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[9] 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[10] 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
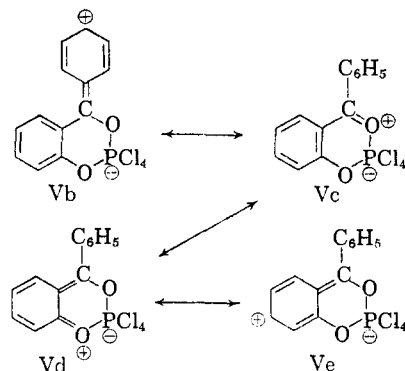
A molecular orbital picture would involve a delocalization of the positive charge from the trigonal carbon into the two benzene rings and the two oxygens. Further studies designed to elucidate the requirements for the unusual charge separation are in progress.

Acknowledgments.—The authors express appreciation to the Public Health Service, National Institutes of Health, for support of this work under Research Grant No. CY-3753 and acknowledge the help of Mr. C. G. Moseley in the synthesis of N-benzylsydnone and purification of acetonitrile.

(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[1]

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.[2]

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–AgClO₄ reference electrode, 0.1 M in AgClO₄, 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[3] and of the electron spin resonance spectrometer[4] are described elsewhere. Polarographic studies, both d.c. and a.c., also were made.[5] The oscillopolarograms 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. Oscillopolarograms 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⁻ 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[6] (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⁻ except that the TCNP solution yields a spectrum with narrower lines. A comparison of the optical absorption spectrum of TCNE⁻ in DMF and the solution obtained by reduction of TCNP in DMF shows that the characteristic band (λ_{max} = 4320 Å.) of TCNE⁻ reported by Phillips, et al.,[2] is present in both solutions, and that the TCNP solution also contains additional bands. Oscillopolarograms 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. Hirshon 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. Sancen and W. W. Pritchard, J. Org. Chem., 25, 1440 (1960).

$a^N = 1.574 \pm 0.005$ gauss
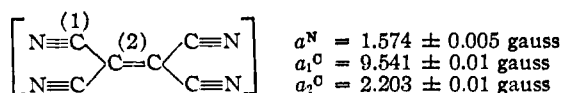$a_1{}^O = 9.541 \pm 0.01$ gauss
$a_2{}^O = 2.203 \pm 0.01$ gauss

Fig. 1.—Hyperfine splitting constants of TCNE⁻ in DMF and in acetonitrile. These results are independent of the parent compound used to generate the radical.

These various lines of evidence prove that the primary reduction product of TCNP is TCNE⁻. Other products are formed in small concentrations which do not give rise to an observable e.s.r. spectrum.

The d.c. polarogram of 1,1,2,2-tetracyanoethane[7] in DMF shows a long gradual wave of small slope starting at −1.1 v. At −2.0 v. there is a high, sharp wave which shows a maximum. Electrolysis at potentials below −2.5 v. produces a light yellow solution which shows no e.s.r. spectrum. At −2.5 v., violent bubbling takes place at the surface of the mercury-pool cathode, and the e.s.r. spectrum of TCNE⁻ is obtained. Thus, just as in TCNP, the reduction product of the ethane is TCNE⁻. The line widths in the e.s.r. spectrum obtained from the ethane are also narrower than in the spectrum obtained by starting with TCNE.

The narrowness of the lines in the e.s.r. spectrum of TCNE⁻ obtained by the reduction of TCNP or tetracyanoethane undoubtedly arises from the absence of an electron exchange reaction between TCNE and TCNE⁻. The excellent resolution obtained permits the identification of all the carbon-13 splittings arising from carbon-13 nuclei in natural abundance. A total of 20 lines attributable to carbon-13 nuclei is observed,[8] and these lines as well as the nine lines arising from the four equivalent nitrogen atoms, have intensity ratios which are in excellent agreement with the predicted ratios. The e.s.r. data obtained are summarized in Fig. 1. Phillips, et al., found $a^N = 1.56$ gauss and $a_1{}^C = 6a^N = 9.4$ gauss in their original investigation.[2,8]

We wish to thank Dr. L. L. McCoy for advice regarding the chemistry of these compounds and Dr. W. H. Reinmuth for assistance with electrochemical problems and for the use of his polarographic equipment. We are indebted to Dr. T. L. Cairns of E. I. du Pont de Nemours for the original sample of TCNE.

(7) Made by the procedure given by W. J. Middleton, R. E. Heckert, E. L. Little and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

(8) W. D. Phillips and J. C. Rowell have also recently observed the carbon-13 splitting from the ethylenic carbon atoms (private communication).

(9) National Science Foundation Coöperative Fellow.

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A DEHYDROXYLATION REACTION

Sir:

We wish to report an apparently general method for the conversion of 1,2-glycols and epoxides to olefins. The reaction consists in pyrolysing the glycol in the presence of equimolar amounts of anhydrous oxalic acid at 200–240°. To our knowledge the only recorded instance of this reaction is the well-known conversion of glycerol to allyl alcohol.[1] A typical example is the conversion of meso-2,3-butanediol to a mixture containing 20% cis- and 50% trans-2-butene. Less than 0.4% butadiene and less than 0.01% isomeric butenes were present in this mixture.[2]

$$CH_3-CHOH-CHOH-CH_3 \xrightarrow{\substack{COOH \\ | \\ COOH}} CH_3-CH=CH-CH_3$$
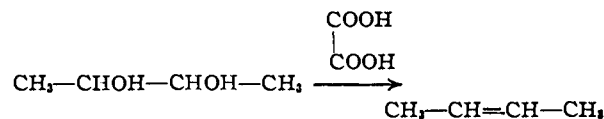
Alicyclic glycols smoothly undergo this conversion in yields ranging from 10–60%. Thus cis- and trans-cyclohexane-1,2-diol, cis- and trans-3,4-dihydroxytetrahydrofuran,[3] trans-cyclopentane-1,2-diol, as well as the corresponding epoxides were transformed into cyclohexene, 2,5-dihydrofuran and cyclopentene, respectively.

The major side reactions are those to be expected when glycols are treated with a dibasic acid namely, (a) the pinacol rearrangement: this becomes the dominating reaction with ditertiary glycols, only; (b) polyester formation: this is more pronounced with simple aliphatic glycols, e.g., ethylene glycol and (c) the decomposition of the monoöxalate ester intermediate to the formate ester of the glycol.

Although the evidence is not compelling, our experiments suggest that a cyclic ester of type I is *not* the important intermediate in this reaction.

I   IIa
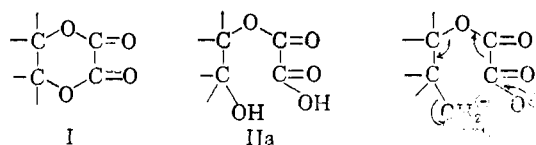
We believe that the monoester and/or its corresponding ion pair (IIa and IIb) decompose in the concerted manner shown. The evidence rests upon these observations: (1) the cyclic oxalic ester of trans-cyclohexane-1,2-diol (m.p. 110.7–111.3°, anal., found for $C_8H_{10}O_4$: C, 56.4; H, 5.94) when pyrolyzed furnished among other products cyclohexanone but *no* cyclohexene. (2) When anhydrous oxalic acid is added to cyclohexene oxide an exothermic reaction ensues and a *blue*[4] oil is formed. Pyrolysis of this oil discharges the blue color and furnishes, among other products, cyclohexane.

The tentative reaction scheme formalized with IIb lends itself to the following working hypothesis. Since IIb does not represent a quasi-six membered ring transition state, no great stereospecificity should be expected. Our experiments with the cis- and trans-cyclohexanediols (yielding 19

(1) O. Kamm and C. S. Marvel in H. Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, N. Y., 1948, p. 45 (ref. 1 and 2).

(2) The assistance of the Shell laboratories, Amsterdam, Holland, in the analysis of this mixture is acknowledged gratefully.

(3) E. G. E. Hawkins, *J. Chem. Soc.*, 253 (1959).

(4) Compare the blue color which develops when carotenoid epoxides are treated with acid, P. Karrer and E. Jucker, *Helv. chim. acta*, **28**, 300 (1945); a conversion of epoxides to olefins *via* the iodohydrin has been achieved by J. W. Cornforth, R. H. Cornforth and K. K. Mathew, *J. Chem. Soc.*, 112 (1959). P. Bedos and A. Ruyer, *Compt. rend.*, **188**, 962 (1929), obtained traces of cyclopentane carboxaldehyde upon treatment of cyclohexene oxide with oxalic acid. G. Darzens, *ibid.*, **150**, 1243 (1910), reports the conversion of glycidic esters by treatment of hydrogen iodide to the corresponding acrylates.