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OXYPHOSPHIRANE INTERMEDIATES IN THE ELECTROCHEMICAL REDUCTION OF α,α'-DIHALOPHOSPHINATES

Albert J. Fry* and Ling-Ling Chung
Hall-Atwater Laboratory of Chemistry, Wesleyan University
Middletown, Connecticut 06457

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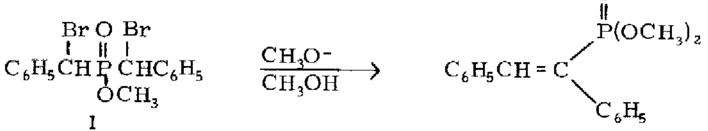
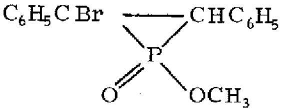
Burns, Capozzi, and Haake[1] found that methyl α,α'-dibromodibenzylphosphinate (1) reacts with sodium methoxide in the manner shown in equation 1, and they pointed out the fact that the reaction



1

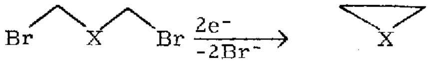
(1)

can best be understood as involving an oxyphosphirane (2). We have been interested



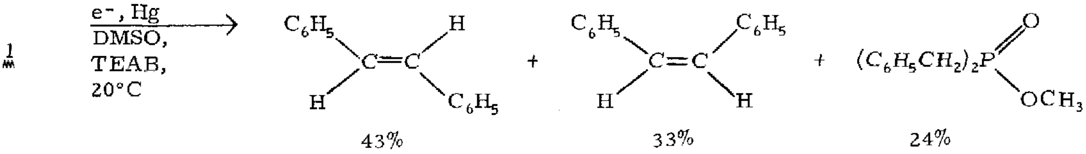
2

in the electrochemical reductive cyclization of 1,3-dibromides, i.e.,

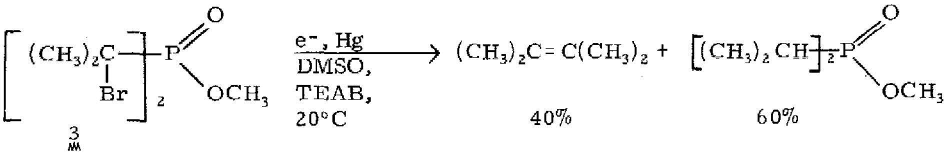


and have reported the results of our investigations for the cases where X= CH$_2$[2] and C=O[3]. It is clear that such cyclizations often proceed very efficiently.[2-4] Furthermore, although the study by Haake, et al.,[1] had shown that compounds such as 2 are labile to base, the electrochemical reduction of halides can be affected under aprotic conditions,[5] hence we were encouraged to examine the electrochemical behavior of α,α'-dihalophosphinates as a possible synthetic route to oxyphosphiranes (5). Our results indicate that such species are indeed so formed, but are labile under the conditions of our experiments.

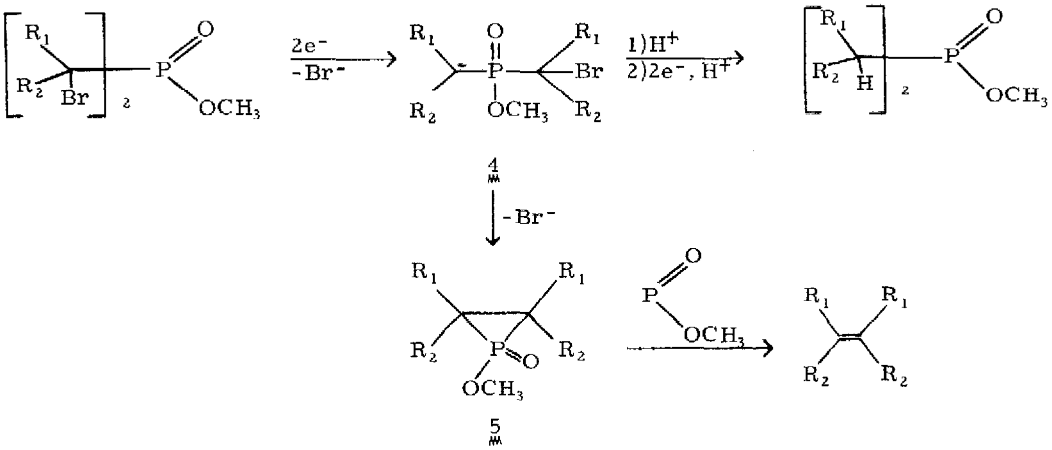
The reaction between N-bromosuccinimide and methyl dibenzylphosphinate in chloroform afforded a mixture of mono-, di-, and tribromides, from which **1** (a mixture of diastereomers) could be separated by column chromatography over silica gel;[1] pure meso-**1** could be obtained from the dibromide mixture by taking advantage of its lower solubility in ether.[6] Meso-**1** and methyl α,α'-dibromodiisopropylphosphinate[7] (**3**) each exhibited a single polarographic wave in dimethylsulfoxide (DMSO) containing 0.1M tetraethylammonium bromide (TEAB)(**1** : 0.0V ; **3** : -0.8V ; potentials are relative to Ag/AgBr). Under these conditions methyl dibenzylphosphinate is not reduced before -2.0V. Controlled-potential coulometric reduction of **1** at a mercury pool resulted in the consumption of 2.1 ± 0.2 electrons/molecule of dibromide. Extraction of the solution from electrolysis of meso-**1** with pentane afforded in good yield a mixture of cis- and trans-stilbene and methyl dibenzylphosphinate i.e.,



A similar result was obtained upon electrochemical reduction of **3**:



We believe that the products can be rationalized in terms of a common intermediate, bromoanion **4**. Protonation



of **4** by adventitious water or by a Hoffmann elimination upon TEAB[8], followed by further reduction, would afford the simple dehalogenated phosphinate. On the other hand, ejection of bromide from **4** would lead to oxyphosphirane **5**, and final thermal decomposition of **5** to alkene would not be unreasonable by analogy to the known thermal instability of, e.g., episulfones.[9] Denney has in fact observed decomposition at-78°C of pentacoordinate phosphorus contained in a three-membered ring.[10] Evidence that **4** lies on the pathway to alkene formation was obtained by electrolysis of **1** in acetonitrile containing 0.1M water,[11] whereupon the relative yields of stilbenes and methyl dibenzylphosphinate became 1:56, as opposed to 3:1 in DMSO; presumably protonation of **4** by water is more efficient in acetonitrile.[12]

The fate of the other (presumed) product from decomposition of **5**, i.e., $P(=O)OCH_3$, remains unknown; no water-insoluble phosphorus-containing materials (other than methyl dialkylphosphinate) are formed in the reaction, but this intermediate might easily be expected to be very reactive toward DMSO, to produce ionic, water-soluble products. Nucleophilic addition to the phosphorus atom in **5** by either dimethylsulfoxide or bromide ion, followed by decomposition of the resulting adduct, would constitute an alternate route to olefin obviating the need to postulate $P(O)OCH_3$ as an intermediate. This species has recently been invoked as an intermediate in base-promoted reactions of methyl phosphinate.[13]

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