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Preliminary Note

Fluoride-ion-free difluoromethylene olefination reactions

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The preparation of terminal difluoromethylene olefins has been facilitated by the reaction of difluoromethylene triphenylphosphorane [$(C_6H_5)_3P=CF_2$] (I) with aldehydes[1] and perfluoroalkyl ketones[2].

$$C_6H_5COCF_3 + (C_6H_5)_3P + CF_2ClCO_2Na \xrightarrow[\text{diglyme}]{100^\circ}$$
$$F_2C=C(C_6H_5)CF_3 + (C_6H_5)_3PO + NaCl + CO_2$$

The usual mode of generation of (I) has been *via* the decarboxylation of alkali metal salts of chlorodifluoroacetic acid. As we have previously demonstrated, the mechanism of this reaction does *not* involve trapping of a fluorocarbene, but probably involves the formation and decomposition of the phosphobetaine salt [$(C_6H_5)_3\overset{+}{P}CF_2CO_2^-$] directly to the ylid (I)[2,3].

Further application of this synthetic route in our laboratory has demonstrated one severe limitation of this method; namely, that fluoride ion addition and isomerization reactions accompany this reaction. For example, when the perfluoroalkyl group is other than trifluoromethyl, fluoride ion isomerization occurs[4].

$$C_6H_5COCF_2CF_3 + CF_2ClCO_2Na + (C_6H_5)_3P \xrightarrow[\text{diglyme}]{100^\circ}$$
$$CF_3C(C_6H_5)=CFCF_3$$
cis and *trans*

$$C_6H_5COCF_2CF_3 + CF_2ClCO_2Li + (C_6H_5)_3P \xrightarrow[\text{DMF}]{100^\circ}$$
$$F_2C=C(C_6H_5)CF_2CF_3$$

The use of lithium chlorodifluoroacetate provided a temporary means around this difficulty[4], since only the terminal olefin was formed with ketones such as C_6H_5-$COCF_2CF_3$ and $C_6H_5COCF_2CF_2CF_3$ with lithium chlorodifluoroacetate.

Subsequent extention of the synthetic route in our laboratory has shown that even the use of lithium chlorodifluoroacetate will not always prevent isomerization or HF-addition (when isomerization is not possible). For example, when *m*-bromophenyl trifluoromethyl ketone is reacted under the normal ylid reaction conditions, only the HF-addition product of the initially formed olefin is isolated[5].

$$m\text{-}BrC_6H_4COCF_3 + (C_6H_5)_3P + CF_2ClCO_2Li \xrightarrow[DMF]{100^\circ} m\text{-}BrC_6H_4CH(CF_3)_2$$

Similarly, when *m*-bromophenyl pentafluoroethyl ketone is reacted under these conditions, the internal olefins are the major products[6].

$$m\text{-}BrC_6H_4COCF_2CF_3 + (C_6H_5)_3P + CF_2ClCO_2Li \xrightarrow[DMF]{100^\circ} \underset{cis \text{ and } trans}{m\text{-}BrC_6H_4(CF_3)C{=}CFCF_3} + m\text{-}BrC_6H_4(C_2F_5)C{=}CF_2$$

Extensive study of this reaction has shown that when a good carbanion stabilizing group, such as Br, I, CN, NO_2, is substituted on the aromatic ring, only the isomerized or addition product can be isolated[5,6], and this method is completely unsuccessful as a route to these terminal difluoromethylene olefins.

This communication describes a synthetic route for the preparation of difluoromethylene olefins *via* ylid (I) which completely avoids any fluoride ion isomerization or addition reactions. The ylid (I) is generated *in situ* from the reaction of dibromodifluoromethane, CF_2Br_2 (II), with triphenylphosphine. Solvents such as dry diglyme, triglyme, or DMF can be successfully employed. Temperatures of ~ 70° provide a convenient rate of reaction.

$$CF_2Br_2 + 2(C_6H_5)_3P + RCOR_f \xrightarrow[\text{diglyme, 24 h}]{70^\circ} F_2C{=}C(R)R_f + (C_6H_5)_3PBr_2 + (C_6H_5)_3PO$$

TABLE 1

$$RCOR_f + \underset{\substack{\text{or}\\ CF_2Br_2}}{CF_2ClCO_2M} \xrightarrow{(C_6H_5)_3P} F_2C{=}C(R)R_f + CF_3CF{=}C(R)R_f + CF_3CH(R)R_f$$

		Yield of product[a] (%)					
		Terminal olefin		Internal olefins		HF addition	
R	R_f	CF_2Br_2	CF_2ClCO_2M	CF_2Br_2	CF_2ClCO_2M	CF_2Br_2	CF_2ClCO_2M
C_6H_5	CF_3	85	68[b]	—	—	—	—
p-ClC_6H_4	CF_3	86	32[b]	—	—	—	37[b]
m-BrC_6H_4	CF_3	83	2[c]	—	—	<1	65[c]
C_6H_5	C_2F_5	82	42[d]	<1	2[d]	—	—
m-BrC_6H_4	C_2F_5	87	42[e]	<1	54[e]	<1	—[f]

[a] GLC yield based on starting ketone; [b] M = Na, Reference 2; [c] M = Li, Reference 5; [d] M = Na, Reference 4; [e] M = Li; [f] 7% yield of unidentified product which may be the HF-addition compound.

Under these conditions no HF-addition or fluoride ion catalyzed isomerization reactions have been observed (except in trace amounts), and only the terminal difluoromethylene olefins are formed. Some representative examples of the utility of this reaction as compared to the chlorodifluoroacetate route are summarized in Table 1.

It should be noted that not only are these reactions with (II) free of fluoride ion complications, but also the yields of products are generally much higher than in the acetate salt method, and the reaction is cleaner and easier to carry out (the hygroscopic salts need not be prepared). The ease of availability of (II)* also makes this reaction attractive.

Consequently, this synthetic route provides a convenient, unequivocal, route to terminal difluoromethylene olefins, and is undoubtedly the method of choice as compared to the acetate salt route. The scope and mechanism of this reaction are under detailed study in our laboratory and will be reported in subsequent papers.

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* Commercially available as Freon 12B2 from E. I. du Pont de Nemours and Co., Inc.