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Preliminary communication

SOME UNEXPECTED REACTIONS OF PERFLUOROALKYNYLMAGNESIUM HALIDES

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Summary

$R_FC{\equiv}CMgX$ reacts with Ac_2O to give not only $MeC(O)C{\equiv}CR_F$ but also $MeC(O)CX{=}C(R_F)C(O)Me$, and with CF_3COOPr it gives $CF_3C(O)CH{=}C(OPr)R_F$ not $CF_3C(O)C{\equiv}CR_F$; $R_FC{\equiv}CMgBr$ reacts with Cl_2 to give $R_FC{\equiv}CBr$ rather than $R_FC{\equiv}CCl$, while with Br_2 $R_FC{\equiv}CMgI$ similarly gives $R_FC{\equiv}CI$ rather than $R_FC{\equiv}CBr$.

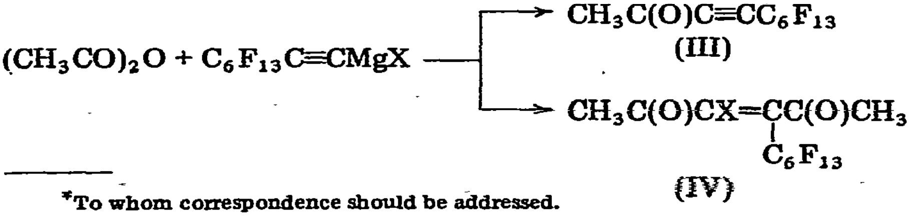
One aim of our studies of perfluoroalkyl compounds is to recognize the differences between their behaviour and that of their hydrocarbon analogues [1]. We report below examples of unexpected reactions of perfluoroalkynylmagnesium halides.

The perfluoroalkynylmagnesium halides (I) were prepared by the exchange reaction [2]:

$$\underset{\text{(II)}}{R_FC{\equiv}CH} + RMgX \xrightarrow[\text{reflux}]{Et_2O} \underset{\text{(I)}}{R_FC{\equiv}CMgX} + RH$$

$R_F = C_6F_{13}, C_8F_{17}$; Ia, $X = Br$, $R = C_2H_5$; Ib, $X = I$, $R = CH_3$

When treated with one molar equivalent of acetic anhydride at −30°C, compounds I gave as major products the ethylenic diketones IV. Only in the case of X = Br was any of the expected acetylenic ketone III isolated.



$$(CH_3CO)_2O + C_6F_{13}C{\equiv}CMgX \longrightarrow \begin{cases} CH_3C(O)C{\equiv}CC_6F_{13} & \text{(III)} \\ CH_3C(O)CX{=}C(C_6F_{13})C(O)CH_3 & \text{(IV)} \end{cases}$$

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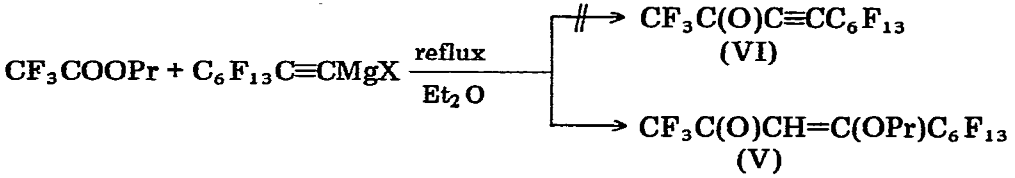
IVa, X = Br, 25%; IVb, X = I, 50% yields in isolated products. NMR: IVa: $\delta(CH_3)$ 2.35 and 2.45, $\delta(CF_2\alpha)$ 106.2; IVb: $\delta(CH_3)$ 2.45 and 2.32; $\delta(CF_2\alpha)$ 101.6 ppm. IR: IVa: $\nu(C{=}O)$ 1715, $\nu(C{=}C)$ 1625; IVb: $\nu(C{=}O)$ 1710, $\nu(C{=}C)$ 1610 cm^{-1}. III was isolated in 17% yield for X = Br. NMR: $\delta(CH_3)$ 2.4; $\delta(CF_2\alpha)$ 101.8 ppm.

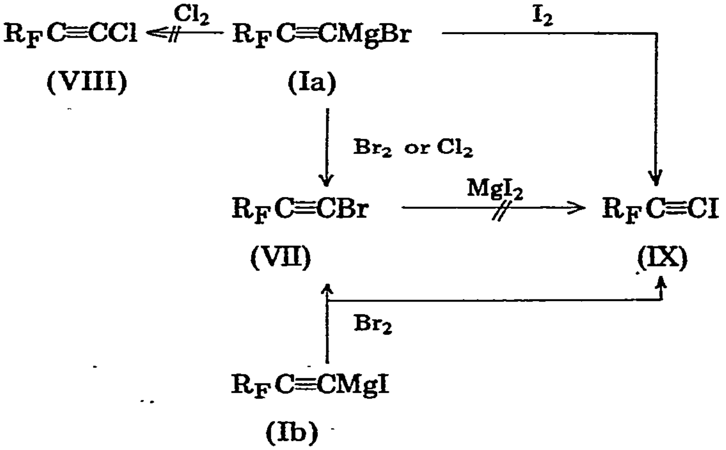
Similarly the ethylenic ketone V was the principal product from I and CF_3COOPr, not the expected acetylenic ketone VI.



(X = I: 30%; X = Br: 40% yields in isolated compounds).

The reaction may be regarded as an addition of a propoxy group to VI, and this would be consistent with the enhanced electrophilic character of the triple bond. V: NMR: $\delta(CH)$ 6.27, $\delta(OC\underline{H}_2CH_2CH_3)$ 4.35, $\delta(OCH_2C\underline{H}_2CH_3)$ 1.87, $\delta(CH_3)$ 1.07, $\delta(CF_3C(O))$ 78.3, $\delta(CF_2\alpha)$ 107.1, $\delta(CF_3)$ 81.6 ppm; IR: $\nu(C{=}O)$ 1730, $\nu(C{=}C)$ 1620 cm^{-1}.

Other unexpected reactions were observed when the alkynylmagnesium halides I were treated with elemental halogens. Thus with chlorine Ia gave the bromoalkyne VII (isolated in 55% yields) rather than the expected chloroalkyne VIII. On the other hand, Ia reacted with bromine or iodine to give the normal products, viz. the bromoalkyne VII (50%) and the iodoalkyne IX (80%). There is only one report of such an exchange in hydrocarbons; viz. the chlorination of 1-heptynylmagnesium bromide to give 1-bromoheptyne (15%) [3].



$R_F = C_6F_{13}$

VII: b.p. 123-126°C/760 mmHg. NMR: $\delta(CF_2\alpha)$ 99.4 ppm; IR: $\nu(C{\equiv}C)$* 2230 cm^{-1}. IX: b.p. 48-53°C/15 mmHg; NMR: $\delta(CF_2\alpha)$ 97.8 ppm; IR: $\nu(C{\equiv}C)$ 2200 cm^{-1}.

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*The IR stretching frequencies are in accordance with those reported for $\nu(C{\equiv}C)$ in $CF_3C{\equiv}CX$ [4].

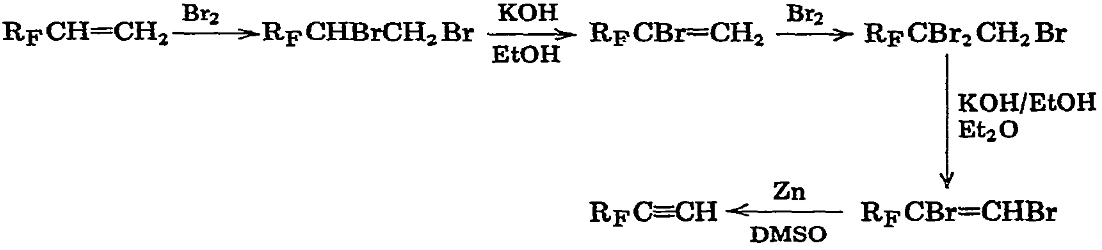
Similarly, Ib reacted with bromine to give not the bromoalkyne VII, but the iodoalkyne IX. Thus it appears that the "abnormal" product is formed when the alkynylmagnesium halide reacts with a lighter halogen. These results cannot be accounted for in terms of exchange of halogen in the 1-haloalkyne, since no trace of IX was found when VII was treated by an ethereal solution of MgI_2 [5] under the same conditions.

It is noteworthy that we could not obtain the bromoalkynes by treatment of II by bromine in alkaline solution under standard conditions [6]. The above reaction thus provides a useful route to the 1-bromo- and 1-iodo-perfluoro-1-alkynes.

In contrast, the usual types of products were obtained from the reaction of I with PhCHO and MeCOCl, though in the second case the tertiary alcohol was recovered as its acetate $CH_3C(C{\equiv}CC_6F_{13})_2OC(O)CH_3$. $C_6F_{13}C{\equiv}CCH(OH)C_6H_5$ (50%): b.p. 120°C/20 mmHg; NMR: $\delta(CH)$ 5.15; $\delta(CF_2\alpha)$ 101.6 ppm; $^5J(H{-}F)$ 4.5 Hz; IR: $\nu(C{\equiv}C)$ 2220 cm^{-1}.

$CH_3C(C{\equiv}CC_6F_{13})_2OC(O)CH_3$ (75%): b.p. 80-85°C/0.3 mmHg; NMR: $\delta(CH_3C(O))$ 2.16, $\delta(CH_3C)$ 2.05, $\delta(CF_2\alpha)$ 99.4 ppm; IR: $\nu(C{\equiv}C)$ 2270, $\nu(C{=}O)$ 1780 cm^{-1}.

The alkynes II were prepared by the following sequence of reactions [7]:



$$\begin{tikzcd}
R_FCH{=}CH_2 \arrow[r, "Br_2"] & R_FCHBrCH_2Br \arrow[r, "KOH", "EtOH"'] & R_FCBr{=}CH_2 \arrow[r, "Br_2"] & R_FCBr_2CH_2Br \arrow[d, "KOH/EtOH", "Et_2O"'] \\
 & & R_FC{\equiv}CH & R_FCBr{=}CHBr \arrow[l, "Zn", "DMSO"']
\end{tikzcd}$$

$R_F = C_4F_9, C_6F_{13}, C_8F_{17}$.

However, the bromination and debromination could not be performed by the procedures reported for the lower homologues [8]. Instead, nearly quantitative brominations were achieved thermally or photochemically. Similarly, debromination by zinc dust is ineffective in refluxing ethanol, but proceeds smoothly in dimethylsulfoxide at 90-100°C (80-85% yield).

All the new compounds gave satisfactory elemental analyses and mass spectra. The ^1H and ^{19}F chemical shifts are relative to TMS and $CFCl_3$, respectively.

Acknowledgements

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