

## Resins from Formaldehyde. CIV. Hydroxymethylation of Diisopropyl Ketone with Formaldehyde\*

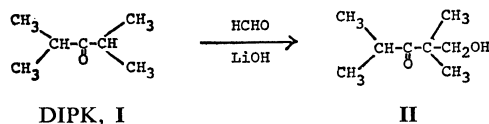
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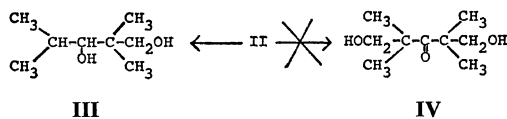
In order to prepare a novel kind of photo-degradable thermoplastic resin, a study about the introduction of a methylol group into 2,4-dimethyl-3-pentanone(I, diisopropyl ketone, DIPK) was made.



The desired 2,2,4-trimethyl-1-pentanol-3-one (II) can be easily prepared by the reaction of DIPK with formaldehyde(F) in an alkaline aqueous medium. When lithium hydroxide was used as a catalyst, the following kinetic equation was obtained

$$\text{Rate} = -d[\text{F}]/dt = k[\text{F}][\text{DIPK}][\text{LiOH}] \quad (1)$$

Further reaction of F with II gave 2,2,4-trimethyl-1,3-pentanediol (III) instead of the expected 2,2,4,4-tetramethyl-1,5-pentanediol-3-one (IV).



The preparation of II was briefly described by Decombe<sup>2</sup> in 1936, using the same procedure as the present paper. But the preparative method of the compound III by the reaction of II and

F seems to be novel. In 1927, III was prepared from isobutyraldehyde by Krestinski, *et al.*<sup>3</sup>

### EXPERIMENTAL

Diisopropyl ketone(DIPK) was of highly pure commercial grade. Formaldehyde(F) was applied as commercial 37-% water solution, containing about 10-% methanol.

#### Procedures for kinetic study

A 100-cm<sup>3</sup> three-necked flask equipped with a reflux condenser, a stirrer, and a thermometer was adjusted at 50°C. Twenty-five cm<sup>3</sup> of methanolic solution containing DIPK, 25 cm<sup>3</sup> of aqueous solution of 37-% F, and 3 cm<sup>3</sup> of aqueous solution of lithium hydroxide were mixed and diluted with methanol up to 60 cm<sup>3</sup> in order to let the mixture become homogeneous. This reaction mixture was placed into the flask mentioned above. At each fixed time, 5 cm<sup>3</sup> of an aliquot was pipetted out and the concentration of formaldehyde was determined by the sodium sulfite method. Plotting the quantities of consumed formaldehyde vs. reaction time gave a straight line. The slope of the line represents the reaction rate of DIPK with F.

#### Preparation of 2,2,4-trimethyl-1-pentanol-3-one(II)

A homogeneous reaction system was obtained by mixing 36 cm<sup>3</sup> of 37-% F, 17.3 g of DIPK, 25 cm<sup>3</sup> of 1-N LiOH, 250 cm<sup>3</sup> of water, and 137 cm<sup>3</sup> of methanol. This solution was refluxed for 24 hr. After distilling off most of the methanol, the remained product was extracted with benzene. The benzene layer was washed with diluted

\* For Part 103 of this series, see ref 1.

sulfuric acid and water and distilled *in vacuo*. The compound **II** was obtained in a yield of 15.4 g (70.5%); bp 96.5–98°C/20 mmHg (lit.<sup>2</sup> 97–98°C/20 mmHg),  $n_D^{25}$  1.4379,  $d_4^{25}$  0.9565; IR (NaCl) 3470  $\text{cm}^{-1}$ , ( $\nu_{\text{OH}}$ ) 1700  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ).

#### Preparation of 2,2,4-trimethyl-1,3-pentandiol (**III**)

To a homogeneous solution, which was prepared by heating a mixture of 20.0 g of paraformaldehyde, 100  $\text{cm}^3$  of water, and 70  $\text{cm}^3$  of methanol, 25.0 g of **II** and 64  $\text{cm}^3$  of 1-*N* LiOH were added. This mixture was refluxed for 48 hr. After distilling off the methanol, the reaction mixture was extracted with benzene. From the benzene extract, the compound **III** was isolated by distillation, bp 112–113°C/10 mmHg. After recrystallization from *n*-hexane, it became a colorless table crystal; Yield 3.93 g (15.5%), mp 51.5–52.2°C (lit.<sup>3</sup> 52°C). IR(KBr) gave no signal of  $\nu_{\text{C=O}}$  at 1700  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR\* (CDCl<sub>3</sub>)  $\delta$  82.8 (d, C<sup>c</sup>), 72.9 (t, C<sup>a</sup>), 39.1 (s, C<sup>b</sup>), 29.2 (d, C<sup>d</sup>), 23.4 (q, C<sup>e</sup>, C<sup>h</sup>), 19.9 and 16.8 ppm (q, C<sup>e</sup> or q, C<sup>f</sup>); mass spectrum *m/e* 146 (M<sup>+</sup>). Anal. Calcd for C<sub>8</sub>H<sub>18</sub>O<sub>2</sub>: C, 65.67; H, 12.43. Found: C, 65.52; H, 12.85. Mol wt 146.

## RESULTS AND DISCUSSION

### Effects of the Concentration of Reagents

Figure 1 shows the effects of [DIPK], [F], and [LiOH] on the rate of reaction. From this figure, it was concluded that the rate of reaction could be expressed by the following equation.

$$R = \frac{-d[F]}{dt} = k[F][\text{DIPK}][\text{LiOH}] \quad (1)$$

### Comparison between the Rates of Reactions of Formaldehyde with DIPK and with 2,2,4-Trimethyl-1-pentanol-3-one

The results are shown in Figure 2. The conditions for reaction were the same as those mentioned above. The "prepared formaline" described in Figure 2 means an aqueous formaldehyde solution which was prepared by boiling paraformaldehyde in distilled water. From these two lines the values of *k* were

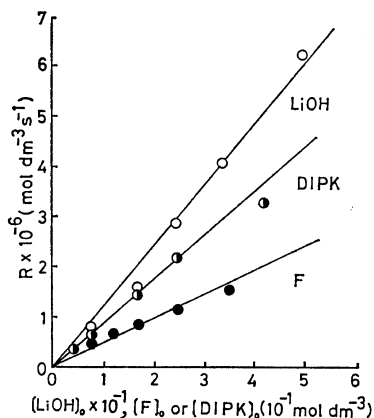
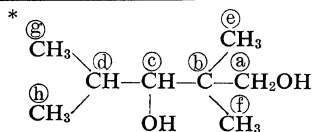


Figure 1.  $-d[F]/dt$  vs. [DIPK]<sub>0</sub>, [F]<sub>0</sub>, and [LiOH]<sub>0</sub> at 50°C: ○, [DIPK]<sub>0</sub>=0.17 mol dm<sup>-3</sup>, [F]<sub>0</sub>=0.17 mol dm<sup>-3</sup>, [LiOH]<sub>0</sub> varied; ◐, [DIPK]<sub>0</sub> varied, [F]<sub>0</sub>=0.17 mol dm<sup>-3</sup>, [LiOH]<sub>0</sub>=8 × 10<sup>-3</sup> mol dm<sup>-3</sup>; ●, [DIPK]<sub>0</sub>=0.17 mol dm<sup>-3</sup>, [F]<sub>0</sub> varied, [LiOH]<sub>0</sub>=8 × 10<sup>-3</sup> mol dm<sup>-3</sup>.

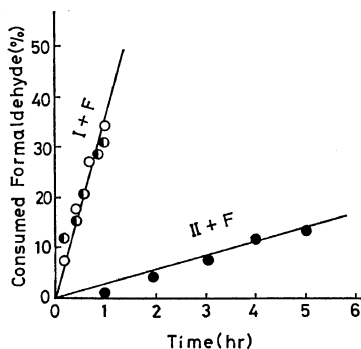


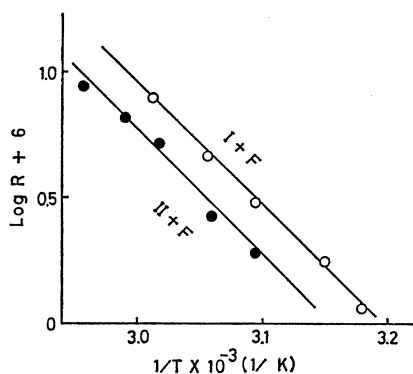
Figure 2. Rate of reaction of **I** and **II** with **F** at 50°C: [F]<sub>0</sub>=0.17 mol dm<sup>-3</sup>; [LiOH]<sub>0</sub>=0.12 mol dm<sup>-3</sup>; [I]<sub>0</sub>=[II]<sub>0</sub>=0.17 mol dm<sup>-3</sup>; ○, ●, commercial formaline; ◐, prepared formaline.

Table I. Rate constants at 50°C

Substance	<i>k</i>
	dm <sup>6</sup> mol <sup>-2</sup> s <sup>-1</sup>
<b>I</b>	5.04 × 10 <sup>-3</sup>
<b>II</b>	0.37 × 10 <sup>-3</sup>

calculated according to eq 1 and are listed in Table I. As in the case of the reaction of **II** with **F**, eq 1 was assumed to be applicable.

It is very interesting that the rate of DIPK was 14 times faster than that of 2,2,4-trimethyl-1-pentanol-3-one. However, the activation energies



**Figure 3.** Determinations of activation energy at 41–65°C.  $[I]_0 = [II]_0 = 0.17 \text{ mol dm}^{-3}$ ;  $[F]_0 = 0.17 \text{ mol dm}^{-3}$ ;  $[LiOH]_0 = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$ (I),  $0.17 \text{ mol dm}^{-3}$ (II).

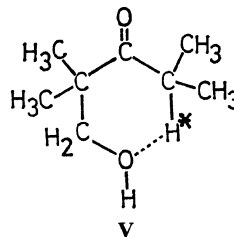
**Table II.** Activation energy and Arrhenius preconstant

Substance	<i>E</i>	<i>A</i>
	$\text{kJ mol}^{-1}$	$\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$
I	93.7	$7.03 \times 10^{12}$
II	95.8	$1.12 \times 10^{12}$

of the reactions in both cases were almost the same, as shown in Figure 3 and Table II.

Accordingly, the large difference between the rate constants of DIPK and 2,2,4-trimethyl-1-pentanol-3-one was due to the difference of entropy terms.

The reason why the compound IV could not be prepared may be explained by the following formula of V.



In such a case, the reactive hydrogen ( $H^*$ ) makes a six-membered ring intramolecularly with the introduced OH group. According to the "six-number rule,"<sup>4</sup> the substitution reaction at  $C-H^*$  in the above structure is deemed quite difficult. Thus a crossed Cannizzaro's reaction takes place between the  $C=O$  group and F to give 2,2,4-trimethyl-1,3-pentandiol(III).

#### REFERENCES

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