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REACTIONS OF ORGANIC ANIONS. XXVI.[x] CATALYTIC ALKYLATION OF KETONES IN AQUEOUS MEDIUM

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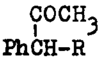
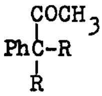
In continuation of the previously reported studies on catalytic alkylation of arylacetonitriles /1/, indene and fluorene /2/ we found recently that ketones can be readily transformed into α-alkylated products when reacted with alkyl halides in the presence of 50 % aqueous NaOH and catalytic amounts of triethylbenzylammonium chloride /TEBA/. The catalytic effect of the latter on the reaction yield was particularly strong in the case of weakly active alkylating agents. Thus, phenylacetone and Bu-Br in 50 % NaOH gave about 5% of 3-phenyl-2-heptanone /I,R=C_4H_9/, whereas in the presence of TEBA the yield increased to 90 %.

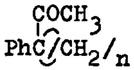
Best results were obtained in the case of ketones with an aromatic substituent at the α-CH_2 group; phenylacetone and desoxybenzoin yielded monoalkyl derivatives /I/[xx]; with active alkylating agents, e.g. benzyl or allyl chloride, used in excess, α,α-disubstitution /II/ occurred. In some cases, e.g., with isopropyl bromide, formation of enolic ethers was observed.


$\mathrm{PhCH(COCH_3)-R}$

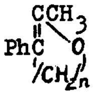
I


$\mathrm{PhC(COCH_3)(R)-R}$

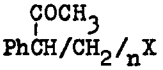
II


$\mathrm{PhC(COCH_3)/CH_2/_n}$

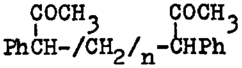
III


$\mathrm{PhC{=}C(CH_3)O/CH_2/_n}$

IV


$\mathrm{PhCH(COCH_3)/CH_2/_nX}$

V


$\mathrm{PhCH(COCH_3)-/CH_2/_n-CH(COCH_3)Ph}$

VI

With α,ω-dihaloalkanes X-/CH_2/$_n$-X /n=1-5/, four types of products

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[x] Part XXV. M.Mąkosza and M.Jawdosiuk, Chem.Comm., 648 /1970/

[xx] Examples are given for phenylacetone.

/III-VI/ resulted; depending on the reaction conditions the required compound can be prepared in good yield. For example, 54 % of the cyclopropane derivative /III, n=2/, was obtained. This is the essential advantage of the catalytic procedure as compared with routine methods.

Cyclic ketones with the methylene group activated by the presence of an aromatic ring, e.g. 1-acenaphthenone and 2-tetralone, undergo disubstitution irrespectively of the alkylating agent. Yields of dialkyl derivatives of 1-acenaphthenone increased considerably when DMSO was added to the reaction mixture. Catalytic alkylation of other ketones, e.g., acetophenone, cyclohexanone and acetone, yielded mixtures of mono-, di- and O-alkylated products, monoalkyl derivatives being usually preponderant.

The new method provides a convenient route for the synthesis of α-substituted ketones. It eliminates inflammable solvents and unstable condensing agents /$NaNH_2$, tert - alkoxide , Ph_3CNa, BuMgBr/ used in the procedures described earlier /3/. The yields are in many cases superior to those reported in literature.

References

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