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PREPARATION OF VARIOUS ALKYL(F-ALKYL)KETONES AND THEIR REACTIVITY TOWARDS NUCLEOPHILES

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Various routes to polyfluorinated ketones, some of them constituting a hitherto unknown class of carbonyl compounds, were investigated.

Hemifluorinated ketones R-CO-R_F, in which an F-alkyl chain (C_8F_{17} or C_6F_{13}) is directly bound to the carbonyl group, were first prepared from F-alkyl Grignard reagents. The reaction of acyl anhydrides $(RCO)_2O$ upon these organometallic derivatives constitutes a particularly competitive route to these ketones, compared, for example, to that of the corresponding acyl chlorides.

The methyl(F-alkyl)ketones CH_3-CO-R_F could also be obtained by the mercuric sulfate catalyzed hydration of (F-alkyl)alkynes R_F-C≡C-H ; in this hydration reaction, no trace of the corresponding aldehyde was detected.

Polyfluorinated ketones R-CO$(CH_2)_n$-R_F, wherein one or two methylene groups separate the R_F chain from the carbonyl, have been synthesized by different classical ways. Also, were prepared various types of α-β unsaturated polyfluorinated ketones, which are different in the positions of respectively the double bond and the carbonyl group versus the F-alkyl group, for example R_F-CO-CH=CH-CH_3 and R_F-CH=CH-CO-CH_3.

The reactivity of these ketones towards some organometallic derivatives and nucleophiles such as amines was studied. Thus, in the case of the reaction of Grignard reagents containing β-hydrogens on the ketones R-CO-R_F, reduction was mainly observed (more than 90%). On the other hand, organolithium derivatives (C_4H_9Li for example) lead only to the addition product. Also, primary amines react, in very mild conditions, to give stable polyfluorinated imines.

These results are discussed in terms of the influence not only of the large inductive effect of the fluorinated alkyl groups attached to the carbonyl,but also of some steric hindrance of these groups.