

PRELIMINARY NOTE

Tributylarsonium-2,2,3,3,4,4-hexafluorocyclobutane Ylide. Preparation and Cleavage

DONALD J. BURTON and PAUL D. VANDER VALK

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242 (U.S.A.)

SUMMARY

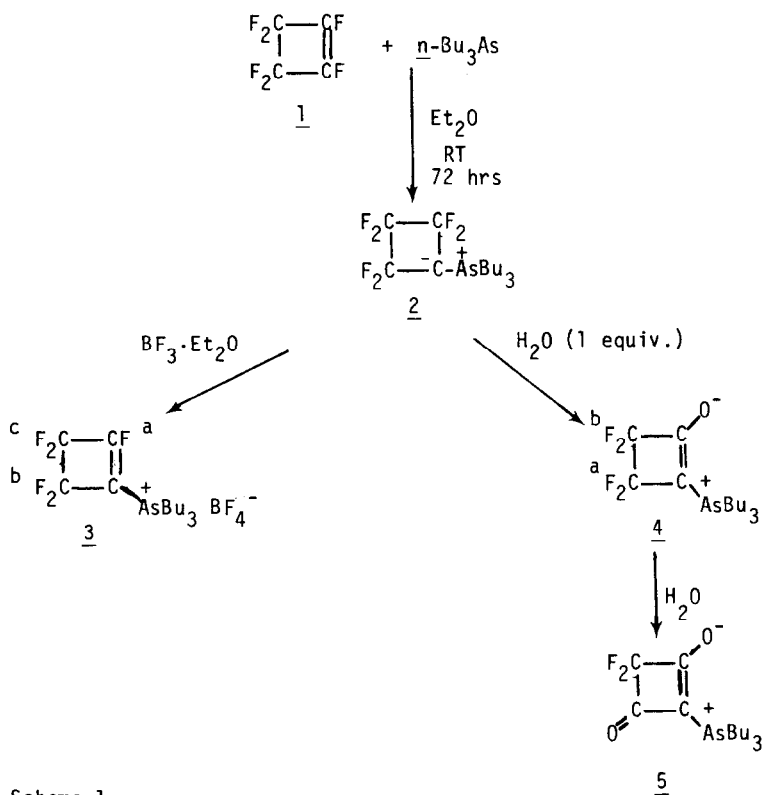
F-cyclobutene forms a stable ylide with n-tributylarsine. In contrast to the halogen cleavage of the analogous phosphonium ylide, which gives 1,1-dihaloalkanes, the arsonium ylide reacts with bromine and iodine to give the 1-halo-F-cyclobutenes.

Recent reports from our laboratory have documented the formation of stable phosphonium ylides from cyclic F-olefins [1] and acyclic olefins [2]. Similar stable ylide formation was found in the reaction of tertiary amines with F-cyclobutene [3].

Herein, we wish to report the first example of a stable fluorinated arsenic ylide and to contrast some of its chemistry with the phosphonium and ammonium analogues.

In contrast to the facile reaction of F-cyclobutene, 1, with triphenylphosphine [1], triphenylarsine did not react with 1 under a variety of conditions. However, n-tributylarsine reacted smoothly (albeit slowly) with 1 in ether or THF to give a quantitative conversion to the arsenic ylide, 2 (see Scheme 1). The <sup>19</sup>F NMR spectrum of 2 consisted of two multiplets in the ratio of 2:1 at  $\delta^*$  82.4 and 122.4 ppm, respectively. Similar chemical shifts and multiplicity patterns were observed in the phosphonium [1] and ammonium [3] analogues.

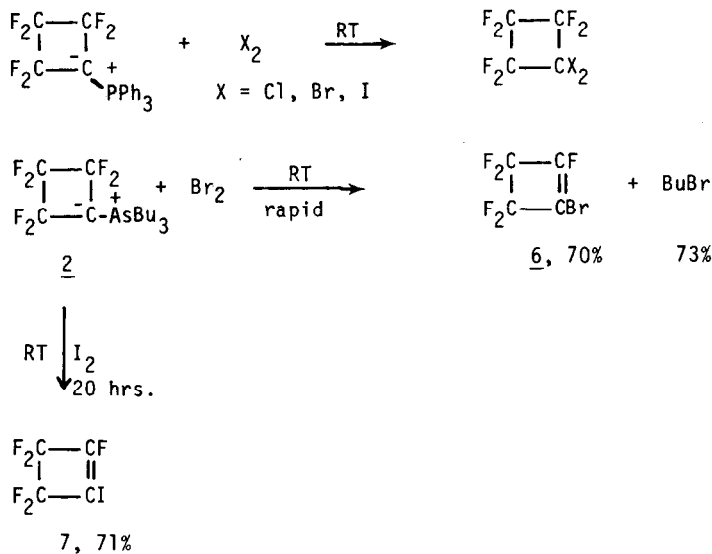
Similar to the phosphonium and ammonium ylides, 2 reacted with boron trifluoride etherate to form the tetrafluoroborate salt [2,3]. Although 2 forms the tetrafluoroborate salt readily, reaction of this salt with KF did not regenerate 2, whereas the analogous phosphonium and ammonium tetrafluoroborate salts easily reformed ylide on reaction with KF. 2 reacts with water to form (sequentially) the mono- or bis- hydrolysis products.  $^{19}\text{F}$  NMR spectrum of 4 exhibits two multiplets in a 1:1 ratio at  $\delta^*$  100.3 and 120.3 ppm, respectively for Fa and Fb. 5 shows a singlet in the  $^{19}\text{F}$  NMR spectrum at 118.1 ppm. 3 shows four absorptions in the  $^{19}\text{F}$  spectrum at  $\delta^*$  82.2 (rel area 1, F<sup>a</sup>),  $\delta^*$  108.9 (rel area 2, F<sup>b</sup>),  $\delta^*$  117.0 (rel area 2, F<sup>c</sup>) and  $\delta^*$  148.1 ppm (rel area 4, BF<sub>4</sub><sup>-</sup>). These values are in reasonable agreement with the analogous phosphonium and ammonium analogs. Thus, the behavior of 2 is identical to the phosphorus and nitrogen ylides in these reactions.



Scheme 1

However, the halogenation of 2 exhibits a radically different mode of behavior compared to the analogous phosphonium ylides [2]. Whereas the phosphonium ylides are readily cleaved to give F-dihaloalkanes [2] or F-dihalocycloalkanes [4], 2 reacts with bromine or iodine to give the 1-halo-F-cyclobutenes 6 and 7 as illustrated in Scheme 2. The yield of compounds 6 and 7 were determined via  $^{19}\text{F}$  NMR vs.  $\text{PhCF}_3$  as an internal standard. 6 and 7 were identified by comparison of their GLPC retention times and  $^{19}\text{F}$  NMR spectra to authentic samples prepared in this laboratory by an alternate method. The butyl bromide is believed to be formed by decomposition of  $\text{Bu}_3\text{AsFBr}$ , since a control reaction of  $\text{Bu}_3\text{As}$  and  $\text{Br}_2$  gave a quantitative yield of  $\text{BuBr}$  after five minutes. The mechanism of this cleavage reaction is unclear at this time.

These results illustrate that some caution should be used in extrapolating the results of the F-phosphonium ylides to other F-ylides. The onium center in the ylide obviously plays an important role in the fate of the cleavage reaction intermediate. Work continues in our laboratory to assess the role of the onium center in a variety of cleavage processes and to explore these unusual and interesting carbanions.



Scheme 2

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- 3 D.J. Burton, R.D. Howells and P.D. Vander Valk, J. Amer. Chem. Soc., 99 (1977) 4830.
- 4 Unpublished work of P.D. Vander Valk.