922 (1923).

An examination of these formulas will show that there is no possibility of isomerism in the homologs of mesityl oxide, mesitylene or phorone, while that of isophorone may have either of the following space formulas,



or



the two being mirror images.

Since little is known of xylitone, nothing can be said with certainty concerning the possible nature of its homologs.

Throughout the remainder of this paper, for simplicity and for lack of better nomenclature, homologs of mesityl oxide will be designated by the term "homomesityl oxide," homologs of phorone by the term "homophorone," and homologs of isophorone by the term "homo-isophorone."

For the examination of homomesityl oxide and phorone the products of oxidation should be of value. Homomesityl oxide should give upon oxidation a mixture of diethyl ketone and acetic acid. Homophorone should also yield upon oxidation diethyl ketone and acetic acid.

For the differentiation between homophorone and homo-isophorone the molecular refraction exaltation should serve. A determination of the unsaturation value would also give an indication as to the identity of the compound in question, for it will be seen that homophorone has two double bonds whereas homo-isophorone contains only one.

Experimental Part

The sodium ethylate was prepared after the method of Claisen, described by Lassar-Cohn.[2] As prepared by this process it was a light, porous substance, nearly pure white, and quite hygroscopic. It proved to be an excellent condensing agent and much more efficient than that prepared without precautions having been taken to avoid oxidation and to remove the alcohol of crystallization.

Condensation.—The diethyl ketone used was a very pure product, boiling at 101–103° (corr.). Sodium ethylate was used in amounts calculated to furnish sodium in the proportion, 1 Na : $4(C_2H_5)_2CO$. It was pulverized and gradually added to the ketone while the latter was cooled and shaken. The mixture was protected from moisture by means of a calcium chloride tube and kept at a temperature in the neighborhood of 10°.

After twelve days' standing, an equal volume of water was added to the mixture to decompose any unaltered sodium ethylate. The solution was then extracted thrice

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[2] "Arbeitsmethoden für Organisch-Chemische Laboratorien," 1907, p. 729.

with ether in volumes equal to that of the solution. The combined ethereal solutions were washed with water until the reddish-brown water-soluble waste products were removed and the washings no longer gave an alkaline reaction. The ethereal solution was allowed to remain overnight over anhydrous sodium sulfate, protected from the atmosphere. After filtering off the sodium sulfate, the ether was distilled. The remaining liquid was a clear yellow oil with a decidedly fragrant odor, reminding one of certain wild flowers.

Separation of the Products.—The unchanged ketone was distilled at atmospheric pressure, after which the distillation was continued at 20 mm., because the oily products of the condensation decompose when they boil under atmospheric pressure.

Due to the rather high cost of diethyl ketone, only 220 g. was available for the entire research.

From 45 g. of sodium ethylate and 220 g. of diethyl ketone, 190 g. of raw product was obtained. From the initial distillation at 630 mm. (atmospheric pressure at Boulder) 60 g. of diethyl ketone was obtained at 100–120°. The distillation was continued at 20 mm. pressure and the following fractions obtained.

Temp., °C. . .	85–117	117–140	140–166	166–170	170–180	180–189	above 189
Wt., g.	20	10	25	30	20	20	15
Product.	Homomesityl oxide		Homophorone or homo-isophorone				Residue

At this point occurred the greatest difficulty of the entire research, that of separating the products in pure condition. Fractionation is at best a more or less inefficient means of purification, and in this particular instance there was the added difficulty that the fractions indicated in the above table represent nearly constant-boiling mixtures. This fact was corroborated by the evidence that combustion data and refractive indices for these fractions varied through a wide range. The same difficulty was experienced by the investigators of acetone[3] and by Ekeley and Howe[1] in their work with methylethyl ketone. As many as ten refractionations sufficed to separate them only partially. A small but gradual polymerization took place during every refractionation so that the final yields of semi-pure products were rather small, as will be seen below.

In the attempt to isolate a homomesityl oxide, the fractions from 85° to 140° (20 mm.) were refractionated several times, yielding finally about 12 g. of a fraction boiling at 98–102° (20 mm.).

Similarly, in attempting to isolate a homophorone or a homo-isophorone, the fractions from 140° to 180° (20 mm.) were redistilled repeatedly, yielding two fractions, 160–163° and 164–166° (20 mm.). Combustion data on these fractions varied considerably. The larger of these two fractions, that from 160° to 163°, was then refractionated, at 8 mm., giving three fractions, 125–134°, 134–137° and 137–140°, of approximately 5 g. each. The last of these fractions gave satisfactory combustion data and was accordingly investigated further.

Homomesityl Oxide from Diethyl Ketone, $C_{20}H_{18}O$

Physical Constants.—Homomesityl oxide from diethyl ketone is a nearly water-white, mobile liquid with a strong mint-like odor and taste; b. p., 98–102° (20 mm.);

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[3] Kerp and Muller, *Ann.*, 299, 212 (1897).

d_4^{20}, 0.8535; n_4^{20}, 1.4501; M_D, calc. (without exaltation), 47.92; plus exaltation for mesityl oxide (0.89) calc., 48.81; found, 48.56; mol. wt., calc., 154.1; found (average of five ebullioscopic determinations with Menzies' apparatus), 153.4.

Analyses. Calc. for $C_{20}H_{18}O$: C, 77.87; H, 11.77. Found: C, 77.28; H, 11.75.

Oxidation of Homomesityl Oxide

Three grams of homomesityl oxide was shaken with 100 g. of water, and a 5% solution of potassium permanganate added gradually while the mixture was shaken until no more was decolorized after standing for 24 hours. Slightly more than four molecules of permanganate were required to one of homomesityl oxide. The solution was filtered and evaporated to 150 cc. The odor of diethyl ketone was plainly recognized during the evaporation. The solution was then made acid with dil. sulfuric acid, whereupon carbon dioxide was evolved. The acid solution was extracted thrice with ether and the ether evaporated. The acid residue was exactly neutralized with dilute sodium hydroxide solution and the solution evaporated to dryness. A small portion of the sodium salt thus obtained was heated with concd. sulfuric acid, and ethyl alcohol added. The odor of ethyl acetate was clearly recognized. Another portion of the salt was heated with *p*-toluidine, giving aceto-*p*-toluide; m. p., 147°.

The oxidation, then, must take place as follows: $(C_2H_5)C = C(CH_3)COCH_2CH_3 + 3\ O_2 = (C_2H_5)_2CO + 2CH_3COOH + CO_2$ proving the structure of homomesityl oxide to be as indicated above.

Homo-isophorone from Diethyl Ketone, $C_{15}H_{26}O$

Physical Constants.—Homo-isophorone from diethyl ketone is a pale yellow, slightly viscous oil with a faint floral odor; b. p., 137–140° (8 mm.); d_4^{20}, 0.91456; n_D^{20}, 1.4831; M_D, calc. (without exaltation) 68.81; plus exaltation for phorone (1.1) = 69.91; found, 69.34 (calc. M_D for a corresponding homophorone is 73.54); mol. wt., calc. 222.2; found (mean of six ebullioscopic determinations with Menzies' apparatus), 224.7.

Analyses. Calc. for $C_{15}H_{26}O$: C, 81.00; H, 11.79. Found: C, 80.92; H, 11.72.

In order to establish further the fact that this compound is a homo-isophorone and not a homophorone, an attempt was made to show that it adds only two bromine atoms, by the usual method for the determination of unsaturation values; 0.4040 g. of the liquid was found to absorb 0.1381 g. of bromine, whereas 0.4040 g. should absorb 0.1689 g. of bromine if the compound contains one double bond. While not a very accurate result, this should be taken to demonstrate the fact that the compound certainly does not contain more than one double bond.

Not a sufficient quantity of this oil was obtained to permit the preparation of any derivatives or the investigation of the products of oxidation.

Combustion analyses were made and molecular refractions determined for every fraction taken during the distillations in an effort to find a compound whose constants would indicate the existence of a homophorone. None was found. The work on methylethyl ketone indicated that acid condensing agents tended to yield homophorones whereas alkaline condensing agents tended to form the closed-ring homo-isophorones. Since the present research does not attempt an investigation of the influence of acid condensing agents, it is reasonable to assume that if any homophorone occurred among the products it was either in such negligible amounts as to escape attention or else the ring was closed under the influence of the alkaline condensing agent to form homo-isophorone.

It is further assumed in this paper that the molecular refraction exaltations for mesityl oxide, phorone and isophorone are applicable, within a certain small amount of error, to the homologs of these compounds herein discussed.

Summary

1. The action of sodium ethylate on diethyl ketone has been investigated.
2. Two compounds have been isolated, one a homolog of mesityl oxide, and the other a homolog of isophorone.
3. The important constants of these compounds have been determined.
4. The homomesityl oxide has been shown to possess the structure $(C_2H_5)_2C{=}C(CH_3)COC_2H_5$.
5. The probable structure of the homo-isophorone has been discussed.

Boulder, Colorado

[Contribution from the Chemical Laboratory of the University of Texas]

SYMMETRICAL DICYCLOHEXYL HYDRAZINE AND RELATED COMPOUNDS

By H. H. Harkins[1] and H. L. Lochte

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Kizhner reported that he was able to reduce cyclohexylidene-azine by sodium in alcohol.[2] He obtained unsymmetrical dicyclohexyl hydrazine instead of the expected hydrazo compound. The mechanism of this peculiar rearrangement has never been explained.[3]

In view of recent successes in the reduction of azines and other compounds containing the C=N complex, by means of the Skita method of catalytic reduction using colloidal platinum as catalyst,[4] it was decided to attempt also the reduction of the ketazine produced through the interaction of two molecular equivalents of cyclohexanone and one of hydrazine hydrate, to determine whether the reported rearrangement would take place on catalytic reduction.[5]

[1] Part of the work included in this paper is from a thesis presented by H. H. Harkins in partial fulfilment of the requirements for the degree of Master of Arts at the University of Texas, 1923.

[2] Kizhner and Byelov, *J. Russ. Phys. Chem. Soc.*, **43**, 577 (1911); *C. A.*, **6**, 347 (1912).

[3] Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, **1913**, p. 95.

[4] (a) Lochte, Noyes and Bailey, This Journal, **44**, 2556 (1922). (b) Neighbors and Bailey, *ibid.*, **44**, 1561 (1922).

[5] Taipale [*Ber.*, **56**, 1247, 1794 (1923)] reports the results of his work on the reduction of the same type of compounds. Unfortunately most of the work of Taipale,