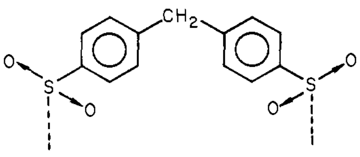
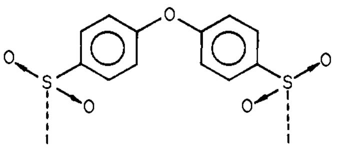
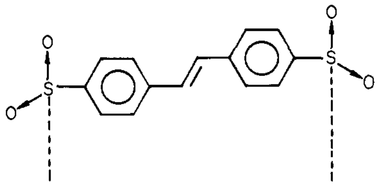
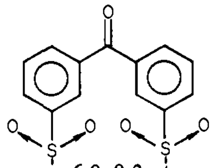
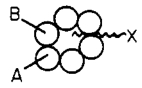
Table II. Estimated Distance (nm) between Two Reacting Sites of Some Capping Reagents

			
9.0–11.0 (9.7)[5]	8.6–11.4 (10.2)[5]	ca. 13.5	6.0, 8.3 9.8
near perpendicular, near coplanar conformation	do	planar	*Z*-oid, near perpendicular, *E*-oid

8 H); IR (KBr) 1650, 1180 cm^{-1}. A similar procedure gave **3a** in 20% yield.

These capped cyclodextrins were readily converted to the corresponding diiodo derivatives (AC and/or AD) by treatment with KI in DMF at 80–90 °C for 2 h;[7] these were further converted to dideoxy derivatives by treatment with $NaBH_4$. Spectral characteristics of the capped cyclodextrins and corresponding diiodo and dideoxy derivatives were satisfactory, but no appreciable difference has been observed between AC and AD isomers. Most characteristic is the ^{13}C NMR spectrum where the AC and AD isomers exhibit practically identical absorptions: 102.03 (C_1), 81.39 (C_4), strong peak centered at 72.11 (C_2, C_3, C_5), 59.87 (C_6 adjacent to hydroxyl), and 9.50 (C_6 adjacent to iodine) for the AC isomer and 101.91 (C_1), 81.39 (C_4), strong peak centered at 72.11 (C_2, C_3, C_5), 59.87 (C_6 adjacent to hydroxyl), and 9.50 (C_6 adjacent to iodine) for the AD isomer. The possibility of an AB isomer is easily excluded on the basis of ^{13}C NMR chemical shifts of the present capped cyclodextrins listed above which are slightly but appreciably different from that of the AB isomer expected from the α-A,B,X isomer, **7**.[8]

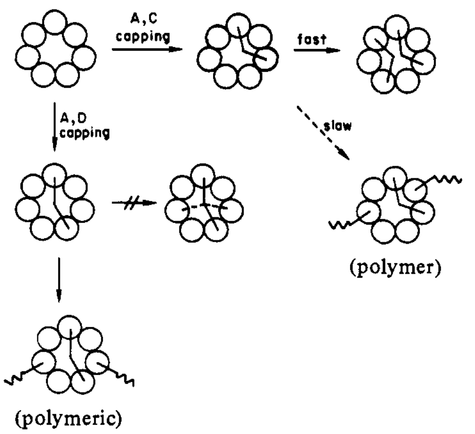


7

The A,C capping with **2b** was strongly supported by our results of formation of the doubly capped β-cyclodextrin with **2b**[9] in good yield (ca. 35% based on cyclodextrin used, which is very close to the yield of single A,C capping of 40%), since any double capping is not possible from a A,D capping reagent (Table I). Actually A,D capping reagent **2a**[10] leads to polymeric material almost exclusively, and double cap was obtained in less than 2.5% yield under the conditions of **2b** capping (Scheme II).

The presence of AC and AD isomers was first proved by Breslow[4] for C in Scheme I, the observed isomer ratio being dependent on the nature of the capping reagent (**2c** and **2d**). This structural dependence of regioselectivity, not remarkable for such similar capping reagents as **2c** and **2d**, is dramatically shown in the present examples. Judging from the CPK molecular model, the major determining factor of the present regiospecific AC and AD capping is concluded to be the "looper's walk" mechanism of the capping reaction, i.e., the first functionalization determines the site of the second functionalization at the "best fit" position, considering the distance between two reacting sites (see Table II), strain in a transition state, direction of approach of an entering group, etc. This mechanism seems to be generally applicable to regiospecific multifunctionalization of large molecules to afford models of enzymes or other biologically important molecules.

Scheme II



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(7) Polymeric materials, the (hydrolyzed) capping reagent, and monosulfonate–monosulfonic acid were removed through flash column chromatography, and the resultant crude capped cyclodextrin was converted to the corresponding diiodo derivative according to the procedure described.[6]

(8) Boger, J.; Brenner, D. G.; Knowles, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 7630.

(9) Double cap was obtained as a sharp round spot on TLC (silica gel, *n*-PrOH/H_2O/AcOEt/25% NH_3 = 5:3:2:1, R_f double cap 0.64, single cap 0.54, β-CD 0.18, polymeric 0; CH_3CN/H_2O = 5:1, R_f double cap 0.6, single cap 0.2, β-CD 0), and the ^1H NMR intensity of the corresponding pure tetradeoxy derivative ($NaBH_4$ reduction of the tetraiodide) was satisfactory. Impure compound was contaminated with benzophenone-3,3'-disulfonic acid ascertained by ^1H NMR of the cap, which was successfully eliminated by repeated reprecipitation with tetrachloroethylene. Electronic and IR spectra were also satisfactory. Details will be described in a forthcoming article.

(10) Structure of the A,D cap was ascertained by its photochemistry. Two well-separated peaks, P_1 and P_2, were observed for the *cis*-stilbene-4,4'-disulfonyl cap, where P_2 was identical with the cis cap, derived from the present *trans*-stilbene-4,4'-disulfonyl cap by irradiation in every respect. Since neither P_1 nor P_2 was an AB isomer, the present stilbene cap is concluded to have the AD structure.

Facile Degradation by Superoxide Ion of Carbon Tetrachloride, Chloroform, Methylene Chloride, and *p,p'*-DDT in Aprotic Media

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Although there is ample evidence that superoxide ion ($O_2^-\cdot$) is an effective nucleophile in aprotic sovlents,[1] studies have been limited to alkyl halides[2–5] and esters.[6–8] Kinetic studies confirm

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(1) Sawyer, D. T.; Gibian, M. J. *Tetrahedron* **1979**, *35*, 1471 and references therein.

(2) Merritt, M. V.; Sawyer, D. T. *J. Org. Chem.* **1970**, *35*, 2157.

(3) Dietz, R.; Forno, A. E. J.; Larcombe, B. E.; Peover, M. E. *J. Chem. Soc. B* **1970**, 816.

(4) San Fillipo, J., Jr.; Chern, C.-I.; Valentine, J. S. *J. Org. Chem.* **1975**, *40*, 1678.

(5) Johnson, R. A.; Nidy, E. G. *J. Org. Chem.* **1975**, *40*, 1680.

(6) San Fillipo, J., Jr.; Romano, L. J.; Chern, C.-I.; Valentine, J. S. *J. Org. Chem.* **1976**, *41*, 586.

(7) Magno, F.; Bontempelli, G. *J. Electroanal. Chem.* **1976**, *68*, 337.

(8) Gibian, M. J.; Sawyer, D. T.; Undermann, T.; Tangpoonpholvivat, R.; Morrison, M. M. *J. Am. Chem. Soc.* **1979**, *101*, 640.

0002-7863/81/1503-712$01.00/0

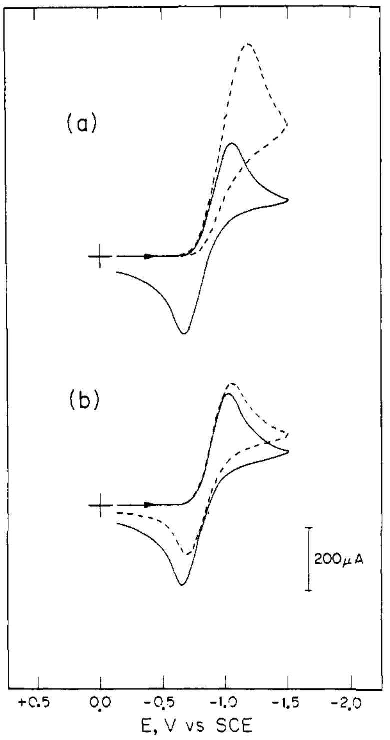

Figure 1. Cyclic voltammograms for the reduction of 4 mM O_2 (1 atm) in dimethylformamide (0.1 M tetraethylammonium perchlorate) at a platinum electrode (area, 0.23 cm^2) in the absence (—) as well as in the presence (- - -) of (a) 3 mM CCl_4 and (b) 3 mM CH_3Cl. The cathodic peak (upper) height from an initial negative scan at a rate of 0.1 V s^{-1} is proportional to O_2 concentration at the electrode surface. The anodic peak (lower) height that results from reversal of the scan direction is proportional to the $O_2^{-\cdot}$ concentration (produced by the reduction of O_2) that diffuses to the electrode surface during the life of the experiment. Saturated calomel electrode (SCE) vs. NHE, +0.244 V.

that the reactions are first order in substrate,[9,10] the rates follow the order primary > secondary ≫ tertiary for alkyl halides and tosylates[4,5] and I > Br > Cl,[3,4,10] and the attack by $O_2^{-\cdot}$ on alkyl halides results in an inversion of configuration.[4,5] Thus, the alkyl halide–$O_2^{-\cdot}$ reaction occurs via an S_N2 mechanism and yields dialkyl peroxide as an overall product.

We wish to report that CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl, and *p,p'*-DDT react rapidly with superoxide ion in dimethylformamide (DMF) and dimethyl sulfoxide (Me_2SO). The overall reactions for the chloromethane substrates are multistep processes that consume one or more $O_2^{-\cdot}$ ions per chloride to yield oxygenated products. An especially surprising result is that the relative rates of reaction for the primary rate-limiting step follow the order CCl_4 > $CHCl_3$ > *p,p'*-DDT > CH_3Cl > CH_2Cl_2. The second-order rate constants for reaction of CCl_4 and $CHCl_3$ with $O_2^{-\cdot}$ indicate that these are among the fastest displacement reactions yet reported for superoxide ion.

The solid curves of Figure 1 illustrate the cyclic voltammetric reduction of O_2 to $O_2^{-\cdot}$ and the reoxidation of the latter. The effect on the process of adding CCl_4 and CH_3Cl to the solutions is illustrated by the dashed curves of Figure 1. All alkyl halides exhibit the same general effect upon the $O_2/O_2^{-\cdot}$ electrochemistry. The reduction peak is enhanced, which implies an intermediate reaction step that generates O_2 from $O_2^{-\cdot}$, and the oxidation peak for the reverse scan (due to $O_2^{-\cdot}$) is diminished or absent. The latter indicates that $O_2^{-\cdot}$ is being removed by reaction with the substrates.

Table I. Stoichiometries and Kinetics for the Reaction of 0.1–4 mM $O_2^{-\cdot}$ with Polychloromethanes and *p,p'*-DDT in Dimethylformamide (0.1 M Tetraethylammonium Perchlorate) at 25 °C[a]

substrate (S), 0.1–5 mM	$O_2^{-\cdot}$ per S	Cl^- released per S	O_2 released per S	k_2, M^{-1} s^{-1}
CH_3Cl	1 ± 0.2	1 ± 0.1		80 ± 10
CH_2Cl_2	2 ± 0.4	2 ± 0.2	1.2 ± 0.3	9 ± 2
$CHCl_3$	4 ± 0.5	3 ± 0.2		460 ± 60
CCl_4	6 ± 0.5	4 ± 0.2	4.2 ± 0.3	1300 ± 200
p,p'-DDT	3 ± 0.5	2 ± 0.2		130 ± 20

[a] Overall reactions: (1) $CH_3Cl + O_2^{-\cdot} \rightarrow {}^1/_2CH_3O{-}OCH_3 + Cl^- + {}^1/_2O_2$; (2) $CH_2Cl_2 + 2O_2^{-\cdot} \rightarrow CH_2O + 2Cl^- + {}^3/_2O_2$; (3) $CHCl_3 + 4O_2^{-\cdot} \rightarrow HC(O)OO^- + 3Cl^- + {}^5/_2O_2$; (4) $CCl_4 + 6O_2^{-\cdot} \rightarrow CO_4^{2-} + 4Cl^- + 4O_2$; (5) *p,p'*-DDT + $3O_2^{-\cdot} \rightarrow$ products + $2Cl^- + {}^3/_2O_2$.

The overall reactant and product stoichiometries for the degradation of polychloro substrates by $O_2^{-\cdot}$ in DMF and Me_2SO are summarized in Table I.[11] Combination of CCl_4 with 6 equiv of $O_2^{-\cdot}$ in Me_2SO yields a product solution which, after dilution with water, can be titrated with aqueous HCl. The stoichiometry and titration curve are consistent with those for an authentic sample of Na_2CO_3 in the same medium. Because peroxides are known to oxygenate Me_2SO to dimethyl sulfone ($DMSO_2$),[12] a reasonable conclusion is that the overall product from the reaction of CCl_4 with excess $O_2^{-\cdot}$ is CO_4^{2-} and that it reacts with this solvent to yield the CO_3^{2-} which is determined by the HCl titration.

When $CHCl_3$ is combined with 4 equiv of $O_2^{-\cdot}$ in DMF, a basic product solution is obtained. Dilution with water and titration with HCl yield a titration curve with a stoichiometry (monoprotic) and an apparent pK_a (6.7) that are consistent with peroxyformate ion.[13] The acidified product solution oxidizes I^- to I_2, which is a further indication of a peroxide species.

On the basis of these experiments and the stoichiometries, overall reactions are proposed for the degradation of polychloro substrates (see Table I). The second-order rate constants for the reaction of $O_2^{-\cdot}$ with several polychloro substrates are summarized in Table I.[14]

The data for CH_3Cl in Table I are in accord with previous studies of the reactivity of $O_2^{-\cdot}$ with *n*-alkyl halides; the value of the rate constant (80 M^{-1} s^{-1}) is 25 times greater than the values for *n*-BuCl in Me_2SO.[2] Likewise, previous kinetic data for the reaction of $O_2^{-\cdot}$ with methylene bromide and related halides confirm the order of reactivity for CH_2Cl_2 and CH_3Cl in Table I (CH_3Br reacts 25 times faster than CH_2Br_2 with $O_2^{-\cdot}$).[10] This and the data for the other substrates in Table I are consistent with the conclusion that the primary step (first order in $O_2^{-\cdot}$ and first order in substrate) for all of the substrates is rate limiting.[15]

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(9) Magno, F.; Seeber, R.; Valcher, S. *J. Electroanal. Chem.* **1977**, *83*, 131.

(10) Danen. W. C.; Warner, R. J.; Arudi, R. L. *ACS Symp. Ser.* **1978**, *No. 69*, 244–257.

(11) These were determined for CCl_4 and $CHCl_3$ by incremental titration with substrate of a known amount of $O_2^{-\cdot}$ (~2 mM, prepared by controlled-potential coulometry). The residual $O_2^{-\cdot}$ concentration was determined by positive-scan voltammetry after each substrate addition and equilibration. The O_2 that results from the stoichiometric combination of substrate and $O_2^{-\cdot}$ in a sealed cell was determined by cyclic voltammetry. In Me_2SO, Cl^- was determined by anodic cyclic voltammetry at +0.95 V vs. SCE. The analysis for Cl^- was confirmed for CCl_4 and *p,p'*-DDT by titration with $AgNO_3$ after dilution of the reaction mixture with aqueous 0.02 M HNO_3. The stoichiometries for the substrates which react more slowly were determined by the addition of substrate to an excess of superoxide ion or by constant current coulometric titration with $O_2^{-\cdot}$.

(12) Goolsby, A. D.; Sawyer, D. T. *Anal. Chem.* **1968**, *40*, 83.

(13) The pK_a values for peroxycarboxylic acids typically are 3.2–3.5 units larger than the parent acid (formic in this case; pK_a = 3.6). See: Swern, D. "Organic Peroxides"; Wiley: New York, 1970; Vol. I, p 460.

(14) These were evaluated by adding the substrate to superoxide ion in a DMF solution and monitoring the rate of disappearance of $O_2^{-\cdot}$ with a rotating platinum disk electrode. At a control potential of −0.3 V vs. SCE, the current was directly proportional to the instantaneous concentration of $O_2^{-\cdot}$. The reaction rates for CCl_4 and $CHCl_3$ were measured under second-order conditions with an excess of superoxide ion present. Both substrates yield linear second-order plots for order-of-magnitude variations in $O_2^{-\cdot}$ and substrate concentrations. For the slower reactions of CH_2Cl_2 and CH_3Cl with $O_2^{-\cdot}$, the rates were measured under pseudo-first-order conditions by the use of an excess of substrate (the semilogarithmic plots are linear).

A subsidiary observation is that hydroxide ion (as 25% tetraethylammonium hydroxide in methanol) reacts rapidly with CCl_4 and $CHCl_3$ in aprotic solvents. For example, the reaction with CCl_4 is so rapid in Me_2SO that it can be titrated with a stoichiometry of 4 mol of OH^- per mol of CCl_4. The ultimate product presumably is CO_2, which probably cannot be further titrated to CO_3^{2-} in Me_2SO.

In the presence of a fourfold excess of OH^-, the rate of disappearance of $O_2^{-}\cdot$ by reaction with CCl_4 is measurably reduced. Analysis of the kinetics for such experiments indicates that the assumed second-order rate constant for the $OH^- + CCl_4$ reaction is 0.7 ± 0.3 of that for the $O_2^{-}\cdot + CCl_4$ reaction.

For the solution conditions of Table I, thiocyanate ion (SCN^-) does not react to a significant extent with CCl_4 in Me_2SO (second-order rate constant $<10^{-2}\ M^{-1}\ s^{-1}$). Hence, $O_2^{-}\cdot$ and OH^- appear to be unique, exceptionally strong nucleophiles with respect to their reactivity toward alkyl halides in aprotic media.

Although strong bases are known to eliminate HCl from $CHCl_3$ and *p,p′*-DDT via an S_N1cB mechanism to give dichlorocarbene and $(p\text{-}ClC_6H_4)_2C{=}CCl_2$,[16] there is not any evidence that such processes are competitive with the displacement reactions of Table I. However, the stoichiometry for the reaction of *p,p′*-DDT indicates that only two of the three alkylchloro atoms are removed. Hence, subsequent to the first step, there may be a dehydrohalogenation to give a chloro-substituted alkene. Such a product may have limited reactivity with $O_2^{-}\cdot$; for example, 1,1,2-trichloroethene (trichloroethylene) reacts extremely slowly.

That the rate constants for CCl_4 and $CHCl_3$ are much larger than that for CH_3Cl is surprising and in conflict with their extreme steric inhibition of an S_N2 process. Although a direct electron transfer is an attractive alternative mechanism (reaction 1), the

$$CCl_4 + O_2^{-}\cdot \rightarrow CCl_4^- + O_2 \tag{1}$$

redox potentials for CCl_4 ($E°'$, −1.3 V vs. SCE) and O_2 ($E°'$, −0.9 V vs. SCE) in DMF do not favor a rapid and complete reaction. However, formation of an adduct, $CCl_4(O_2^{-}\cdot)$, as a transition state prior to concerted intramolecular electron transfer, displacement of Cl^-, and formation of $CCl_3O_2\cdot$ would facilitate a rapid reaction and overcome the thermodynamic inhibition of reaction 1. Hence, reasonable and self-consistent initial reactions for the $O_2^{-}\cdot$–CCl_4 system in DMF are

$$CCl_4 + O_2^{-}\cdot \rightarrow [CCl_4(O_2^{-}\cdot)]_{tr} \rightarrow CCl_3O_2\cdot + Cl^- \tag{2}$$

$$CCl_3O_2\cdot + O_2^{-}\cdot \rightarrow CCl_3O_2^- + O_2 \tag{3}$$

These are followed by additional rapid displacement and reduction steps to give the overall reaction of Table I. Analogous mechanistic pathways are proposed for the other substrates. There is not any evidence that the C–H bond of $CHCl_3$ is broken or that aromatic chlorides (*p,p′*-DDT) are displaced within the time frame of our experiments (less than 1 h).

The exceptional reactivity of $O_2^{-}\cdot$ with polychloro hydrocarbons in aprotic solvents provides a convenient means to their degradation and detoxification. For example, a controlled-potential electrolysis cell with an air-saturated Me_2SO–tetraalkylammonium chloride electrolyte could be used to generate $O_2^{-}\cdot$, which would convert CCl_4 wastes (added to the cell) to CO_3^{2-} and Me_2SO_2.

Slater[17] has suggested that the hepatotoxicity of CCl_4 is due to a CCl_4-stimulated peroxidation of unsaturated fatty acids via the $Cl_3CO_2\cdot$ radical. Because this species is believed to be the primary product for the reaction of $O_2^{-}\cdot$ with CCl_4 in aprotic media (eq 2), similar chemistry may occur with in vivo generated $O_2^{-}\cdot$ and represent the mechanism of CCl_4 toxicity.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-7922040. We thank Professors R. C. Neuman, Jr., and T. R. Fukuto of this department for helpful discussions and for providing a sample of *p,p′*-DDT (T.R.F).

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[15] During the course of the kinetic measurements 10–20% of the $O_2^{-}\cdot$ decomposed. Presumably, this was due to residual water and impurities in the aprotic solvents (Burdick and Jackson "Distilled in Glass" grade). Water would produce OH^- and HO_2^- via the net reaction

$$2O_2^{-}\cdot + H_2O \rightarrow O_2 + HO_2^- + OH^-$$

However, these nucleophiles (OH^- and HO_2^-), at most, would be present at a tenfold lower concentration than $O_2^{-}\cdot$. Their contribution to the total reaction rate with CCl_4 would be less than 5% (less than the experimental error of the measurements).

[16] March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 342–343.

[17] Slater, T. F. *Ciba Found. Symp.* **1979**, *65*, 143–163.

Ferrocenyl-Stabilized Two-Coordinate Phosphorus Cations: Synthesis, Coordination Chemistry, and Mössbauer Spectroscopy

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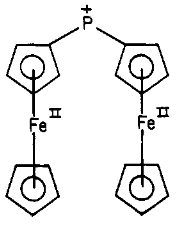
Halide abstraction from bis(dialkylamino)halophosphines with Lewis acids to form two-coordinate phosphorus cations (phosphenium ions) is well established,[1,2] but there are no unequivocal examples of phosphenium ions featuring two P–C bonds.[3] Since the remarkable ability of the ferrocenyl moiety (Fc) to stabilize carbenium ions is well documented,[6] it seemed appropriate to attempt the stabilization of phosphenium ions by using this substituent. The purpose of the present communication is to report the synthesis of $(Fc)_2P^+$ (**1**), the first example of a low-coordinate noncarbon main group cation stabilized by ferrocenyl groups. We also report initial results on the coordination chemistry of **1**.



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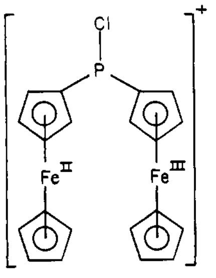

2

Treatment of Fc_2PCl[7] with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2 at −78 °C, followed by warming to room temperature, resulted in a deep red solution. The ^{31}P NMR spectrum of this

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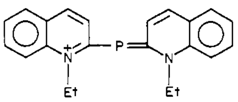
[1] (a) Maryanoff, B. E.; Hutchins, R. O. *J. Org. Chem.* **1972**, *37*, 3475–3480. (b) Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534–2540. (c) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Ibid.* **1977**, *16*, 994–1001.

[2] For a recent review, see: Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789–797.

[3] On treatment with acid, the phosphamethinecyanines are protonated at the phosphorus center;[4] thus the predominant resonance form must be, e.g.,



This viewpoint is confirmed by the fact that the ^{31}P NMR chemical shifts (~25–50 ppm) fall well outside the range observed for phosphenium ions.[2] Interestingly, even though Gamon and Reichardt[5] regard their phosphatrimethinecyanine as a predominantly P=C bonded species, in fact, the ^{31}P chemical shift (+355.8 ppm) is indicative of the presence of appreciable positive charge on phosphorus.

[4] Dimroth, K.; Hoffmann, P. *Chem. Ber.* **1966**, *99*, 1325–1331.

[5] Gamon, N.; Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 404–405.

[6] (a) Cais, M. *Organomet. Chem. Rev.* **1966**, *1*, 435–454. (b) Watts, W. E. *J. Organomet. Chem. Libr.* **1979**, *7*, 399. (c) Hill, E. A.; Wiesner, R. *J. Am. Chem. Soc.* **1969**, *91*, 509–510.

[7] Sollott, G. P.; Peterson, W. R. *J. Organomet. Chem.* **1969**, *19*, 143–159.

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