

downfield in the spectrum of II; this would be expected from the closer positions of oxygen in this structure compared to that of I as shown by inspection of molecular models. The same interpretation is used in the spectra of III and IV and the results are consistent with this type of reasoning.

The rate of reactivation of Sarin inhibited eel acetylcholinesterase at pH 7.4, 25°, in the presence of  $7.2 \times 10^{-3} M$  acetylcholine by *syn*-4-formyl-1-methylpyridinium iodide oxime, III, was reported previously<sup>7</sup> as 140 M.<sup>-1</sup> min.<sup>-1</sup> while that of the *anti* isomer, IV, was 56 M.<sup>-1</sup> min.<sup>-1</sup>. These results do not agree with the molecular complementarity theory advanced by Wilson which predicted that the *anti* isomer would be the more active reactivator.

(7) E. J. Poziomek, B. E. Hackley, Jr., and G. M. Steinberg, *J. Org. Chem.*, **23**, 714 (1958).

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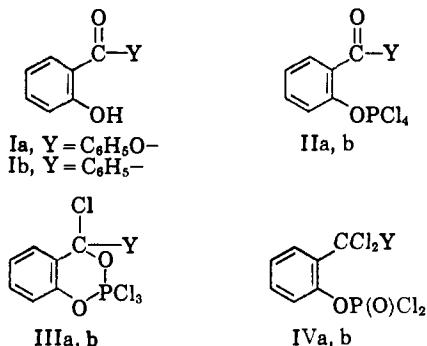
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#### AN UNUSUAL HETEROCYCLIC SYSTEM INVOLVING CHARGE SEPARATION AND HEXACOVALENT PHOSPHORUS

Sir:

In a previous study<sup>1</sup> of the product from the reaction of phenyl salicylate (Ia) and phosphorus pentachloride, the absence of an infrared carbonyl stretching band served to eliminate structure IIa originally proposed by Michaelis and Kerkhof.<sup>2</sup> Structure IIIa was preferred over IVa on the basis of the available evidence. Since structure IIIa can be considered to be formed by the covalent sharing



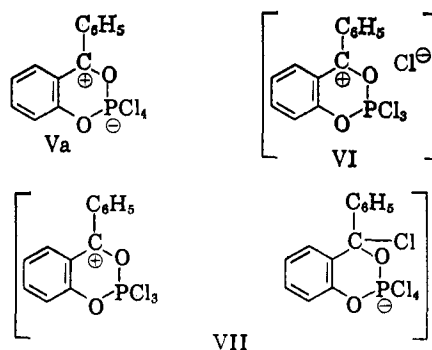
by phosphorus and oxygen of the  $\pi$  electron pair originally from the ester carbonyl group, it seemed that a more easily polarizable carbonyl such as that of a ketone would undergo a similar ring closure. Indeed, the infrared spectrum of the compound obtained from the reaction of *o*-hydroxybenzophenone (Ib) (practically quantitative yield) also showed no trace of a carbonyl stretching band. The product, which was very soluble in most common organic solvents, was recrystallized as colorless rods, m.p.

(1) A. G. Pinkus, P. G. Waldrep and P.-H. Ko, Abstracts, 132nd ACS Meeting, Chicago, Illinois, Sept. 7-12, 1958, p. 48-P.

(2) A. Michaelis and W. Kerkhof, *Ber.*, **31**, 2172 (1898).

65.4–66.2° from cyclohexane. *Anal.*<sup>3</sup> Calcd. for C<sub>13</sub>H<sub>9</sub>Cl<sub>4</sub>PO<sub>2</sub>: C, 42.20; H, 2.45; Cl, 38.33; mol. wt., 370.0. Found: C, 42.08; H, 2.62; Cl, 38.21; mol. wt.,<sup>4</sup> 372.8. The compound was remarkably resistant to hydrolysis in contrast to the extreme sensitivity to moisture of the 1:1 products of a variety of phenols and phosphorus pentachloride.<sup>6</sup> For example, when a solid<sup>5a</sup> sample of the compound was shaken for several minutes with water, the filtrate gave no precipitate with silver nitrate. The compound was completely hydrolyzed, however, back to *o*-hydroxybenzophenone (81% yield) by refluxing with aqueous sodium hydroxide.

The dipole moment of the compound was surprisingly high (9.17 D. at 30° in benzene)<sup>6</sup>—much higher than that estimated on the basis of IIIb or IVb. A structure in full accord with the high dipole moment and other experimental data is V which incorporates a novel type of intracyclic charge separation. The accurate molecular weight determination eliminates a simple ionization such as VI as an explanation. The conductance of a benzene solution was too low to be measured. Furthermore, appreciable ionization would not be expected in benzene, a non-ionizing solvent. In acetonitrile, a more favorable solvent for ionization, the conductance was of a low order of magnitude. For example, the equivalent conductivity of a 0.04913 M solution was 0.05374 ohm<sup>-1</sup> cm.<sup>2</sup>. This can be compared with a value of 30.0 ohm<sup>-1</sup> cm.<sup>2</sup> for a 0.0495 M solution of phosphorus pentachloride in acetonitrile<sup>7</sup> and 73.8 ohm<sup>-1</sup> cm.<sup>2</sup> for a 0.0570 M solution of triphenyl phosphite dichloride in acetonitrile.<sup>8</sup> The low conductivity excludes appreciable amounts of an ionic dimer (VII) type of structure which would not be excluded by the molecular weight determination.



The ultraviolet spectrum of the compound (cyclohexane) shows the absence of the low intensity long wave length band at 336 m $\mu$  present in the spectrum

(3) Carbon and hydrogen analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

(4) Cryoscopic in benzene.

(5) R. Anschütz and W. D. Emery, *Ann.*, **239**, 301 (1887); A. G. Pinkus and P. G. Waldrep, *J. Org. Chem.*, **24**, 1012 (1959).

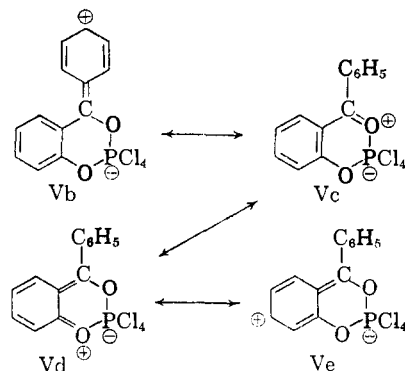
(5a) NOTE ADDED IN PROOF.—Solutions of the compound, however, hydrolyze at a faster rate; thus, all manipulations of solutions of the compound were carried out in a dry-box.

(6) A check determination on a known compound having a high dipole moment was made. The value obtained for *N*-benzylsydnone, 6.36 D., at 30° in benzene, checks closely with the value 6.27 D. at 25° in benzene reported by R. A. W. Hill and L. E. Sutton, *J. Chem. Soc.*, 746 (1949).

(7) D. S. Payne, *ibid.*, 1052 (1953).

(8) G. S. Harris and D. S. Payne, *ibid.*, 3038 (1956).

of *o*-hydroxybenzophenone which is due to an electronic transition involving the carbonyl group. The high solubility of the compound in organic solvents resembles similar solubility characteristics of some mesoionic compounds<sup>9</sup> which also have high dipole moments and involve a separation of charge within the five-membered ring. It should be pointed out, however, that compound V should not be classified as a mesoionic compound even though it cannot be represented by a wholly covalent structure. Although a sextet of electrons<sup>10</sup> is available, they are not associated with *all* of the atoms comprising the ring—notably the phosphorus. Thus, structure V is a novel system involving intracyclic charge separation. The remarkable stability of the compound is also explicable on the basis of structure V. At least twenty-two resonance hybrids can be written, of which five examples (Va–Ve) are shown



A molecular orbital picture would involve a delocalization of the positive charge from the trigonal carbon into the two benzene rings and the two oxygens. Further studies designed to elucidate the requirements for the unusual charge separation are in progress.

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(9) W. Baker and W. D. Ollis, *Quart. Revs.*, **11**, 15 (1957).

(10) Two from each oxygen and two from the benzo ring.

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#### ELECTRON SPIN RESONANCE STUDIES OF ELECTROLYTICALLY REDUCED TETRACYANOETHYLENE DERIVATIVES<sup>1</sup>

Sir:

We wish to report the investigation by electron spin resonance of the electrolytic reduction products of tetracyanoethylene, 1,1,2,2-tetracyanocyclopropane, and 1,1,2,2-tetracyanoethane. The anion radical of tetracyanoethylene dissolved in tetrahydrofuran was first studied by Phillips, Rowell and Weissman.<sup>2</sup>

(1) Supported in part by the U. S. Air Force through the Office of Scientific Research.

The electrolyses were performed in a cell with a platinum anode and a mercury-pool cathode. The solvent was *N,N*-dimethylformamide (DMF), acetonitrile, or mixtures of the two, and the supporting electrolyte was 0.1 *M* tetra-*n*-propylammonium perchlorate. The solvents were degassed carefully and most of the studies were made with solutions 5 mM. in reducible material. A Ag–AgClO<sub>4</sub> reference electrode, 0.1 *M* in AgClO<sub>4</sub>, was employed which, with DMF as solvent, has a potential about –0.5 v. with respect to the standard calomel electrode. The details of the electrolytic cell<sup>3</sup> and of the electron spin resonance spectrometer<sup>4</sup> are described elsewhere. Polarographic studies, both d.c. and a.c., also were made.<sup>5</sup> The oscillograms were performed at a number of frequencies in the range from 0.1 to 100 cps.

Tetracyanoethylene (TCNE) is reduced to the anion radical merely by dissolving it in DMF. The resulting solution is pale yellow. A potential of –0.2 v., corresponding to the half-wave potential, is required to reduce TCNE in acetonitrile, and the radical produced gives an e.s.r. spectrum identical with that observed from the DMF solution. Oscillograms in acetonitrile show that the reduction is reversible. TCNE in solvent mixtures of acetonitrile and DMF gives this same e.s.r. spectrum for mole fractions of acetonitrile less than 0.5 except that the intensity of the spectrum decreases and the line width increases as the amount of acetonitrile is increased. The increased line width undoubtedly arises from the exchange reaction between TCNE<sup>-</sup> and the unreduced TCNE. Passage of current in the DMF solution of TCNE increases the line width of the e.s.r. spectrum. This phenomenon has not been explained.

The half-wave potential of 1,1,2,2-tetracyanocyclopropane<sup>6</sup> (TCNP) in DMF is –1.4 v. Reduction at this potential gives a bright red-orange solution and bubbling is observed at the mercury-pool cathode. The e.s.r. spectrum obtained is identical with that found for TCNE<sup>-</sup> except that the TCNP solution yields a spectrum with narrower lines. A comparison of the optical absorption spectrum of TCNE<sup>-</sup> in DMF and the solution obtained by reduction of TCNP in DMF shows that the characteristic band ( $\lambda_{\max} = 4320 \text{ \AA}$ ) of TCNE<sup>-</sup> reported by Phillips, *et al.*,<sup>2</sup> is present in both solutions, and that the TCNP solution also contains additional bands. Oscillograms of TCNP in acetonitrile indicate that the reduction is irreversible, and they exhibit a strong oxidation wave at approximately –0.2 v. This is the half-wave potential of TCNE in acetonitrile. Small waves corresponding to other reduction products also are observed. Finally, when TCNP in acetonitrile is reduced completely by electrolysis, the resulting solution gives a strong oxidation wave at –0.2 v.

(2) W. D. Phillips, J. C. Rowell and S. I. Weissman, *J. Chem. Phys.*, **33**, 626 (1960)

(3) P. H. Rieger, I. Bernal and G. K. Fraenkel, to be published.

(4) J. M. Hirsion and G. K. Fraenkel, *Rev. Sci. Instr.*, **26**, 34 (1955); H. L. Strauss and G. K. Fraenkel, *J. Chem. Phys.*, in press.

(5) D. E. Smith and W. H. Reinmuth, *Anal. Chem.*, submitted for publication, and D. E. Smith, Thesis, Columbia University, New York, 1961.

(6) Made according to the procedure given by R. M. Schreiber, G. N. Saucen and W. W. Pritchard, *J. Org. Chem.*, **25**, 1440 (1960).