

The condensation of ketones of the aliphatic series with formaldehyde in the presence of hydroxides of calcium, sodium, and potassium and carbonates of alkali metals is known to take place readily [1–3]; the condensation of aliphatic-aromatic ketones with formaldehyde proceeds with considerably more difficulty.

We have investigated the products of the condensation of the following arylmethylketones with formaldehyde: 1) methyl-*p*-tolylketone; 2) methyl-*m*-xylylketone; and 3) methyl- $\beta$ -naphthylketone.

Hydroxides of calcium and barium, barium carbonate, caustic potash, and ammonium chloride were used as the condensing agents.

Condensation of the ketones indicated with formaldehyde was performed in an aqueous or alcohol medium as heating was carried out on a water bath and the reaction mass was mixed.

For a molar ratio of ketone to formaldehyde of 1:3, condensation proceeds via the following scheme:

*[insert from Russian page xxx]*

At the same time, dihydric keto alcohols —  $\text{Ar-CO-CH}(\text{CH}_3\text{OH})_2$  — were obtained in various quantities.

In all cases condensation went forward at a high rate and with better yields in an alcohol solution in the presence of caustic potash and potassium carbonate.

Table of Basic Parameters\*

Starting substances	Condensation agent	Molar ratio of ketone to formaldehyde	Substances obtained	Yield (%)	$T_{\text{boil}}$ (°C/mm)	$T_{\text{melt}}$ (°C)	Analytical data
$\text{CH}_3\text{C}^*\text{H}_4\text{COCH}_3$	$\text{NH}_4\text{Cl}$ aqueous solution	1:3	$\text{CH}_3\text{C}_6\text{H}_4\text{COC}(\text{CH}_2\text{OH})_3$	30.5	158/10	—	$M(\text{found}) = 226$ , $M(\text{calc.}) = 224$ . Found (%): C 64.05, H 7.01. $\text{C}_{11}\text{H}_{16}\text{O}_4$ . Calc. (%): C 64.23, H 7.14. OH number: found 2.89, calc. 3.0.
Same	$\text{K}_2\text{CO}_3$ aqueous solution	same	a) $\text{CH}_3\text{H}_6\text{H}_4\text{COC}(\text{CH}_2\text{OH})_3$ b) $\text{CH}_3\text{C}_6\text{H}_4\text{COCH}(\text{CH}_2\text{OH})_2$	21 10	149/10	—	$M(\text{found}) = 195.8$ , $M(\text{calc.}) = 194$ . Found (%): C 67.80, H 7.45. $\text{C}_{11}\text{H}_{14}\text{O}_3$ . Calc. (%): C 68.01, H 7.21. OH number: found 1.92, calc. 2.
Same	$\text{K}_2\text{CO}_3$ alcohol solution	same	$\text{CH}_3\text{C}^*\text{H}_4\text{COC}(\text{CH}_2\text{OH})_3$	55.6			
Same	KOH alcohol solution	same	$\text{CH}_3\text{C}_6\text{H}_4\text{COC}(\text{CH}_2\text{OH})_3$ $\text{CH}_3\text{H}_6\text{H}_4\text{COCH}(\text{CH}_2\text{OH})_3$	26 22			
Same	KOH alcohol solution	1:1	$\text{CH}_3\text{C}_6\text{H}_4\text{COCH}=\text{CH}_2$ (polymer)	42		—	$M = 146$ . Found (%): C 81.72, H 7.19. $\text{C}_{10}\text{H}_{10}\text{O}$ . Calc. (%): C 82.19, H 6.84.
$(\text{CH}_3)_2\text{C}^*\text{H}^*\text{COCH}^*$	$\text{NH}_4\text{Cl}$ aqueous solution	1:3	$(\text{CH}_3)_2\text{C}_6\text{H}_3\text{COC}(\text{CH}_2\text{OH})_3$	32.6	164– 166/10	—	$M(\text{found}) = 236$ , $M(\text{calc.}) = 238$ . Found (%): C 65.33, H 7.77. $\text{C}_{13}\text{H}_{11}\text{O}_4$ . Calc. (%): C 65.54, H 7.56. OH number: found 3.06, calc. 3.
Same	$\text{K}_2\text{CO}_3$ aqueous solution	same	$(\text{CH}_3)_2\text{C}^*\text{H}_3\text{COCH}(\text{CH}_2\text{OH})_2$	69.4	150– 153/10	—	$M(\text{found}) = 210.4$ , $M(\text{calc.}) = 208$ . Found (%): C 62.05, H 7.90. $\text{C}_{12}\text{H}_{11}\text{O}_5$ . Calc. (%): C 62.23, H 7.69. OH number 1.91.
Same	KOH alcohol solution	same	$(\text{CH}_3)_2\text{C}^*\text{H}_3\text{COC}(\text{CH}_3\text{OH})_3$ $(\text{CH}_3)_2\text{C}^*\text{H}_3\text{COCH}(\text{CH}_2\text{OH})_2$	25.5 50.6	—	—	

\* Translator's note: In this table, individual illegible digits (all of which are subscripts) are replaced with a single asterisk (\*).

Starting substances	Condensation agent	Molar ratio of ketone to formaldehyde	Substances obtained	Yield (%)	$T_{\text{boil}}$ (°C/mm)	$T_{\text{melt}}$ (°C)	Analytical data
Same	KOH alcohol solution	1:1	$(\text{CH}_3)_2\text{C}_6\text{H}_3\text{COCH}=\text{CH}_2$ (polymer)	40			$M = 160$ (monomer). Found (%): C 82.27, H 7.72. $\text{C}_{11}\text{H}_{13}\text{O}$ . C 82.50, H 7.50.
$\text{C}_{10}\text{H}_7\text{CO}\cdot\text{CH}_3$ ( $\beta$ -naphthylmethylketone)	$\text{NH}_4\text{Cl}$ aqueous solution	1:3	$\text{C}_{10}\text{H}_7\text{COC}(\text{CH}_3\text{OH})_3$	30.5	175–178/7	184.5	$M(\text{found}) = 262$ , $M(\text{calc.}) = 260$ . Found (%): C 69.05, H 6.32. $\text{C}_{1*}\text{H}_{10}\text{O}$ . Calc. (%): C 69.23, H 6.15.
Same	$\text{K}_2\text{CO}_3$ aqueous solution	same	same	19			
Same	KOH alcohol solution	same	same	35			
Same	KOH alcohol solution	1:1	$\text{C}_{10}\text{H}_7\text{COCH}=\text{CH}^*$ (polymer)	39			$M = 182$ . Found (%): C 85.66, H 5.67. $\text{C}_{1*}\text{H}_{10}\text{O}$ . Calc. (%): C 85.71, H 5.49.

For a molar ratio of arylmethylketones to formaldehyde of 1:1, instead of the expected formation of keto alcohols having the composition  $\text{Ar}-\text{CO}-\text{CH}_{[\textit{illegible}]}-\text{CH}_2\text{OH}$ , in all cases resins corresponding to the formula  $\text{Ar}-\text{CO}-\text{CH}=\text{CH}_2$ , that is, arylvinylketones in their polymeric form, were precipitated when condensation was performed in an alcohol solution in the presence of small amounts of KOH. For purification, the resins were washed with hot water and reprecipitated with alcohol from a benzene solution. The resins were transparent, thermoplastic, insoluble in water and ethyl alcohol, and soluble in benzene and chloroform.

When melted with phthalic anhydride, trihydric keto alcohols yielded alkyd-type resins.

The table presents data on and analyses of the arylketo alcohols obtained.