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Abstract

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PREPARATION OF A HEXACYCLIC PRODUCT OF THE SELF-CONDENSATION OF CYCLOHEXANONE

Recently we showed (^{1}) that, as a result of the self-condensation of cyclohexanone under the influence of solid sodium hydroxide at room temperature, a tricyclic dioxiketone, $C_{18}H_{30}O_3$, is formed. The condensation of cyclohexanone in an acidic medium under ordinary conditions has been little studied. It is known that, on standing for 24 hours, a mixture of equal parts by weight of cyclohexanone and 60% aqueous sulfuric acid forms 2-cyclohexylidenecyclohexanone (^{2}). It was of interest to clarify the behavior of cyclohexanone under ordinary conditions in the presence of more concentrated sulfuric acid.

In the present work it has been found that, when cyclohexanone is allowed to react with methanolic sulfuric acid (Table 1), a solid product of empirical formula $C_{36}H_{52}O_2$ (I) is formed. In order to obtain data on the formation reaction and structure of I, the possibility of synthesizing it under other conditions was also studied. It proved that, in the presence of methanol, *n*-butanol, or water and

Table 1

Experiments on the self-condensation of cyclohexanone and 2-cyclohexylidenecyclohexanone (duration of syntheses 8–12 days, temperature 20–25°)

Experiment No.	Ketone	Amount, g	Solvent	Amount, g	Sulfuric acid, g	Yield, g: dodecahydrotriphenylene	Yield, g: $C_{36}H_{52}O$	Found*, %: C	Found*, %: H	Mol. wt.
1	Cyclohexanone	240	Methanol	390	460	2.4	80	83.52	10.05	520
2	Same	240	*n*-Butanol	400	460	12.0	40	83.47	10.13	517
3	Same	240	Water	150	460	1.0	25	–	–	520
4**	Same	240	Methanol	790	240	14.5	2.5	–	–	495
5***	Same	240	Water	100	160	–	10	83.34	9.86	490
6	2-Cyclohexylidenecyclohexanone	350	Methanol	550	650	5.0	120	83.57	10.23	505

* $C_{36}H_{52}O_2$. Calculated, %: C 83.65; H 10.15. Mol. wt. 516.8.
** The reaction mixture was boiled for 15 hours (^{3}).
*** Duration of synthesis 20 days.

concentrated sulfuric acid (experiments 1, 2, and 3), one and the same product of cyclohexanone condensation, of composition $C_{36}H_{52}O_2$, is obtained. It follows from this that the solvent does not participate in the formation of the compound obtained, and that the latter is a product of the self-condensation of cyclohexanone. It should be noted that, under the conditions of self-condensation of cyclohexanone in dodecahydro-1,2,3,4,5,6,7,8,9,10,11,12-triphenylene (^{3}), we also succeeded in isolating, in small yield (about 1%), the above-mentioned product of composition $C_{36}H_{52}O_2$ (experiment 4). It was further found that the bicyclic product of the self-condensation of cyclohexanone, 2-cyclohexylidenecyclohexanone (^{2}), in the pres-

in the presence of methanolic sulfuric acid is converted into the same compound $C_{36}H_{52}O_2$ (experiment 6). Under the conditions for the synthesis of 2-cyclohexylidenecyclohexanone, if the duration of the experiment is increased (experiment 5), along with the target product compound I is also formed, which on fractionation proved to be homogeneous. At the same time, the tricyclic products of cyclohexanone autocondensation—2-[2-(Δ'-cyclohexenyl)-cyclohexylidene]-cyclohexanone (^{1}) and 2,6-dicyclohexenylcyclohexanone (^{4})—do not form I on interaction with methanolic sulfuric acid. Therefore it may be assumed that the autocondensation of cyclohexanone to compound $C_{36}H_{52}O_2$ proceeds through the stage of formation of 2-cyclohexylidenecyclohexanone

$$2C_6H_{10}O \rightarrow C_{12}H_{18}O + H_2O, \qquad (1)$$

Fig. 1. UV absorption spectrum of I in ethyl alcohol

Figure 1: Fig. 1. UV absorption spectrum of I in ethyl alcohol

$$3C_{12}H_{18}O \rightarrow C_{36}H_{52}O_2 + H_2O. \qquad (2)$$

I

In experiments 1, 2, 3, and 6, dodecahydrotriphenylene is obtained as a by-product of the autocondensation of cyclohexanone. The formation of the latter during the autocondensation of 2-cyclohexylidenecyclohexanone (experiment 6) is noteworthy. This phenomenon can be explained by the occurrence of a reversible aldol condensation reaction ($^{4-6}$).

I is not hydrolyzed on heating to the boiling point at atmospheric pressure with dilute aqueous solutions of acids and alkalis; on boiling with concentrated nitric acid it is oxidized to adipic acid; on heating to 250°, a molecule of water is split off from compound I and compound $C_{36}H_{50}O$ is formed. The product $C_{36}H_{52}O_2$ does not add hydrogen under the usual conditions of catalytic hydrogenation in the presence of platinum oxide (^{7}), whereas hydrogenation of 2-cyclohexylidenecyclohexanone under the same conditions gives, in quantitative yield, a saturated bicyclic ketone (^{8}). Compound I does not give the usual derivatives of carbonyl compounds.

Fig. 1. UV absorption spectrum of I in ethyl alcohol

Compound $C_{36}H_{52}O_2$ cannot contain tertiary alcohol groups, since the latter are readily split off under the influence of sulfuric acid as a dehydrating agent. In the UV spectrum of compound $C_{36}H_{52}O_2$ (Fig. 1), the maximum absorption occurs at $\lambda_{\max} = 258$ mμ and $\varepsilon_{\max} = 50300$. Such an absorption maximum is characteristic of α, β, β-trisubstituted α, β-unsaturated carbonyl compounds and is close to the absorption maximum for 2-cyclohexylidenecyclohexanone ($\lambda_{\max} = 254$ mμ) (^{9}). The molar absorption coefficient, increased in comparison with 2-cyclohexylidenecyclohexanone, can apparently be explained by the fact that I contains two carbonyl groups, each of which is conjugated with an ethylene bond, the two systems being isolated from each other, since otherwise the absorption maximum would lie in the region of longer wavelengths (not less than 300 mμ) (^{10}). Thus, on the basis of reactions (1) and (2), the elemental composition, and the UV spectrum of compound $C_{36}H_{52}O_2$, it is a hexacyclic diketone containing three double bonds. Two of the double bonds are conjugated with carbonyl groups, and one is isolated.

Experimental Part

Preparation of diketone $C_{36}H_{52}O_2$ **(I).** A mixture of 390 g of methanol, 460 g of concentrated sulfuric acid, and 240 g of cyclohexanone (experiment 1) was left standing for 8 days and stirred from time to time.

The reaction mixture was diluted with 6 liters of water, the aqueous layer was removed, and the residue was dissolved in 300 ml of ether. The white precipitate that separated at this point was filtered off and washed with ether (2 portions of 50 ml). After drying, 2.4 g of dodecahydrotriphenylene was obtained, m.p. 232° (from benzene), showing no depression with an authentic sample of dodecahydrotriphenylene (1). The filtrate was slowly poured, with stirring, into 2 liters of methanol. The thick mass thus formed was washed with 100 ml of methanol, dissolved in 200 ml of ether, and again precipitated in 2 liters of methanol. After a third such operation (150 ml of ether and 2 liters of methanol), the solid product that separated was filtered off and washed with methanol (2 portions of 100 ml). After drying in air, 80 g of substance I was obtained as a yellowish powder with an indistinct melting point (m.p. 80–120° with decomposition), readily soluble in ether, benzene, and pyridine, sparingly soluble in methanol, and insoluble in water.

In an analogous manner, substance I was isolated in experiments 4, 5, and 6. The isolation of I in experiments 2 and 3 differed only in that the reaction mixture was first poured into methanol. The results of all experiments and the analytical data are summarized in Table 1.

Fractionation of I. 20 g of substance I with mol. wt. 520 was dissolved in 1500 ml of acetone. After filtration, 150 ml of water was slowly added, with stirring, to the yellow solution; the precipitate that separated was filtered off and washed with 50 ml of methanol. After drying in air, 6.5 g of substance I was obtained as a slightly yellowish powder with mol. wt. 525. A further 250 ml of water was added to the filtrate. After filtration, washing, and drying of the precipitate, 5.5 g of I was obtained as a yellow solid product with mol. wt. 505. In the present work the molecular weights were determined cryoscopically in benzene.

Heating of I. 14 g of substance I was heated for 2 h at 250°. After cooling, the transparent dark-red melt was ground, dissolved in 100 ml of ether, the ethereal solution was filtered, and slowly, with stirring, precipitated in 500 ml of methanol. The precipitate that separated was filtered off and washed with 50 ml of methanol. After drying in air, 8 g of a yellow powder was obtained.

Mol. wt. 493; for $C_{36}H_{50}O$ calculated 498.8.

Found, %: C 86.78; 86.25; H 10.12; 10.33
$C_{36}H_{50}O$. Calculated, %: C 86.70; H 10.10

Oxidation of I. To 250 ml of concentrated nitric acid, with cooling, 25 g of I was slowly added. After this mixture had been boiled under a reflux condenser for 24 h, the reaction mass was diluted with 250 ml of water; the precipitate that separated was filtered off, washed with water, and dried in air. 1 g of a solid product was obtained as a yellow powder, which was not investigated further. On evaporation on a water bath, 30 g of product was obtained. 10 g of this residue was stirred with 25 ml of ether, and the almost white precipitate was filtered off. 4 g of adipic acid was obtained, m.p. 152° (from water), showing no depression with a known specimen.

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