Perfluoroalkyl Calcium Derivatives: Reactions with Carbonyl Compounds

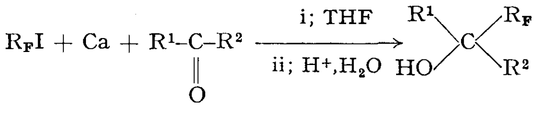
By GEORGES SANTINI, MAURICE LE BLANC, and JEAN G. RIESS*
(*Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS, Institut de Mathématiques et Sciences Physiques, Parc Valrose,* 06034 *Nice Cedex, France*)

Summary Perfluoroalkylcalcium derivatives, prepared by the action of perfluoroalkyl iodides on amalgamated calcium in ethers, react with aldehydes and ketones to give the expected alcohols in 20—70% yields.

GRIGNARD reagents have not found the wide use in fluorocarbon chemistry that they have in hydrocarbon chemistry, although they have recently received renewed attention.[1] Perfluoroalkyl derivatives of many elements have been reported,[2] but none of them have found general use in synthesis, and a perfluoroalkylating agent which would be as universal and versatile as the Grignard reagent in hydrocarbon chemistry has not yet been found.

We now report the first use of perfluoroalkylcalcium intermediates as perfluoroalkylating agents in their reactions with carbonyl compounds.

Perfluoroalkyl iodides react at room temperature with finely divided calcium and carbonyl compounds in basic solvents such as tetrahydrofuran (THF), dioxan, or diethyl ether, according to equation (1).



$$R_FI + Ca + R^1\text{–}\underset{\underset{\displaystyle O}{\|}}{C}\text{–}R^2 \xrightarrow[\text{ii; H}^+\text{,H}_2\text{O}]{\text{i; THF}} \begin{matrix}R^1 & & R_F\\ & C & \\ HO & & R^2\end{matrix} \qquad (1)$$

$R_F = C_2F_5$ or C_6F_{13}

The formation of a perfluoroalkylcalcium intermediate is supported by the nature of the hydrolysis product and by the reaction products formed with carbonyl compounds.

When pure calcium metal was used, the reaction started vigorously after an induction period of *ca.* 30 min, and large proportions of undesired R_FH were produced, the proportion increasing with temperature. This disadvantage was partially overcome by using amalgamated calcium. Using a mercury amalgam, which is easily prepared by heating the two metals together under an argon atmosphere, the reaction starts immediately and proceeds smoothly. The consumption of R_FI is complete after *ca.* 2 h at room temperature or *ca.* 10 h at −20°C. No reaction was observed in more basic solvents such as triethylamine, ethylenediamine, or tetramethylethylenediamine, which are known to form complexes with R_FI.[3]

The reactions with ketones and aldehydes were carried out at −20 to 40 °C, using two methods: (i) addition of the carbonyl compound after the reaction of R_FI with calcium was complete. In this case the expected alcohol was generally accompanied by large amounts of the reduction by-product R_FH; (ii) by performing the reaction in the presence of the carbonyl compound (Barbier method), which significantly lowered the proportion of R_FH and increased the yield of the alcohol.

The following examples were performed in THF, according to the second method, with a 10% excess of calcium and 5% excess of R_FI. The alcohols were isolated after hydrolysis of the reaction mixture and purified either by vacuum distillation or by column chromatography on neutral Al_2O_3 (II—III, elution by 5% ethyl acetate in pentane). All the products were characterised by their ^1H and ^{19}F n.m.r., i.r. and mass spectra and gave satisfactory elemental analysis.

The reaction of $Et_2C{=}O$ with $C_6F_{13}I$ and Ca–Hg gave the tertiary alcohol $Et_2C(OH)C_6F_{13}$ in 70% yield, and cyclohexanone gave 60% of the expected perfluorohexylcyclohexanol. The reaction of the more hindered di-isopropyl ketone, for which free-radical reactions were expected to be favoured, gave, after 20 h at -20°C, the tertiary alcohol $Pr^i_2C(OH)(C_6F_{13})$ (40%) (b.p. = 86—92°C at 13 mm Hg) and the coupling by-product $C_{12}F_{26}$ (35%) (b.p. = 54—60 °C at 13 mm Hg). Tridecafluorohexylmethylphenylcarbinol was formed in 30% yield from acetophenone along with a brown viscous fluorine-containing polymeric substance.

In the case of acetone both the tertiary alcohol $Me_2C(OH)(C_6F_{13})$ (40%) (b.p. = 47 °C at 15 mmHg; m.p. = 38 °C), and the compound $MeC(OH)(C_6F_{13})CH_2C(Me_2)(OH)$ (30%) (b.p. = 130 °C at 0·05 mmHg), which results from an addition on the diacetone alcohol, were formed. Similarly ethyl methyl ketone yielded $EtMeC(OH)C_6F_{13}$ (31%) and $EtC(OH)(C_6F_{13})CH_2C(OH)EtMe$ (10%) which results from the addition on the ketolisation by-product. Benzaldehyde gave the expected secondary alcohol $PhCH(R_F)(OH)$ [$R_F = C_2F_5$ (70%), $R_F = C_6F_{13}$ (60%)]. The existence of a chiral centre results in two doublets in the ^1H n.m.r. spectrum while the CF_2 group α to the asymmetric carbon gives an AB system. Salicylaldehyde similarly gave *o*-$OHC_6H_4CH(C_6F_{13})OH$ (20%) (m.p. = 75—79 °C), but crotonaldehyde did not give the expected alcohol but a fluorine containing polymeric substance.

Perfluoroalkylcalcium derivatives appear to exhibit the same general behaviour as Grignard reagents[1] or alkyl calcium derivatives.[4] However, the presence of ketolisation by-products in several cases indicates that their basic properties are enhanced.

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