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Synthesis and Anomalous Reactivity of 5-Bromo-3,5- Di-t-Butyl-2-Phenyl-1,2-Oxaphosphol-3-Ene 2-Oxide and its 4-Bromo Analog

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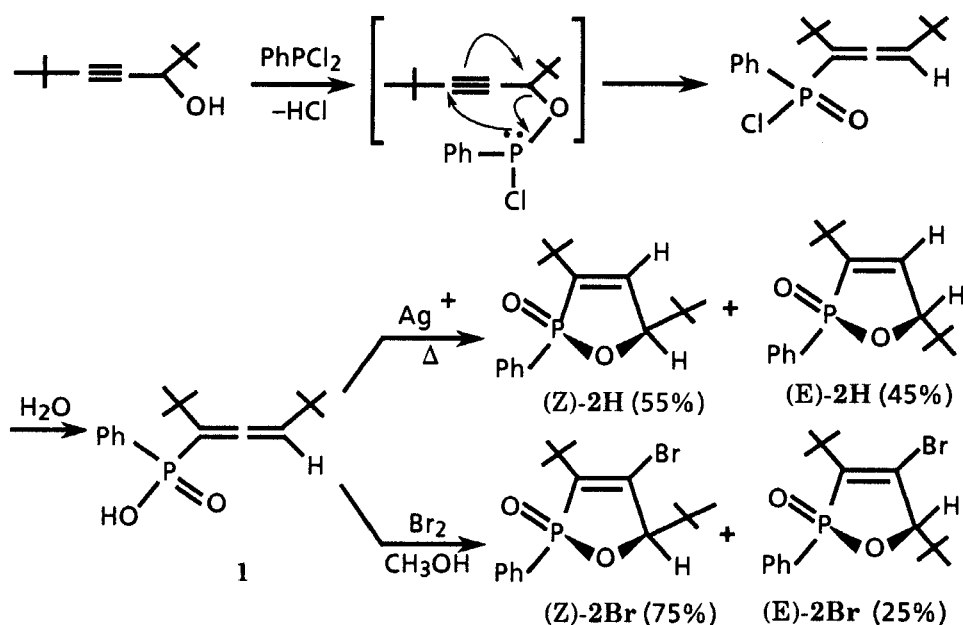
SYNTHESIS AND ANOMALOUS REACTIVITY OF 5-BROMO-3,5-DI-*t*-BUTYL-2-PHENYL-1,2-OXAPHOSPHOL-3-ENE 2-OXIDE AND ITS 4-BROMO ANALOG

Roger S. Macomber*, Daniel E. Rardon, and Douglas M. Ho

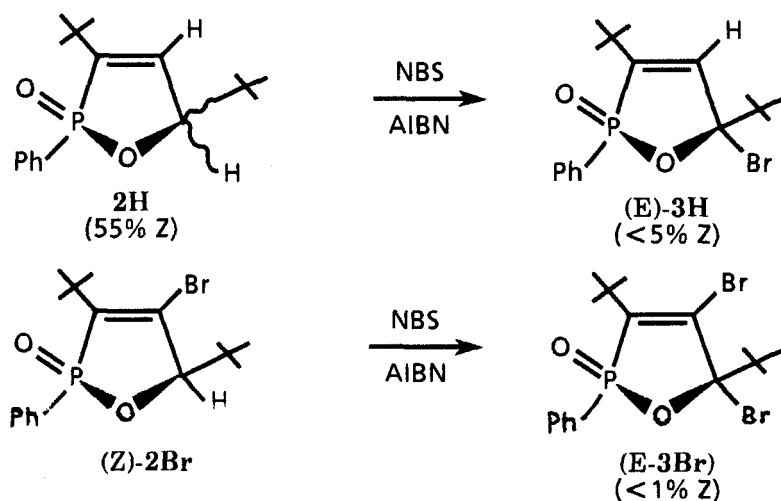
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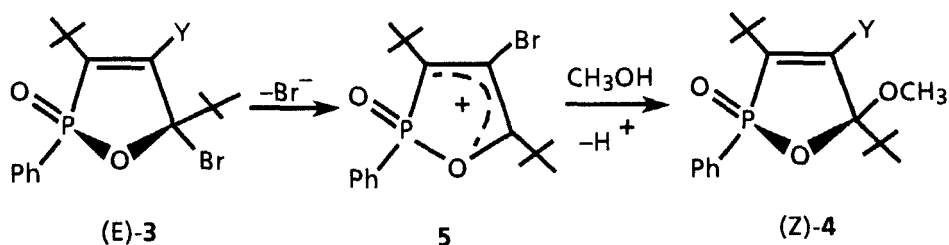
Reaction of 2,2,6,6-tetramethyl-4-heptyn-3-ol with dichlorophenylphosphine leads to 2,2,6,6-tetramethyl-3,4-heptadien-3-yl phenyl phosphinic acid (1), which undergoes Ag^+ -catalyzed cyclization to 3,5-di-*t*-butyl-2-phenyl-1,2-oxaphosphol-3-ene 2-oxide (2H, 75-55% Z, 25-45% E). Electrophilic bromination of 1 affords 2Br, the 4-bromo derivative of 2H, as a 75% Z, 25% E diastereomer mixture from which pure (Z)-2Br can be isolated.



Free radical allylic bromination of (Z/E)-2H and (Z)-2Br leads to the corresponding 5-bromo derivatives 3H and 3Br, each as a single diastereomer. X-ray analysis proved that 3Br has the E configuration, which is therefore also assigned to 3H. All other diastereomeric configurations were assigned on the basis of ^1H NMR.



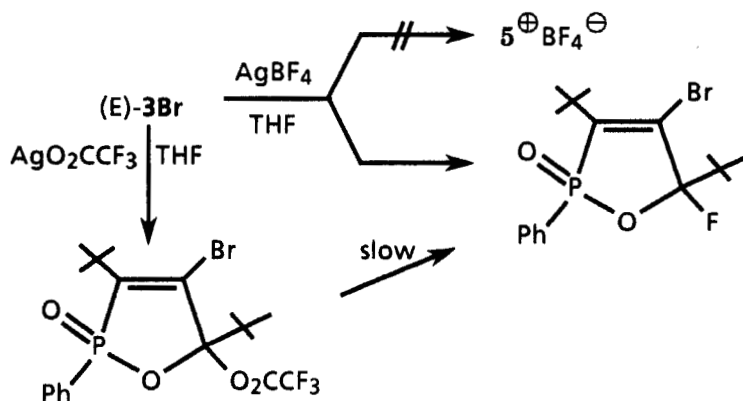
Allylic bromide (E)-3H is at least 1700 times more reactive than (E)-3Br toward methanolysis, though both yield the corresponding 5-methoxy derivatives (4H and 4Br) with predominant inversion of configuration. This is attributed to hydrogen bonding between the phosphoryl oxygen and the attacking methanol molecule.



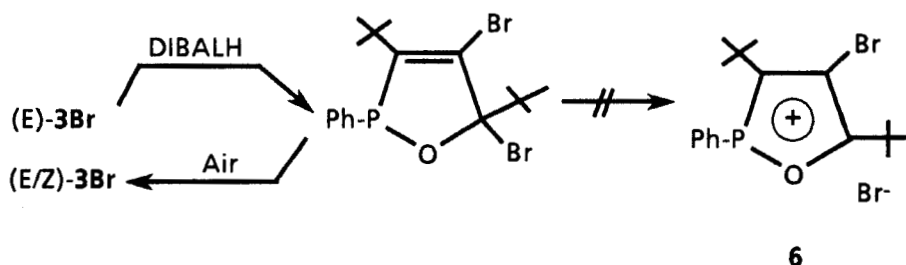
The retardation of (E)-3Br relative to (E)-3H is ascribed to steric interference between the C_4 bromine and the C_5 t-butyl group in the

(potentially anti-aromatic) methanolysis intermediate (5), an effect which is supported by a low-temperature ^1H NMR study of E-3Br.

Reaction of (E)-3Br with AgBF_4 or AgOTFA in THF gives the 5-fluoro and 5-trifluoroacetoxy derivatives, respectively, further indication of the instability of 5.

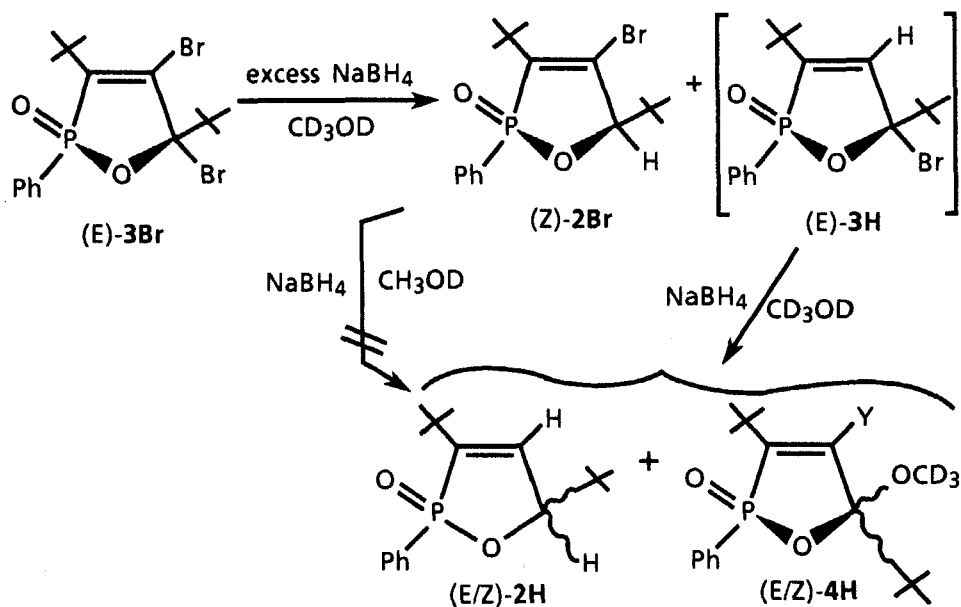


^{31}P NMR indicates that the phosphoryl oxygen in (E)-3Br can be reductively eliminated by DIBALH, but the resulting product is quickly re-oxidized to (E/Z)-3Br by air, rather than ionize to form potentially heteroaromatic ion 6. Reaction of (E)-3Br with NaBH_4 results in reductive



cleavage of the C_4 -bromine as well as the C_5 bromine, leading to the formation of (E/Z)-2H, (Z)-2Br, and (E/Z)-4H. (Z)-2Br is inert under these conditions.

Extended Huckel calculations are in agreement with the stereochemical preferences observed in this work, as well as the solvolysis-rate-retarding



effect of the phosphoryl oxygen. In view of the dramatic solvolysis rate reduction caused by the 4-bromo group in (E)-3Br, the previously noted (Rardon, D.; Macomber, R.S. *J. Org. Chem.* 1990, 55, 1493) high solvolytic reactivity of 7, the 2-hydroxy analog of 3Br, is ascribed to a mechanism involving reversible opening of the 5-membered ring.

