molecule which is converted to 1,3-cyclohexadiene (Ⅵ), and consequently Ⅲ and Ⅳ are formed.

Details of experiments, discussion of mechanism of the reactions, and the chemical behaviors of Ⅲ and Ⅳ will successively be presented.

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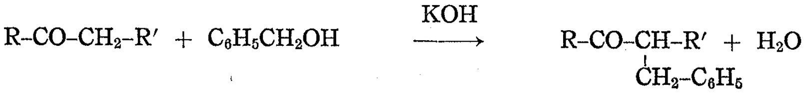
A New Synthesis of α-Benzylketones

In 1956 Sprinzak[1] reported the benzylation of fluorene in 9-position by simply refluxing them with benzyl alcohol and potassium hydroxide. Later this benzylation was applied by Avramoff and Sprinzak[2] to pyridine and quinoline homologs in which active methyl groups were benzylated. Although these reactions seemed fairly general no extensive report has appeared and the active methyl or methylene compounds which underwent the reaction are only fluorenes, α- and γ-picolines, quinaldine and lepidine.

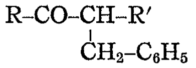
The extension of this benzylation to ketones is now successfully undertaken and this communication deals with a new procedure which allows the preparation of monobenzylated aromatic ketones (I) in satisfactory yield with simple experimental manipulation. The procedure consists of refluxing a mixture of appropriate ketone and benzyl alcohol in the presence of potassium hydroxide. In this highly basic medium aromatic ketones reacted rapidly with benzyl alcohol between 170° and 180° to give good yields of monobenzylation products.



$$\text{R-CO-CH}_2\text{-R}' + \text{C}_6\text{H}_5\text{CH}_2\text{OH} \xrightarrow{\text{KOH}} \underset{\text{CH}_2\text{-C}_6\text{H}_5}{\text{R-CO-CH-R}'} + \text{H}_2\text{O}$$

Chart 1. I

Table I. Monobenzylated Aromatic Ketones



$\underset{\text{CH}_2\text{-C}_6\text{H}_5}{\text{R-CO-CH-R}'}$

R	R′	Reaction time (min.)	Yield (%)[a]
Phenyl	H	15	70.4
〃	CH_3	20	51.2
〃	C_2H_5	20	42.8
〃	C_6H_5	20	73.5
p-Tolyl	H	30	47.0
〃	CH_3	25	42.0[b]
2-Naphthyl	H	20	60.3

a) These percent yields are based on ketones. No attempt has been made to determine the optimum conditions or maximum yields for the reaction.
b) New compound. *Anal.* Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found : C, 85.44; H, 7.82.

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1) Y. Sprinzak : J. Am. Chem. Soc., 78, 466 (1956).
2) M. Avramoff, Y. Sprinzak : *Ibid.*, 78, 4090 (1956).

The reactions are usually complete within 30 minutes when water ceased to distil. By varying R and R′ the method proved to be applicable to the preparation of a variety of aromatic ketones.

All of the products mentioned in the present communication were identified by elementary analyses, infrared spectra or by comparison with compounds synthesized by independent routes. The studies on mechanism and extension of this benzylation to aliphatic and alicyclic ketones are now underway and detailed discussion will be reported in a full paper. The advantage of this reaction is well demonstrated in the synthesis of benzylacetophenone[*1] (I : R=phenyl, R′=H) which is now obtained from acetophenone in one operation in 70% yield. The following procedure is illustrative:

A suspension of potassium hydroxide (3.5 g., 0.062 mole) in benzyl alcohol (30 g., 0.277 mole) in a distilling flask was heated until the temperature of the bath reached 165° at which potassium hydroxide came into solution. To this was added about one third of acetophenone (29.2 g., 0.244 mole) under vigorous stirring and the temperature of the bath was kept between 170° and 180°. Rapid reaction soon took place and the water as it formed started to distil. The rest of acetophenone was run in slowly and heating was continued until the reaction was complete. The water distilled amounted to 3.9 ml. The reaction mixture was filtered hot with suction to remove precipitated potassium benzoate.[*2] The filtrate was fractionated. Benzylacetophenone distilled at 165~166°/4.5 mm. Yield : 36 g. (70.4% based on acetophenone). It solidified to colorless prisms, m.p. 70.5~71° (from ethanol) (lit.[*1] m.p. 72~73°). On admixture with authentic sample no depression of melting point was observed.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found : C, 85.42; H, 6.79. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1681 (ketone CO), no OH band.

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[*1] α-Benzylketones of the type (I) have been prepared by the reduction of benzalketones (For typical example : Reduction of benzalacetophenone to benzylacetophenone. R. Adams, J. W. Kern, R. L. Shriner : Org. Syntheses, Coll. Vol. I, 101) or less commonly by the direct benzylation of ketones with benzyl chloride in the presence of sodamide. (A. Haller, E. Bauer : Compt. rend., **150**, 1576 (1910))

[*2] The formation of a small amount of potassium benzoate was encountered in several instances in Table I as in Sprinzak's benzylation.[1,2)] Though this is considered to be the product of Cannizzaro reaction of benzaldehyde, a possible intermediate of this benzylation, detailed discussion will be given elsewhere.

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