

Figure 1. Interaction diagram between the exocyclic π orbital and a high lying σ orbital to visualize the distortion of the resulting linear combination.

diagram plots of the calculated electrostatic potential fields (EPF).¹² The plot for **3a** is seen to display an intensely positive region above and below the benzene ring, while those for **1** and **2** reflect the absence of meaningful long-range electrostatic interaction. Accordingly, the transition states for uniparticulate electrophilic additions¹³ and for those biparticulate electrophilic processes where closely trailing δ^- fragments are involved can be expected to receive added stabilization when the attacking reagent is positioned above the electron-deficient benzenoid portions of **3a** and **3b**. The transition states which develop during syn attack by *N*-methyltriazolinedione⁹ and *N*-bromosuccinimide (**6**)¹⁴ are representative of our thinking. Since peracid oxidations do not proceed by way of similar charge-separated activated complexes,¹⁰ they are not similarly affected. The stereoselectivity of $^{18}\text{O}_2$ attack is essentially identical with that of the first two of these model reactions and, therefore, the intervention of transition states such as **7** is inferred.

A third factor may come into play if the π electrons of the exocyclic double bond experience partial rehybridization as they come under the influence of the electrostatic field provided by the approaching electrophile. Stabilizing bishomoconjugative interaction can develop when the benzene ring is unsubstituted or endowed with electron-donating groups, and favor anti attack. This effect would be negated by the presence of electron-withdrawing aryl substituents, as solvolytic studies on *anti*-7-benzonorbornenyl sulfonates have so convincingly demonstrated.¹⁵

Whatever the situation, the singlet oxygenations of the 7-isopropylidenenorbornenes are not proceeding under frontier orbital control, the customarily low activation energy of $^{18}\text{O}_2$ ene reactions¹⁶ notwithstanding, nor is the HOMO ($\pi_s - \pi_{ex}$) responsible for the NBS and urazole reactions. This conclusion is supported by the finding that **1** and **2** give nearly identical syn/anti ratios despite the existing differences in the nature of their HOMO's.

To the extent that the electrophile-stereoselectivity profiles employed herein provide valid model comparisons, the intervention of peroxide-like transition states are directly implicated.

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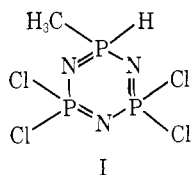
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Hydridocyclophosphazenes. Synthesis via Organocopper Reagents

Sir:

The reactions of organometallic reagents with cyclic phosphazenes, $(\text{NPX}_2)_{3\text{or}4}$ ($\text{X} = \text{Cl}$ or F) normally yield partially alkylated or arylated cyclic phosphazenes and ring-opened species.¹⁻³ We report here the unusual reaction of methylmagnesium chloride with hexachlorocyclotriphosphazene, $(\text{NPCl}_2)_3$, in tetrahydrofuran in the presence of $(n\text{-Bu}_3\text{PCuI})_4$, which gave, after treatment with 2-propanol, high yields (76%) of an air- and moisture-sensitive crystalline product identified as I.

A typical experimental procedure was as follows. Hexachlorocyclotriphosphazene (5.0 g, 0.014 mol) and $(n\text{-Bu}_3\text{PCuI})_4$ (3.0 g, 0.0019 mol) were stirred together in tetrahydrofuran (150 mL) at 0°C , and MeMgCl (25 mL of a 3.0-mol solution in THF) was added dropwise over 30 min. After this



time the reaction mixture was allowed to warm slowly to 25 °C and was stirred for 16 h. The mixture was then cooled to 0 °C and (CH₃)₂CHOH (10 mL) was added carefully. After the evolution of gas had ceased, removal of the solvent in vacuo and sublimation of the residue (0.1 mmHg, 120 °C) gave I (3.2 g, 76%) as air- and moisture-sensitive white crystals.

The structure of I was established from the following data. The proton decoupled ³¹P NMR spectrum⁴ showed a simple AB₂ pattern with peaks at 18.6 ppm⁵ (a doublet with *J*_{PNP} = 12 Hz) and 12.1 ppm (a triplet with *J*_{PNP} = 12 Hz). The peak at 12.1 ppm was significantly larger than expected because of the nuclear Overhauser influence by the hydrogen atom bound to this phosphorus. In the proton-undecoupled ³¹P NMR spectrum, the peak at 12.1 ppm was split into a doublet (*J*_{PH} = 560–570 Hz). The ¹H NMR spectrum⁶ showed the methyl protons at 1.77 ppm (as a doublet, *J*_{PCH} = 16 Hz, of multiplets, *J*_{HPCH} = 3.4 Hz, *J*_{PNPCH} = 4 Hz). The hydride resonance appeared at 7.44 ppm (as a doublet, *J*_{PH} = 568 Hz, of triplets, *J*_{PNPH} = 11 Hz, of multiplets, *J*_{HCPH} = 3.4 Hz). The coupling constants were confirmed by ¹H homo-decoupled NMR experiments.

The infrared spectrum showed bands for the CH₃ group at 3000 (w) and 2910 (w), PH units at 2409 (m) and 2399 (m), and PN bonds at 1220 (s), 1180 (s) and 1160 (s) cm⁻¹. The mass spectrum showed a parent ion at *m/e* 291, with a characteristic Cl₄ isotope pattern. Correct microanalytical data were also obtained.⁷

The only other example of a hydridophosphazene was synthesized by Schmidpeter et al.^{8,9} by rearrangement of a proton from skeletal nitrogen during the condensation of a linear aryl-phosphorus-nitrogen species with a phosphine. Compound I is the first example of a hydridophosphazene formed as the result of the reaction of an organometallic reagent with a preformed cyclic phosphazene. It is also the only example of a cyclophosphazene with both halogen and hydrogen atoms as substituent groups. Thus, it is a valuable synthetic intermediate. For example, the reaction of I with chlorine in carbon tetrachloride led to the formation in high yields of N₃P₃Cl₅CH₃, a compound not readily available by other routes. The P–H bond also generates intriguing possibilities for insertion-type reactions.

The reactions of Grignard reagents with organic substrates in the presence of *catalytic* amounts of copper are well documented, and these reactions are thought to proceed via organocopper intermediates.¹⁰ However, in the reaction reported here, the yield of I *depended* on the copper concentration, and the maximum yield was obtained with copper:phosphazene ratios of ≥0.5:1. Vapor phase chromatography experiments showed that the concentration of (NPCl₂)₃ decreased in proportion to the amount of Grignard added, *but* I was not formed until 2-propanol was added to the mixture.

The 2-propanol was added initially as a Grignard deactivation agent. However, isotope-labeling studies using (CH₃)₂CHOD indicated that the alcohol was the source of the hydrogen atom bound to phosphorus in I. This suggests that I is generated via the intermediate formation of a metallophosphazene species where two phosphazene molecules are associated with one copper atom, and this possibility is being investigated.

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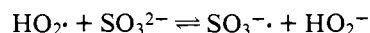
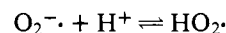
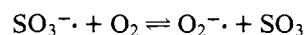
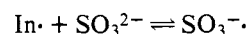
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Photochemical Generation of O₂⁻ by Rose Bengal and Ru(bpy)₃²⁺

Sir:

The photochemical formation of singlet oxygen from dye sensitizers^{1a} has been assumed since Foote and Wexler's^{1b} classic experiments reconfirmed Kautsky's original proposals. Yet there is another possibility when an excited dye, or other excited molecule, encounters molecular oxygen—namely electron transfer.² This latter reaction would produce superoxide and the radical cation from the sensitizer. We report our results regarding this latter possibility herein.

The aerobic oxygenation of sulfite is a sensitive detector of superoxide ion (O₂⁻).³ Superoxide enhances the autoxidation of sulfite, SO₃²⁻, according to the following mechanistic scheme:



In this scheme In· is an initiator. In now classic studies, SO₃²⁻ oxidation was used by Fridovich and Handler in a number of ways—to prove the one-electron reduction using xanthine oxidase,⁴ to demonstrate the inhibiting actions of carbonic anhydrase and myoglobin on the reduction of cytochrome *c* by xanthine oxidase,⁵ and to detect superoxide anion in illuminated dye solutions containing sulfite.^{6,7}

Recently several groups have become concerned with (a) the mechanism of singlet oxygen formation from certain dyes, in particular rose bengal, and (b) the role of superoxide (O₂⁻) in reactions attributed to singlet oxygen.⁸

To study the role that superoxide may play in sensitized photooxidation reactions, we have studied oxygen uptake, with a Clark oxygen electrode, of a solution of sulfite dyes, and the superoxide inhibiting enzyme, superoxide dismutase.

Dark solutions of sulfite and rose bengal were saturated with oxygen at 35 °C buffered at 7.8 pH with phosphate and the oxygen uptake measured. When a solution of sulfite and rose bengal was irradiated at 562 nm with a monochromator, the rate of sulfite oxidation increased severalfold over that of the oxidation in the dark for the same solution. According to the