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PRELIMINARY NOTE

A General Facile Preparation of *F*-Alkylacetylenes

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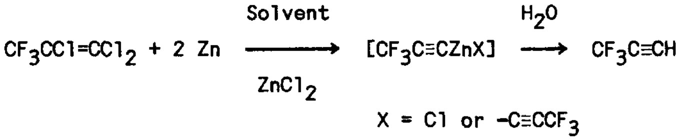
SUMMARY

F-Alkylethylenes can be exhaustively chlorinated under UV irradiation to give *F*-alkylpentachloroethanes in high yields. Subsequent dechlorination with three equivalents of zinc readily gives the *F*-alkylacetylenic zinc reagents, which on hydrolysis with aqueous HCl provide the corresponding *F*-alkylacetylenes in good yields. The methodology is applicable to *F*-alkyl groups of various chain lengths, and the *F*-acetylenic zinc reagent produced as the reaction intermediate can also be utilized in the direct preparation of functionalized *F*-alkylacetylenes.

Several methods have been reported for the preparation of *F*-alkylacetylenes. These early reports were multi-step syntheses and the choice of method depended primarily on the availability of precursors [1-6].

The most simplistic method for the preparation of an *F*-alkylacetylene is the one-pot preparation of 3,3,3-trifluoropropyne described by Finnegan and Norris [7] almost 25 years ago.



$$CF_3CCl{=}CCl_2 + 2\ Zn \xrightarrow[ZnCl_2]{Solvent} [CF_3C{\equiv}CZnX] \xrightarrow{H_2O} CF_3C{\equiv}CH$$

$$X = Cl \text{ or } -C{\equiv}CCF_3$$

Recent work in our laboratory [8-12] and by other workers [13,14] have demonstrated the utility of both *F*-alkyl [8] and *F*-vinylic [4-14] zinc reagents in preparative organofluorine chemistry. Thus, our attention became focused on a practical route to the corresponding *F*-acetylenic zinc

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reagents as a general entry to F-alkylacetylenes and functionalized F-alkyl acetylenes via methodology already amply illustrated for the corresponding F-vinylic zinc reagents [9-14].

The criteria utilized in the selection of our approach were: (1) the precursors must be commercially available or readily prepared via standard methodology; (2) any intermediate steps must be readily carried out on a large scale; (3) the choice of the F-alkyl group must be general; and (4) the reaction sequence must be carried out in standard apparatus. The sequence employed which satisfies these criteria is outlined below in Scheme I.

$$R_FCH{=}CH_2 \ + \ 3Cl_2 \xrightarrow{UV} R_FCCl_2CCl_3$$

$$\begin{tikzcd} R_FCCl_2CCl_3 \arrow[r, "3Zn", "DMF"'] & {[R_FC{\equiv}CZnCl \ + \ (R_FC{\equiv}C)_2Zn]} \arrow[d, "HCl\ aq."] \\ & R_FC{\equiv}CH \end{tikzcd}$$

Scheme I

The F-alkylethylenes are commercially available or can be readily prepared via addition of F-alkyl iodides to ethylene followed by subsequent elimination of hydrogen iodide with base.

Exhaustive chlorination of the F-alkylethylenes readily provides the F-alkylpentachloroethanes. The chlorination has been accomplished via two different procedures. On a small scale (typically 40 mmoles) the chlorination reactions were carried out in 300 ml sealed glass tubes (containing the desired ethylene and four equivalents of chlorine) placed in a Rayonnette photochemical reactor which contained alternating 2537 and 3000Å lamps. This method (Method A) is particularly useful for volatile ethylenes (i.e. $R_F{=}C_3F_7$), but it was not effective for $R_F{=}C_{10}F_{21}$. In this latter case the intermediate chlorination products were solids, which were not soluble in the remaining condensed chlorine and impeded the successful conversion to $C_{10}F_{21}CCl_2CCl_3$. A second chlorination procedure has proven to be convenient for large scale preparations (Method B). The F-alkylethylenes were chlorinated neat (or in Freon 113 solution in the case of

$C_{10}F_{21}$) in an Ace Photochemical reactor (450 W medium pressure immersion lamp) at room temperature. Chlorine gas was simply bubbled thru the solution in the reactor until the reaction was complete (24-74 hours). Both methods gave high yields of the F-alkylpentachloroethanes with F-alkylethylenes of various chain length. These results are summarized in Table I.

TABLE I

Preparation of F-alkylpentachloroethanes from $R_FCH=CH_2$

	Method A		Method B	
R_F	Scale (mmoles)	Yield	Scale (mmoles)	Yield
C_3F_7	40	66%		
C_4F_9	40	79%	1173	90%
C_6F_{13}	40	79%	899	72%
C_8F_{17}	40	89%	370[a]	75%
$C_{10}F_{21}$			102[b]	94%

[a] Reactor temperature kept at 50°C to prevent solidification of products.

[b] Chlorination was carried out in 1M solution in Freon 113.

The zinc dehalogenation reaction was accomplished in DMF (sufficient to yield a final concentration of 1M). With one equivalent of zinc the reaction stopped cleanly at the F-alkyltrichloroethylene stage (isolated yields 64-65%). These trichloroethylenes could be readily dehalogenated to the F-alkylacetylenic zinc reagents as described by Finnegan and Norris [7]. However, it was not necessary to prepare the F-alkyltrichloroethylenes, since the reaction of the F-alkylpentachloroethanes with three equivalents of zinc gave the corresponding F-alkylacetylenic zinc reagents directly. The best yields were obtained when the temperature of the dehalogenation reaction was controlled by addition of the F-alkylpentachloroethanes at a rate which maintained the temperature of the reaction mixture at 90-100°C. To ensure complete dechlorination, the reaction mixture was heated at 100°C for one hour after the initial exotherm had subsided.

The zinc reagents are readily hydrolyzed to the corresponding *F*-alkylacetylenes. Hydrolysis with water gave thick slurries which hampered isolation of the acetylenes. However, hydrolysis with concentrated HCl gave satisfactory results. After hydrolysis, the *F*-alkylacetylenes were flash distilled from the reaction mixture (steam distillation also works well), the distillate washed with water to remove any DMF, and the acetylenes purified by distillation. Table II summarizes these results.

TABLE II

Preparation of *F*-alkylacetylenes from *F*-alkylpentachloroethanes

$$R_FCCl_2CCl_3 \xrightarrow[DMF]{3Zn} [R_FC{\equiv}CZnX] \xrightarrow[H_2O]{HCl} R_FC{\equiv}CH$$

R_F	Yield	^{19}F NMR (ϕ^*)[a]	^1H NMR (δ)[b]	J_{HF}(Hz)	C≡C(FT-IR)[c]
C_3F_7	77%	-100.0	3.0	5.6	2147
C_4F_9	72%	- 99.8	3.0	5.9	2145
C_6F_{13}	64%	- 99.8	3.0	5.9	2150
C_8F_{17}	62%	- 99.8	3.0	5.5	2146
$C_{10}F_{21}$[d]	43%	- 99.9	3.0	5.5	2149

[a] Chemical shift for CF_2 group adjacent to the triple bond, in ppm upfield from $CFCl_3$.

[b] In ppm downfield from TMS (all signals are triplets).

[c] In cm^{-1}.

[d] DMF/THF solvent utilized in this reaction.

In conclusion, a simple, straightforward, general preparation of *F*-alkylacetylenes from commercially available *F*-alkylethylenes is described. In addition, the *F*-alkylacetylenic zinc reagents can be utilized in the preparation of functionalized *F*-alkylacetylenes. Preliminary work in our laboratories has demonstrated that the zinc reagent can be effectively employed in the synthesis of 1-halo-*F*-acetylenes, 1-aryl-*F*-acetylenes, *F*-

diynes and *E*-enynes [15]. Also, a recent report by Bumgardner [16] with the Finnegan and Norris reagent reaffirms the utility of our approach.

This direct general preparation from simple precursors is easily carried out in standard apparatus and should find extensive synthetic utility, and we recommend this approach to researchers interested in *E*-alkylacetylenes and *E*-alkylacetylene derivatives. Future publications will detail additional application of these *E*-alkylacetylenic zinc reagents.

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