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YLID INTERMEDIATES IN THE REDUCTION OF PHOSPHONIUM IONS

Arthur W. Herriott
Department of Chemistry, State University of New York at Albany
Albany, New York 12203

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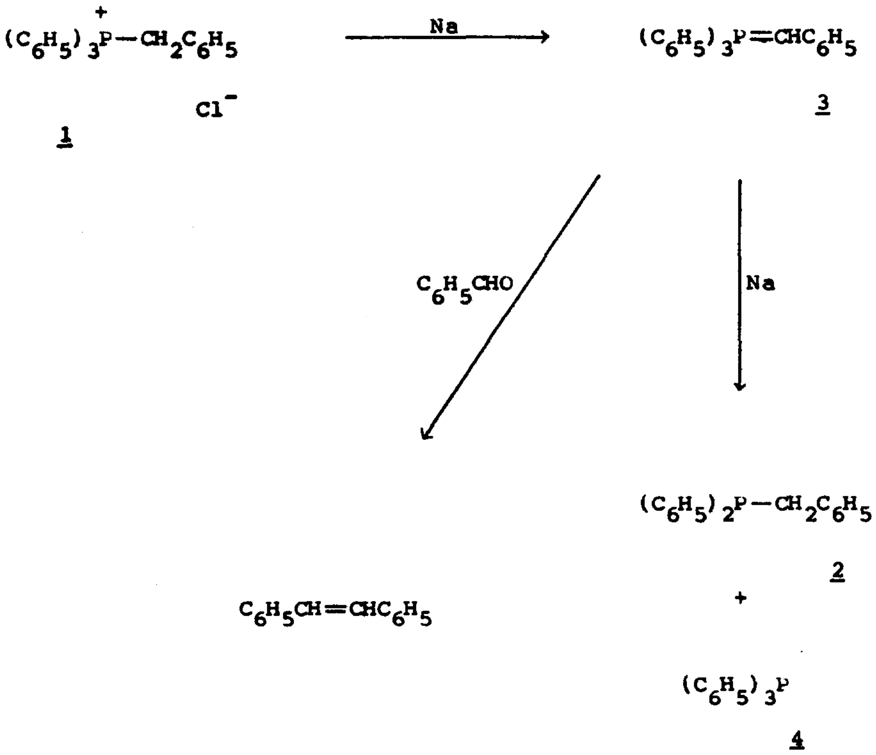
The cleavage of a carbon-phosphorus bond in phosphonium ions usually results in expulsion of the most stable anion or radical. Thus the reaction of benzyltriphenylphosphonium salts with hydroxide ion[1], halide ion[2], hydride ion[3], ultraviolet light[4], or cathodic electrons[5] is reported to give selective removal of the benzyl group in each case. In distinct contrast is the report of Horner, Beck, and Hoffmann[6] that reduction of benzyltriphenylphosphonium chloride 1 with sodium produced benzyldiphenylphosphine 2 in 53% yield. Since we had need of 2 for other work, we have briefly examined the mode of this reduction.

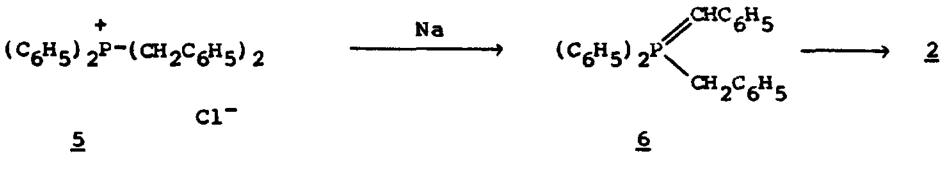
The unusual preference for phenyl cleavage would be explicable if the species reduced is not the phosphonium ion itself, but the ylid derived by prior removal of an acidic benzylic hydrogen.[7] Reduction of the benzylidenephosphorane 3 would be expected to eject a phenyl radical rather than phenyl carbene.[8] The intermediacy of 3 is confirmed by the observations reported herein.

When the reduction of 1 was carried out with molten sodium in refluxing toluene under the conditions of Horner et al,[6] the reaction mixture quickly became dark. In contrast, if reaction temperature was held at 70°, the characteristic red color of 3 appeared rapidly and persisted after 24 hours in the presence of excess sodium; manometric monitoring indicated evolution of 0.5 equivalent of hydrogen. Quenching of an aliquot with benzaldehyde produced cis and trans stilbene in a ratio of 1:2 in 75% yield along with triphenylphosphine oxide; only a trace of benzyldiphenylphosphine was present. When the remaining solution was heated at 100° for 12 hours and worked up with saturated ammonium chloride solution, benzyldiphenylphosphine and triphenylphosphine were obtained in an average ratio of 85:15 along with small amounts of triphenylphosphine oxide and benzyldiphenylphosphine oxide.[9] The relative amounts of phenyl and benzyl cleavage were confirmed in a separate experiment using p-xylene as solvent; benzene and toluene were produced in a ratio of 4:1.[10]

Two additional experiments further established the intermediacy of the ylid. Treatment of 1 with 1.1 equivalents of sodium hydride in toluene generated 3 by an alternate route under similar conditions of solvent and by-products; when this solution was treated with sodium at 100°, phosphines 2 and 4 were obtained in relative yields of 9:1. And reduction of dibenzyldiphenylphosphonium chloride, 5, with sodium in toluene produced only the monobenzylphosphine 2 with no trace of dibenzylphenylphosphine and $<1\%$ of 4. The intermediate in the reduction of 5 is ylid 6, from which a benzyl group is cleaved in complete preference to a phenyl group.

These results demonstrate that ylids are intermediates in the reduction of benzyl phenyl phosphonium salts. The original problem of an apparent preference of phenyl over benzyl cleavage thus appears to be resolved. It is interesting to note, however, that Horner and Neumann have recently reported only phenyl cleavage in the cathodic reduction of dibenzylphenylphosphine oxide, although the yield was low (5%).[11] Ylid intermediates are unlikely in this new reaction and thus a new question of phenyl vs. benzyl cleavage awaits an explanation.


$(C_6H_5)_3\overset{+}{P}-CH_2C_6H_5$ Cl^-
1
Na
$(C_6H_5)_3P=CHC_6H_5$
3
C_6H_5CHO
Na
$C_6H_5CH=CHC_6H_5$
$(C_6H_5)_2P-CH_2C_6H_5$
2
+
$(C_6H_5)_3P$
4


$(C_6H_5)_2\overset{+}{P}-(CH_2C_6H_5)_2$ Cl^-
5
Na
$(C_6H_5)_2P(=CHC_6H_5)CH_2C_6H_5$
6
2

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8. Reduction of ylids with $LiAlH_4$ takes a different course from that of the corresponding phosphonium salt, ref. 3.
9. Analysis was by gas chromatography on a 4-ft. silicone nitrile column at 250°. The yield of *2* relative to *4* varied from 70-95% in several runs; the cause of this variation was not explored.
10. Small amounts (<2%) of biphenyl were also produced.
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