Journal of Fluorine Chemistry
Elsevier Sequoia S.A., Lausanne — Printed in Switzerland

Preliminary Note

A convenient preparation of bromofluoromethylene olefins

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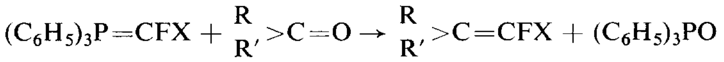
(Received November 1st, 1971)

Previous reports from this laboratory have recently demonstrated the utility of fluorinated ylids in the preparation of difluoromethylene and fluorochloromethylene olefins[1-4], (equation (1)).

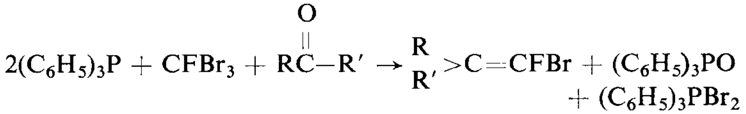


$$(C_6H_5)_3P{=}CFX + \overset{R}{\underset{R'}{}}{>}C{=}O \rightarrow \overset{R}{\underset{R'}{}}{>}C{=}CFX + (C_6H_5)_3PO \qquad (1)$$

$(X = F, Cl;\ R = \text{alkyl or aryl};\ R' = H, \text{or } R_f)$

The earlier acetate salt method (using either CF_2ClCO_2Na or $CFCl_2CO_2Na$) employed for the generation of the ylid[1-3] necessitated the preparation and use of hygroscopic salts, the preparation of expensive materials (especially $CFCl_2CO_2H$), and in the case of the difluoromethylene olefination reaction isomerization and/or HF addition of the product olefin occurred[4]. Later work with difluorodibromomethane (Freon 12B2) circumvented all these difficulties for the preparation of terminal difluoromethylene olefins[4].

This report describes the extention of the Freon 12B2 reaction to the preparation of terminal bromofluoromethylene olefins (equation (2)).



$$2(C_6H_5)_3P + CFBr_3 + R\overset{\overset{O}{\|}}{C}{-}R' \rightarrow \overset{R}{\underset{R'}{}}{>}C{=}CFBr + (C_6H_5)_3PO + (C_6H_5)_3PBr_2 \qquad (2)$$

$(R = \text{alkyl, aryl}, R_f;\ R' = H, \text{alkyl}, R_f)$

The preparation of the bromofluoromethylenetriphenylphosphorane $[(C_6H_5)_3P{=}CFBr]$ (I) can be conveniently carried out *in situ* by the reaction of triphenylphosphine and fluorotribromomethane (II) in dry glyme solvents at ~70°. The method of Birchall and Haszeldine[5] provides a ready source of (II), or it can be purchased commercially*. Similar results can be obtained from fluorodibromoacetic acid as a precursor [6], but this method again is plagued by the same difficulties as the earlier acetate methods. Consequently, the preparation of (I) from (II) is the synthetic method of choice. Some representative examples of the scope of this reaction are summarized in Table 1.

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* Commercially available from PCR, Gainesville, Fla., U.S.A.

TABLE 1

$$2(C_6H_5)_3P + CFBr_3 + RCOR' \xrightarrow[70^\circ]{\text{glymes}} \begin{matrix} R \\ R' \end{matrix} > C{=}CFBr \text{ (III)}$$

R	R′	%(III)[a]	%(III)[b]	*trans/cis* ratio[c]
C_6H_5	CH_3	40	17.6	41/59
C_6H_5	CF_3	97	81.5	46/54
C_6H_5	C_2F_5	77	64.6	60/40
CF_3	CF_3	38[d]	24.0	....
$C_6H_5CH_2$	CF_3	71	58.6	43/57

[a] Conversion percentage.

[b] Based on starting carbonyl compound.

[c] The *trans/cis* ratio of (III) was assigned on the basis of J(H,F) and/or J(CF_3,F). *Trans* is defined as *trans* F and R′.

[d] Ylid pre-formed by reaction of 2:1 $(C_6H_5)_3P$:$CFBr_3$ ratio, then ketone added.

Examination of the properties and scope of (I) relative to the difluoromethylenetriphenylphosphorane (IV) has revealed two distinct and interesting differences. First, (I) is more general in scope than (IV). Whereas (I) gave a 40% conversion of olefin with acetophenone, (IV) has been shown previously to be unreactive with this ketone! In fact, only aldehydes and ketones containing perfluoroalkyl groups react with (IV), and typical non-activated ketones are resistant to (IV). In contrast, (I) appears to react with non-activated ketones. Secondly, (I) is more stable than (IV). Regardless of the mode of generation of (IV)[1, 4], solutions of this reagent exhibit no stability, and the carbonyl trapping agent must be present in solution to intercept (IV). All efforts in this laboratory to pre-generate (IV), followed by subsequent addition of the carbonyl moiety, have been fruitless. In contrast to the instability of (IV), we have found (I) to be extremely stable in solution. For example, when (I) was generated from the reaction of (II) with triphenylphosphine in the absence of any carbonyl trapping agent, *the solution of (I) did not decompose.* After 21 h at 37–38°, this solution of (I) gave a 73% yield of olefin on subsequent addition of trifluoroacetophenone (equation (3)).

$$\begin{array}{lll} 2(C_6H_5)_3P + CFBr_3 \xrightarrow[\text{glyme}]{70^\circ} & \underset{\text{(I)}}{(C_6H_5)_3P{=}CFBr} + & (C_6H_5)_3PBr_2 \\ & & \Big\downarrow \begin{array}{l}(1)\ 21\text{ h at }37^\circ \\ (2)\ CF_3COC_6H_5\end{array} \\ & & C_6H_5(CF_3){=}CFBr\ (73\%) \end{array} \quad (3)$$

Solutions of (I) exhibit greater stability than any other yet reported fluoromethylene ylid**. Consequently, for the first time a fluoromethylene ylid is available for detailed examination.

** Solutions of $[(C_6H_5)_3P{=}CFCl]$ show stability of 1/4–1/2 h[3]. Solutions of $[(C_6H_5)_3P{=}CHF]$ show stability at low temperatures but decompose rapidly on warming to room temperature.[7,8]

Additional work is in progress to explore the scope and mechanism of this method of ylid formation. In addition, a detailed study of the synthetic applicability and transformations afforded by this stable ylid is in progress and will be reported in subsequent papers.

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