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THE SELF-CONDENSATION OF CYCLOHEXANONE AND METHYLCYCLOHEXANONES UNDER VERY HIGH PRESSURE

BY TSUTOMU TAKAHASHI, KIMHIKO HARA AND JIRO OSUGI

The self-condensations of cyclohexanone and its methyl substituted derivatives were investigated under pressures of 20~50 kbar and temperatures of 160~300°C without solvent and/or catalyst. It was found that 2-cyclohexenylcyclohexanone, 2-cyclohexylidenecyclohexanone, 2,6-dicyclohexenylcyclohexanone and dodecahydrotriphenylene were produced from the self-condensation of cyclohexanone. Dodecahydrotriphenylene becomes the main product at the higher pressure and the higher temperature. 2,2'-Methyl-(2-methylcyclohexenyl)-cyclohexanone was obtained from the self-condensation of 2-methylcyclohexanone. The reactivity of 2,6-dimethylcyclohexanone was also examined and no product was obtained under pressures of 20~50 kbar and below temperatures of 250°C.

This condensation is assumed to occur in the liquid phase and to proceed through a series of aldol condensation followed by dehydration. This scheme was confirmed from pressure effects, but the mechanism of this condensation cannot be explained merely by the pressure dependence of auto-protolysis. The non-reactivity for 2,6-dimethylcyclohexanone is reasonable in light of the larger steric hindrance.

Introduction

The mechanism of aldol condensation has been widely studied under atmospheric pressure. Ketones have much lower reactivity as compared with aldehydes¹⁾. The condensation reaction of ketones, particularly cyclohexanones, was reported to be characteristic to the reaction at high pressure or to be highly accelerated by pressure. The condensation of cyclohexanone was caused under pressures up to 5 kbar in the absence of a catalyst and was accelerated by pressure^{2,3)}.

In some groups of organic reactions, the accurate kinetical study has been carried out under pressure up to several kbar. It is interesting, however, to investigate under the higher pressure the other groups of the reactions which occur only at high pressure, even if the relative details are sacrificed.

From this point of view, this paper is concerned with the self-condensation of cyclohexanone, 2-methylcyclohexanone and 2,6-dimethylcyclohexanone under pressures of 20~50 kbar and temperatures of 140~300°C without solvent and/or catalyst. The mechanism of these reactions was discussed

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- 1) H. O. House, "Modern Synthetic Reactions", Chap. 8, W. A. Benjamin Inc., New York and Amsterdam (1965)
- 2) R. H. Sapiro and Shu-lin Péng, *J. Chem. Soc.*, 1938, 1171
- 3) S. D. Hamann, "Physico-Chemical Effects of Pressure", p. 189, Butterworths, London (1957)

by comparison with each other.

Experimental

Materials

Cyclohexanone, 2-methylcyclohexanone and 2,6-dimethylcyclohexanone of guaranteed grade were obtained commercially. They were dehydrated by anhydrous sodium sulfate and were distilled under reduced pressure just before use.

Apparatus

Hydrostatic pressures up to 50 kbar were generated in a compact cubic anvil apparatus, whose calibration techniques and other experimental procedures were reported earlier in detail⁴⁾. The reactant of about 15 mg was inserted into a capsule made of Teflon. Temperature was detected by chromel-alumel thermocouples inserted through the gaps between the anvils. The junction was situated in contact with a glassy-carbon heater.

Analysis of products

All the materials presumed to be produced under pressure were synthesized by other methods described in the references cited^{5,6)}. The reaction products were identified by measuring IR, NMR and Mass spectrum.

The physical properties used for identification are as follows:

2-Cyclohexenylcyclohexanone: b. p. 113°C/2 mmHg. IR absorption, 1710 cm⁻¹, in the C=O vibration.

NMR spectrum, τ -value 4.7 of olefin proton.

2-Cyclohexylidenecyclohexanone: IR absorption, 1685 cm⁻¹, in the C=O vibration resonanced with α - β double bond.

2,6-Dicyclohexenylcyclohexanone: b. p. 172°C/2 mmHg. IR absorption, 1710 cm⁻¹, in the C=O vibration. NMR spectrum, τ -value 4.7 of olefin proton.

Dodecahydrotriphenylene: m. p. 236°C. NMR spectrum, τ -value 7.5 and 8.5 equivalent resonance (α -proton and β -proton)⁷⁾.

2,2'-Methyl-(2-methylcyclohexenyl)-cyclohexanone was synthesized under the pressure of 3 kbar and the temperature of 120~130°C in the presence of *p*-toluenesulfonic acid as catalyst and separated by means of liquid column-chromatography. Parent peak 206 in Mass spectrum. IR absorption, 1710 cm⁻¹, of the C=O vibration. There is no olefin proton and methin proton of α -position of the C=O group.

Determination of yield

The products were separated each other by liquid column-chromatography used silica gel as the adsorbent and chloroform as the developer. Then, each yield was determined by using a calibration

4) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *This Journal*, **34**, 1 (1964); K. Hara, *This Journal*, **40**, 73 (1970)

5) J. Plesák, *Collect. Czech. Chem. Commun.*, **21**, 375 (1956)

6) E. Wenkert, S. K. Bhattacharya and E. M. Wilson, *J. Chem. Soc., Suppl.*, **1964**, 5617

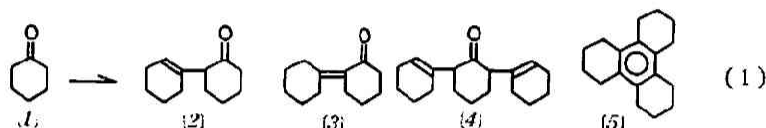
7) V. N. Setkina, A. G. Ginzurt and E. I. Fedin, *Dokl. Akad. Nauk, SSSR*, **158**, 671 (1964)

curve made from the peak intensity of an IR absorption band.

Results and Discussion

Self-condensation of cyclohexanone

It was found that the self-condensation of cyclohexanone [1] produces 2-cyclohexenylcyclohexanone [2], 2-cyclohexylidenecyclohexanone [3], 2,6-dicyclohexenylcyclohexanone [4] and dodecahydrotriphenylene [5] under pressures of 20~50 kbar and temperatures of 180~300°C in the absence of a catalyst.



This condensation does not occur at the temperature below 150°C at 20 kbar and at the temperature below 180°C at 45 kbar, at which acetone is assumed to be the solid phase. The result is shown in Fig. 1. At the temperature between 200° and 300°C, however, the total yield of the products in a given reaction time increases with increasing pressure. And no discontinuous point was observed in the temperature and pressure region where the products were obtained. Therefore, the condensation of cyclohexanone is considered to occur in the liquid phase.

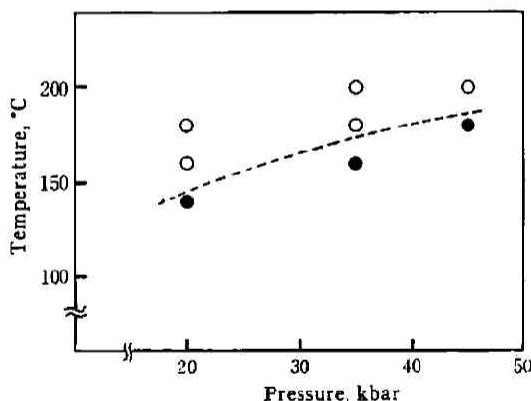


Fig. 1 Reaction diagram for the condensation of cyclohexanone
 ○: Condensation
 ●: No condensation
 ---: Estimated melting curve

The aldol condensation of cyclohexanone in the presence of a catalyst is studied well at atmospheric pressure^{5,6}, *e. g.* in the presence of *p*-toluenesulfonic acid. [2], [4] and [5] were reported to be obtained at 190°C for 1 hour with the yield of 60 wt%, 7 wt% and 1 wt%, respectively.

Sapiro and Shu-lin Peng²⁾ have studied the self-condensation of cyclohexanone up to the pressure of several kbar and the temperature of 100°C in the absence of a catalyst and obtained [2] as only one product with the yield of 72 wt% when the equilibrium was achieved sufficiently. On the other hand, Bengelsdorf⁸⁾ has obtained only [5] from cyclohexanone with the yield of 60 wt% at 35 kbar and 320°C

8) I. S. Bengelsdorf, "Amer. Chem. Soc. Meeting", Sept (1956)

for 15 minutes without catalyst.

It was one of the objects of this research that the difference in the products between the reaction at several kbar and that at several ten kbar would be examined. It was found, however, that even at the pressure of several ten kbar [2], [3] and [4] are also produced besides [5]. Table 1 gives the yield of each product at various temperatures and pressures. The yield of [3] is less than 1% in all the experimental regions.

Table 1 Self-condensation of cyclohexanone

Reaction condition			Yield (wt.%)		
Pressure (kbar)	Temperature (°C)	Time (min)	[2]	[4]	[5]
20	200	30	5	1	Nil*
		60	5	3	Nil
		120	4	4	Nil
	250	30	1	1	12
	35	200	7	2	Nil
		60	1	1	19
45	250	30	1	1	34
		60	1	2	10
	200	30	1	2	13
		60	Nil	2	13
	250	30	1	1	27
		60	1	1	27

* No measurable yield

Following the change in yield with time at a given temperature and pressure, we can find that [2] is produced first of all and then [2] reacting with a cyclohexanone further, [4] and [5] are brought about. Therefore, it is concluded that the self-condensation under very high pressure takes place through the similar process to that at atmospheric pressure. After a sufficient reaction time, [5] becomes a final main product. This can be well explained from the pressure effects, since the molar volume of [5] is smaller than that of [2] or [4].

The yield at the same condition as that in the work of Bengelsdorf⁸⁾, *i. e.* 35 kbar and 320°C, is 45 wt% and somewhat smaller than that of Bengelsdorf. This difference probably comes from the method of the determination of yield. In the work of Bengelsdorf⁸⁾, the amount of the products was determined only by elementary analysis.

Self-condensation of 2-methylcyclohexanone

From the self-condensation of 2-methylcyclohexanone [6], 2, 2'-methyl-(2-methylcyclohexenyl)-cyclohexanone [7] was detected by the measurement of IR spectrum.

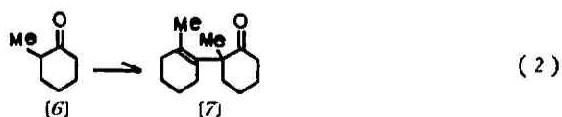


Table 2 gives the yield of [7]. The self-condensation of 2-methylcyclohexanone does not occur in the higher pressure region than about 30 kbar at 200°C, at which 2-methylcyclohexanone is assumed to be

Table 2 Self-condensation of 2-methylcyclohexanone

Pressure (kbar)	Reaction condition Temperature (°C)	Time (min)	Yield (wt%) [7]
20	200	30	10
		60	20
	250	30	18

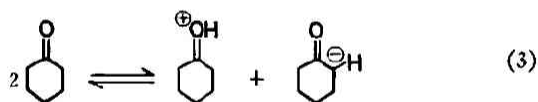
the solid phase. As in the case of cyclohexanone, this is a reaction in the liquid phase.

In the reaction at atmospheric pressure, [7] could never be obtained even in the presence of *p*-toluenesulfonic acid as catalyst. By the application of the pressure of 3 kbar, however, it was obtained at 190°C in the presence of *p*-toluenesulfonic acid. The fact that in the self-condensation of 2-methylcyclohexanone, without catalyst the pressure of several ten kbar, or with catalyst the pressure of 3kbar is needed seems to come from the effect of steric hindrance by methyl group.

Self-condensation of 2, 6-dimethylcyclohexanone

The self-condensation of 2, 6-dimethylcyclohexanone did not occur under the pressure of 20~50 kbar and the temperature of 250°C. It seems reasonable in light of large steric hindrance by methyl groups. It indicates that even the pressure of 50 kbar cannot take it away.

Hamann has explained that the self-condensation of ketones occurs through auto-protolysis followed by the acid or base catalyzed aldol condensation and dehydrations²⁾.



In our results, however, the products through the base catalyzed aldol condensation were not obtained at an early stage of the reaction. Therefore, the mechanism of this condensation cannot be explained merely by the pressure dependence of auto-protolysis, but it is necessary to take into consideration the difference of pressure effects on the reaction rates between the acid and base catalyzed condensation.

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