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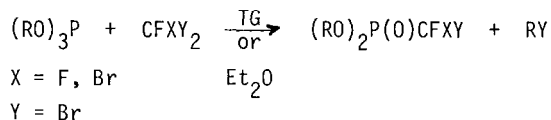
PRELIMINARY NOTE

PREPARATION OF F-METHYLENE BIS PHOSPHONATES

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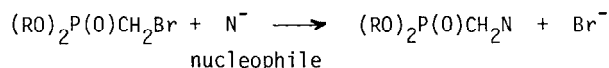
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We have recently reported a facile, high yield synthesis of halo-F-methylphosphonates via the reaction of trialkyl phosphites and halo-F-methanes [1]. These F-methyl phosphonates undergo selective attack at



phosphorus, phosphoryl oxygen, or the -OR group depending on the nature of the attacking nucleophile [2]. Similar type of reactions have been previously observed in non-fluorinated phosphonates, and selective attack of this kind is neither surprising nor unique.

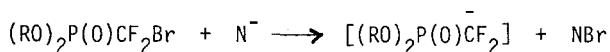
In addition to attack at the above mentioned sites in the phosphonate molecule, S_N2 displacement of halogen from the alpha carbon is another typical reaction of non-fluorinated phosphonates. However, we have



obtained no evidence that such S_N2 displacements occur at the halo-F-methyl carbon of halo-F-methylphosphonates.

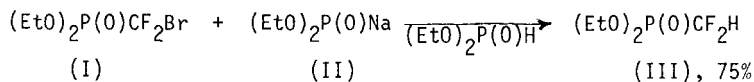
We now wish to report that products which appear to be derived from S_N2 type reactions at the halo-F-methyl carbon are actually formed via

positive halogen abstraction from the halo- $\underline{\text{F}}$ -methylphosphonate. The reactive intermediate is the $\underline{\text{F}}$ -methylene phosphonate ylide. Similar behavior

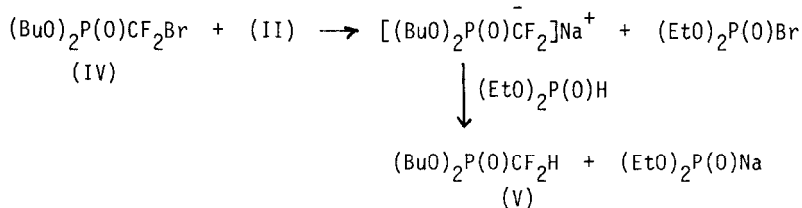


has been previously noted in the chemistry of halo- $\underline{\text{F}}$ -methyl phosphonium salts [3].

For example, when bromo- $\underline{\text{F}}$ -methyldiethylphosphonate (I) is reacted with sodium diethyl phosphite (II) in excess diethyl phosphite, the reduced phosphonate (III), [4], is formed in 75% yield. Other reduced phosphonates can be obtained from related halo- $\underline{\text{F}}$ -methylphosphonates via a similar



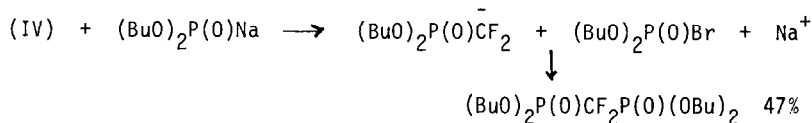
reaction sequence. Positive halogen abstraction and/or carbene formation mechanisms can be rationalized to explain the above result. The mechanism was shown, however, to involve positive halogen abstraction by the following experiment. When bromo- $\underline{\text{F}}$ -methyldibutylphosphonate (IV) was reacted with (II) in excess diethyl phosphite, the only reduced phosphonate observed was $\underline{\text{F}}$ -methyldibutylphosphonate (V). No (III) was detected by ^{19}F NMR. Thus, the mechanism is consistent with attack at halogen to



generate the phosphonate ylide. Subsequent proton capture by the ylide gives (V). The absence of (III) precludes any carbene ($:\text{CF}_2$) intermediates [5].

The acylation of ylides is a well documented reaction. If the mechanistic pathway is as outlined above, further reaction of the initially formed ylide with the phosphoryl bromide (in the absence of dialkyl phosphite) might occur to give the bis phosphonate. Such behavior has now been observed.

When (IV) was reacted with sodium dibutyl phosphite in hexane, a 47% isolated yield of tetrabutyl-F-methylene bis phosphonate [6] was obtained. The major by-product (27%) was the reduced phosphonate (V). Similar



reaction of (I) and (II) in hexane gave 13% isolated yield of tetraethyl-F-methylene bis phosphonate [7,8]. To our knowledge, these syntheses represent the first reported examples of F-methylene bis phosphonates.

The bis phosphonates can also be obtained via direct reaction of CF_2Br_2 with excess sodium dialkylphosphite. However, in our hands this



route gives lower yields and product isolation is more difficult due to increased side product formation.

In summary, reaction of halo-F-methylphosphonates with phosphite anion proceeds via attack on halogen. Positive halogen abstraction generates the F-methylene phosphonate ylide [9]. Subsequent acylation of this ylide with the phosphoryl halide produced in the first step gives a useful route to the F-methylene bis phosphonates.

Our work continues to explore these halo-F-methylphosphonates as well as the F-methylene bis phosphonates.

ACKNOWLEDGEMENT

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REFERENCES

- 1 D. J. Burton and R. M. Flynn, *J. Fluorine Chem.*, **10** (1977), 329.
- 2 Unpublished work of R. M. Flynn.
- 3 M. J. Van Hamme and D. J. Burton, *J. Fluorine Chem.*, **13** (1979), 407 and references therein.
- 4 Authentic samples of the reduced phosphonates were prepared (for comparison) by the method of Soborovskii and Baina, *J. Gen. Chem. USSR*, **29** (1959) 1115.

5 Carbene can be formed by dissociation of the F-methylene phosphonate ylide. Subsequent capture of carbene by (II) followed by protonation would give (III). Related work in our laboratory suggests that the ylide is unstable and can dissociate to carbene and phosphite anion. In the experiment described, proton capture is obviously faster than dissociation.

6 ^{19}F NMR: δ^* 121.6 ppm (t) J 87 Hz; ^1H NMR: δ 0.8-1.1 (m, 3H), δ 1.1-1.9 (m, 4H), δ 4.0-4.4 (m, 2H); ^{31}P NMR: δ - 3.7 (t); ^{13}C NMR: δ 116.3 (t,t) J(C,P) 187 Hz, J(C,F) 279 Hz (-CF₂-). Anal: Calcd for C₁₇H₃₆F₂O₆P₂: % C 46.79, % H 8.26. Found % C 46.79 % H 8.27.

7 ^{19}F NMR: δ^* 122.0 (t) J 87 Hz; ^1H NMR: δ 1.40 (t) J 7 Hz (CH₃), δ 4.39 (d,q) J(H,P) 3.8 Hz, J(H,H) 7 Hz (-CH₂O); ^{31}P NMR: δ - 3.5 (t); ^{13}C NMR: δ 16.4 (s) (CH₃-), δ 65.3 (d) J 2.9 Hz, δ 116.2 (t,t) J(C,P) 187 Hz, J(C,F) 279 Hz (-CF₂-). Anal: Calcd for C₉H₂₀F₂O₆P₂: % C 33.33, % H 6.17. Found % C 33.41, % H 6.32.

8 No attempt has been made to optimize yields or reaction conditions.

9 This work represents the first example of a fluorine-containing phosphonate ylide.

Corrigendum

Journal of Fluorine Chemistry, 14 (1979) 495 - 510. Amino-sulphur-fluorine derivatives as fluoride ion donors: preparation of three- and four-coordinated cations of sulphur(IV) and (VI). R. Mews and H. Henle.

The authors have requested that the text order of this article be changed slightly, as follows:

Page 501: Wie bei den Schwefel(IV).....

to page 502: oder Addukt bildet.

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