

Preliminary Note

Olefination *via* metal dehalogenation of phosphonium salts

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Recently, Corey and Fuchs¹ reported the preparation of 1,1-dibromo-olefins by the reaction of aldehydes with triphenylphosphine, carbon tetrabromide and zinc dust. One of the advantages claimed for this method was that only one equivalent of triphenylphosphine was required. Although these authors did not report any mechanistic studies, presumably the function of the zinc is to dehalogenate the intermediate phosphonium salt, $[(C_6H_5)_3PCBr_3]^+ Br^-$ **.

This report by Corey and Fuchs prompts us to report some of our own work on the metal dehalogenation of phosphonium salts. Our work in this area was initiated by experimental problems which occur in the usual base generation of phosphonium ylids. For example; (a) when alkyl-lithium reagents are employed in the generation of ylids, the intermediate betaine in the Wittig reaction can coordinate with the lithium ion and collapse of the betaine to olefinic products is impeded. Betaine collapse can be accomplished by treatment with potassium *t*-butoxide² which may be unsuitable if the olefinic product is susceptible to base attack; (b) in some cases the initial phosphonium salt may undergo displacement reactions with the alkyl-lithium reagent or may undergo halogen-abstraction reactions³. Either type of reaction generates an undesired ylid resulting in lower yields of product. (c) If one of the reactants is a carbon tetrahalide, the usual mode of ylid generation *via* two equivalents of phosphine and one equivalent of carbon tetrahalide gives one equivalent of dihalotriphenylphosphorane. If the reactant carbonyl compound contains any functional group susceptible to attack by $(C_6H_5)_3PX_2$ ($X = Cl, Br$), competing side reactions again result⁴.

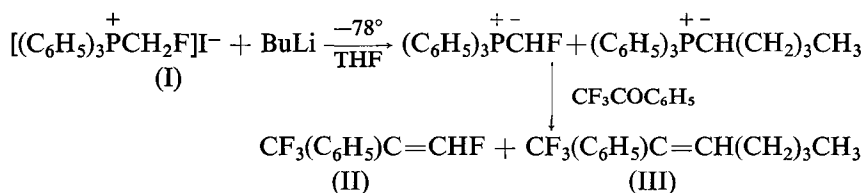
To avoid the type of problems outlined above, we have investigated the use of metal dehalogenation of phosphonium salts, since this procedural modification of the Wittig reaction avoids the use of alkyl-lithium reagents, avoids metal/halogen

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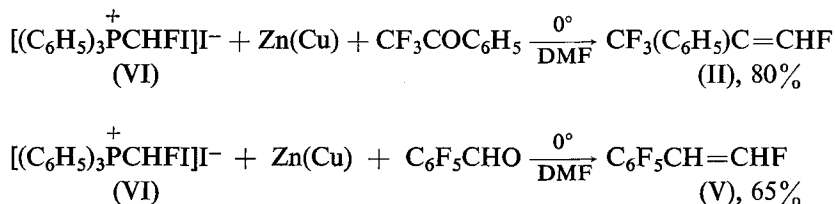
** Other mechanistic possibilities are available, but on the basis of our work with similar phosphonium salts, dehalogenation of the intermediate shown appears to be the most reasonable mechanism.

abstraction or displacement reactions, prevents formation of dihalophosphoranes and allows equivalent amounts of phosphines to be employed in the carbon tetrahalide reactions.

To illustrate the utility of this procedure, the preparation of vinyl fluorides will be detailed. When fluoromethyltriphenylphosphonium iodide (I) was treated with butyl-lithium at -78° and the subsequent ylid solution reacted with trifluoroacetophenone and allowed to warm to room temperature, only small amounts of the desired vinyl fluoride (II) were observed by GLPC. Subsequent treatment of the reaction solution with potassium *t*-butoxide (2 h at 0°) increased the yield of (II) to 50%. In addition to (II), 17% of (III) and 1% of the vinyl ether $\text{CF}_3(\text{C}_6\text{H}_5)\text{C}=\text{CHOBu}^t$ (IV) were observed. The yield of (II) decreased and the yield of (IV) increased with time. Under similar conditions, pentafluorobenzaldehyde gave less than 5% of vinyl fluoride, (V).



In contrast to the problems encountered in the alkyl-lithium generation method, the dehalogenation of fluoro-iodomethyltriphenylphosphonium iodide (VI) with a zinc-copper couple⁵ gave excellent yields of vinyl fluorides (II) and (V).



No complications of new ylid formation, vinyl ether formation, or betaine collapse are encountered in this method. Consequently the yields of desired product are increased and the isolation procedure is simplified. A comparison of the ylid generation procedures is summarized in Table 1. Satisfactory analytical and spectral data were obtained on all olefinic products.

This dehalogenation procedure promises to provide a useful modification of the Wittig reaction. Preliminary work in our laboratory with other phosphonium salts⁶ has shown this reaction to be general, and other examples illustrating the utility of this route to olefins will be described in due course. In addition, the mechanism of these reactions and the use of other metals is under active investigation.

TABLE 1
COMPARISON OF YLID ROUTES TO VINYL FLUORIDES

| Carbonyl component | Olefin | Yield (%) | <i>cis:trans</i> ^a | Method |
|---|---|-----------|-------------------------------|--------|
| CF ₃ COC ₆ H ₅ | CF ₃ (C ₆ H ₅)C=CHF | 50 | 46:54 | BuLi |
| CF ₃ COC ₆ H ₅ | CF ₃ (C ₆ H ₅)C=CHF | 80 | 52:48 | Zn(Cu) |
| C ₆ H ₅ CHO | C ₆ H ₅ CH=CHF | 44 | 44:56 | BuLi |
| C ₆ H ₅ CHO | C ₆ H ₅ CH=CHF | 52 | 41:59 | Zn(Cu) |
| C ₆ F ₅ CHO | C ₆ F ₅ CH=CHF | <5 | — | BuLi |
| C ₆ F ₅ CHO | C ₆ F ₅ CH=CHF | 65 | 54:46 | Zn(Cu) |
| C ₆ H ₁₃ CHO | C ₆ H ₁₃ CH=CHF | 26 | 48:52 | BuLi |
| C ₆ H ₁₃ CHO | C ₆ H ₁₃ CH=CHF | 54 | 43:57 | Zn(Cu) |

^a *Cis:trans* ratios were determined by NMR spectroscopy. In the BuLi method, one of the product isomers was consumed faster than the other by potassium t-butoxide and hence in this case the *cis:trans* ratios are not too meaningful but are merely given for comparative purposes.

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