

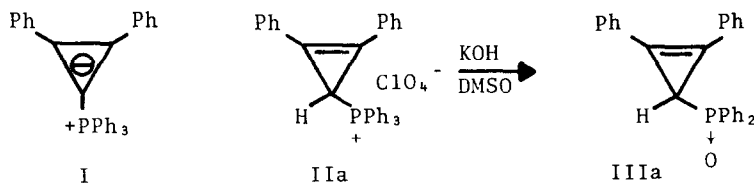
BASE-CATALYZED DECOMPOSITION OF CYCLOPROPENYLPHOSPHONIUM HYDROXIDES

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The concept of antiaromaticity was introduced by Breslow (2) to account for the extraordinarily slower rates of hydrogen-deuterium exchange in cyclopropene derivatives having hydrogen activating groups in the 3-position compared with model cyclopropyl systems. Although these kinetic results infer instability of the cyclopropenyl anion relative to the cyclopropyl anion, supporting data of a more thermodynamic nature is desirable. We now report initial results from a study of the decomposition of some cyclopropenylphosphonium hydroxides which, although kinetic in nature, nevertheless permit the establishment of upper and lower limits to the pKa's of triphenyl- and diphenylcyclopropene.

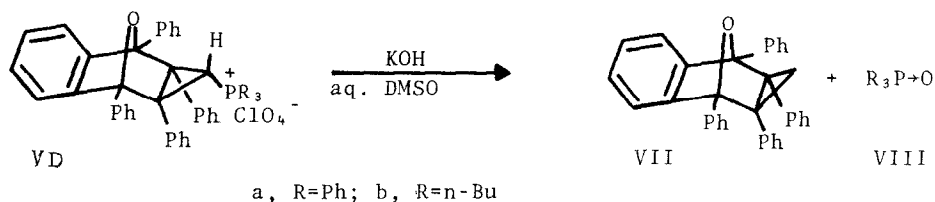
In the attempt to generate the ylid diphenylcyclopropenyliidetriphenylphosphorane (I), a potentially useful intermediate in methylenecyclopropene synthesis, (3) treatment of the phosphonium salt IIa with sodium amide in dimethylsulfoxide (DMSO) followed by aqueous workup afforded cyclopropenylphosphine oxide IIIa in high yield. In order to test whether this product was arising by base-catalyzed decomposition of the corresponding phosphonium hydroxide formed during workup, IIa was hydrolyzed in aqueous DMSO containing potassium hydroxide



to give IIIa in almost quantitative yield. This result appeared to be particularly significant in light of an earlier report of the hydrolysis of cycloheptatrienyltriphenylphosphonium fluoroborate (repeated by us in aqueous DMSO) to give triphenylphosphine oxide and cycloheptatriene, the latter postulated to result from protonation of the antiaromatic cycloheptatrienyl anion. (4)

Since it has been convincingly demonstrated by McEwen and other workers (5) that the most stable anion is preferentially cleaved from phosphorus in base-catalyzed decomposition of quaternary phosphonium hydroxides, the above results suggested a convenient approach for the experimental estimation of the pKa's of diphenyl- and triphenylcyclopropene. Table I summarizes the cleavage products resulting from hydrolysis of a selected series of diphenyl- and triphenylcyclopropenyl phosphonium salts under basic conditions (aqueous DMSO-potassium hydroxide). Cleavage of the diphenylcyclopropenyl salts IIa, IIb and IIc resulted in nearly exclusive formation of benzene and the corresponding cyclopropenylphosphine oxide, IIIa, IIIb and IIIc. On the other hand, hydrolysis of IIc yielded tri-n-butylphosphine oxide (Vc) as the only isolable product from this reaction. The expected hydrocarbon product 1,2-diphenylcyclopropene (IV; R=H) could not be isolated; however, this is not surprising in view of the failure of previous attempts (6) to prepare this as yet unknown and apparently quite reactive disubstituted cyclopropene.

For comparison purposes the cyclopropylphosphonium salts VIa and VIb were prepared by the Diels-Alder reaction of 1,3-diphenylisobenzofuran with IIa and IIc, (7) respectively, and hydrolyzed under identical conditions to those in Table I. Cyclopropane VII and the corresponding phosphine oxides VIIIa and VIIIb



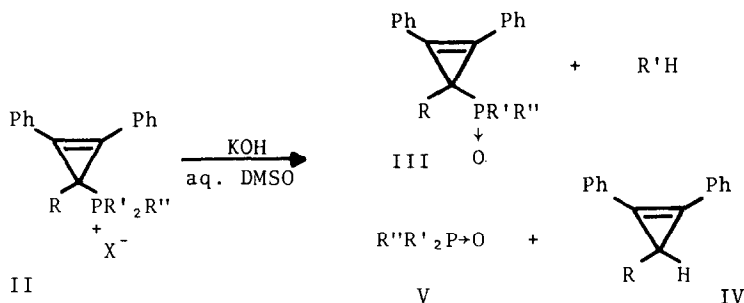


Table I

Cleavage Products in 80-85% Aqueous DMSO ^a

Phosphonium Salt ^b	III	IV	V
IIa R=H; R'=R''=Ph	95	--	--
IIb R=H; R'=Ph; R''=Me	86	--	--
IIc R=H; R'=R''= <u>n</u> -Bu	--	--	89
IIid R=H; R'=Ph; R''=diphenylcyclopropenyl	44	--	trace
IIe R=Ph; R'=Ph; R''=Me	--	80	78
IIf R=Ph; R'=Me; R''=Ph	--	75	50
IIg R=Ph; R'=R''= <u>n</u> -Bu	--	68	58
IIh R=Ph; R'=R''=Ph	--	-- ^d	--

^a The concentration of base, potassium hydroxide, varied in the range 0.14-0.21 M.

^b In all cases when R is H, X is perchlorate; when R is phenyl, X is bromide. Salt concentrations varied from 0.05-0.12 M. ^c Isolated yields ^d The only products obtained were those from hydrolysis of the triphenylcyclopropenyl cation apparently formed from dissociation of the phosphonium salt.

were the only detectable products.

Examination of the products from the hydrolysis of the triphenylcyclopropenylphosphonium salts IIe-g establish a high preference for, if not exclusive, cleavage of the cyclopropenyl carbon-phosphorus bond. Taking the pK_a of benzene to be 37 ⁽⁸⁾ then the pK_a of triphenylcyclopropene can certainly be fixed at less than 37.

From tritium exchange experiments with triphenylmethane and triphenylcyclopropene, Breslow and Dowd ⁽⁹⁾ concluded that the pK_a of triphenylcyclopropene was greater than 33, the value for triphenylmethane. The present results therefore establish an upper limit to this pK_a and place it in the range 33-37. Not surprisingly the diphenylcyclopropenyl anion is found to be less stable, the pK_a of

its conjugate acid, diphenylcyclopropene, being fixed at somewhat greater than 37 but less than 44, the estimated pKa of n-butane. (8) A more quantitative extension of this work to these and other cyclopropenylphosphonium salts is planned in the hopes of obtaining precise estimates of the pKa's of cyclopropene hydrocarbons.

Preparation of the phosphonium salts IIa-c and IIe-h was accomplished by addition of the appropriate phosphine to a slurry of the corresponding cyclopropenyl cation in methylene chloride or benzene. (10) The bis(diphenylcyclopropenyl)phosphonium salt II d was prepared by addition of a tetrahydrofuran solution of lithium diphenylphosphide, prepared from chlorodiphenylphosphine, to a slurry of diphenylcyclopropenyl perchlorate in the same solvent. The structures of these salts and other new compounds prepared in this work were established by elemental analysis and the usual spectral data including mass, ir, uv and nmr. (11)

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References

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(b) National Science Foundation Cooperative Predoctoral Fellow, 1965-1968.
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7. The *exo*-stereochemistry of these adducts is based on analogy to proven structures of adducts of 1,3-diphenylisobenzfuran with cyclopropene and its simpler derivatives (unpublished results, C. T. Sprouse, Jr.).
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10. Two of these phosphonium salts, IIa and IIc, have been recently reported by D. T. Longone and E. S. Alexander, [*Tetrahedron Letters*, 5815 (1968)].
11. Presentation of the nmr results including a discussion of geminal PCH coupling constants will appear in a forthcoming publication.