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 detail[4]. 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. Plesék, *Collect. Czech. Chem. Commun.*, **21**, 375 (1956)

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

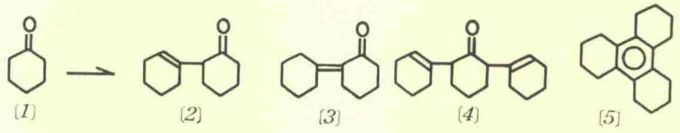
7) V. N. Setkina, A. G. Ginzurt and E. I. Fedin, *Dokl. Akad. Nauk, SSSR*, **158**, 671 (1964)

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.



(1)

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.

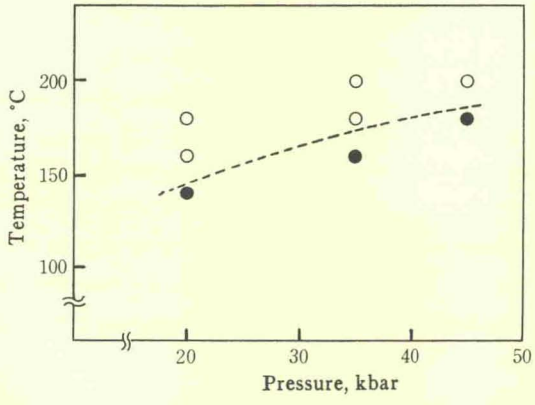


Fig. 1 Reaction diagram for the condensation of cyclohexanone
○: Condensation
●: No condensation
---: Estimated melting curve

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 Pèng[2] 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, Bengelsdorf[8] 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)