

1,10-diol.⁸ Its stereochemistry is assigned all-*trans* because its ultraviolet spectrum^{9a} is similar to that of *trans*-polyenes^{9b} but different from those containing one or more *cis* double bonds.^{9b} Tetraenediol XII reacts with 1 equiv. of excess *N*-phenylmaleimide to give a mono 4,7-adduct, m.p. 303°, which can be dehydrated to the fully conjugated pentaene, m.p. >300° (λ_{\max} 264 and 361 $m\mu$ (ϵ 21,000 and 36,000)). Reaction of XII with *p*-toluenesulfonic acid yields 2,2-diphenyl-5-(6,6-diphenylhexatrienyl)-2,5-dihydrofuran (XIII, 71%), m.p. 132–133° (eq. 4); its structure is consistent with its analysis, spectra,^{10a} and n.m.r. absorption.^{10b} Tetraphenyldiol XIV is converted by *p*-toluenesulfonic acid (eq. 4) to the tricyclic ether XV (45%, m.p. 231°, λ_{\max} 287 $m\mu$ (ϵ 19,500)); the transformation of XIV and proof of structure of XV are analogous to that of X and XI.^{10b}

(8) M. Godchot, *Compt. rend.*, **171**, 198 (1920).

(9) (a) Maxima at 320 $m\mu$ (ϵ 66,000), 306 (70,000), and 294 (52,000); (b) L. Zechmeister and J. H. Pinckard, *J. Am. Chem. Soc.*, **76**, 4144 (1954).

(10) (a) λ_{\max} at 239 and 326 $m\mu$ (ϵ 16,500 and 42,000); (b) the n.m.r. absorption will be discussed in detail in future publications.

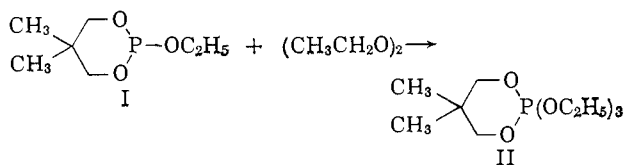
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Pentaalkoxyphosphoranes¹

Sir:

Recently it was reported that a material believed to be pentaethoxyphosphorane could be prepared by reaction of triethyl phosphite and diethyl peroxide.² It is the purpose of this report to describe the preparation of two new pentaalkoxyphosphoranes. They are the cyclic oxyphosphorane II and pentamethoxyphosphorane. The phosphite (I) was allowed to react with diethyl peroxide at room temperature for 20 days. At this



time the n.m.r. spectrum indicated that there was present unreacted phosphite, the phosphate (III) derived from I, a new material, and possibly minor amounts of other substances. Distillation at 65° (block) (0.25 mm.) gave a 60% fraction, whose n.m.r. spectrum indicated it was composed of ca. 15% I, very little III, and a new substance. This substance has been assigned the structure II on the basis of the following data. The phosphorus-31 n.m.r. spectrum taken on a sample 38 days after distillation showed absorption at -124.1, +1.9, +8.9, and +71.6 p.p.m. relative to 85% phosphoric acid. The absorptions can be assigned to I, triethyl phosphate, III, and II, respectively.³ Large positive shifts are characteristic of phosphorus com-

(1) This research has been supported by the National Science Foundation under Grant GP-202.

(2) D. B. Denney and H. M. Relles, *J. Am. Chem. Soc.*, **86**, 3897 (1964).

(3) The proton n.m.r. spectrum of the 38 day old sample showed considerable changes from that obtained on the freshly distilled material. These changes clearly indicate that III was formed over the 38 days.

pounds with five electronegative groups attached to phosphorus.⁴ The proton n.m.r. spectrum of the freshly distilled sample showed a singlet at τ 9.04 and a triplet at 8.98 ($J = 7$ c.p.s.) further split into doublets ($J = 2$ c.p.s.). There was also a complex multiplet centered at τ 6.2. The 9.04 absorption can be assigned to the *gem*-dimethyl group,⁵ the 8.98 to the methyls of the ethyl groups, and the remainder to methylene groups. Some phosphite (I) was also detected by the presence of an absorption at τ 9.3.

The infrared spectrum of II is similar in many respects to those of I and III; however, each can be distinguished from the other by characteristic absorptions. In particular II has broad absorptions at 12.35 and 13.2 μ , I at 12.5 (sharp) and 13.5 μ (broad), and III has strong sharp bands at 11.65 and 12.0 μ . There is also a strong absorption at 7.6 μ in III which is weak in II and absent in I.

Attempted g.l.p.c. analysis, 10-ft. silicone grease column, 175°, injection port 195°, gave at least seven products. Two of the major components were shown to be triethyl phosphate and III by adding each and rechromatographing.

All of the above physical data support the assignment of structure II. The reactions of II lend support to this structural assignment. Benzoic acid reacted exothermically with II⁶ at room temperature to give ethanol, ethyl benzoate (78%), triethyl phosphate (24%), III (42%), and uncharacterized materials. Reaction of II with phenol was mildly exothermic and led to the formation of ethanol, phenetole (78%), III (33%), and triethyl phosphate (19%). Treatment of II with an equimolar amount of butanol gave very little reaction; after 7 days a trace of butyl ethyl ether had been formed. Hydrolysis of II was rapid and resulted in the formation of phosphates and ethanol.

Trimethyl phosphite was allowed to react with dimethyl peroxide in methylene chloride for 2 months in a refrigerator. Evaporation of the methylene chloride afforded a residue whose n.m.r. spectrum in carbon tetrachloride showed two doublets at τ 6.26 ($J = 11$ c.p.s.) and 6.56 ($J = 12$ c.p.s.). A weak doublet with $J = 10$ c.p.s. appeared on the sides of the peaks of the τ 6.56 doublet. The doublet at τ 6.26 was increased in intensity when trimethyl phosphate was added. The small doublet may have been due to trimethyl phosphite; it has the same chemical shift and coupling constant. Distillation at 40° (block) (10 mm.) concentrated the unknown material in the distillate.⁷ Treatment of a carbon tetrachloride solution of this material with water yielded trimethyl phosphate and methanol. Treatment with benzoic acid yielded methyl benzoate (70%) based on the mole ratio determined by n.m.r.,⁷ trimethyl phosphate (100%), and a low-boiling material, possibly methanol. On the basis of these data it is concluded that the reactive material is pentamethoxyphosphorane.⁸

(4) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **85**, 3252 (1963).

(5) It is very interesting to note that the *gem*-dimethyls are not equivalent (τ 9.3 and 8.82) in the phosphite (I) and (τ 9.13 and 8.8) in the phosphate (III), whereas they are apparently equivalent in II.

(6) The material was freshly distilled and by n.m.r. showed ca. 15% I and very little III.

(7) If it is assumed that this material is pentamethoxyphosphorane the mole ratio changed from 0.67:1 to 1.62:1.

(8) Unfortunately it was not possible to obtain a phosphorus-31 n.m.r. spectrum of this material.

The preparation of pentamethoxyphosphorane and II by the phosphite-dialkyl peroxide route indicates its generality.⁹ The physical properties are in accord with those predicted. The chemical reactions illustrate their sensitivity toward acids and suggest possible applications as low-temperature alkylating agents.¹⁰ Extensions of these studies are now in progress.

Acknowledgment. We wish to thank Dr. John R. Van Wazer and the Monsanto Company for their determination of the P^{31} n.m.r. spectrum.

(9) In this connection it should be noted that no difficulty has been experienced in preparing diethyl peroxide whereas two violent explosions have taken place during the work with dimethyl peroxide.

(10) V. A. Kukhtin and K. M. Orekhova [*Zh. Obshch. Khim.*, **29**, 1687 (1959)] have reported that the 1:1 adduct of biacetyl and triethyl phosphite reacts with acetic acid to give ethyl acetate in 60% yield.

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Chemiluminescence of Electrogenerated 9,10-Diphenylanthracene Anion Radical¹

Sir:

Hercules has discussed possible mechanisms for the chemiluminescence of electrogenerated species based on qualitative electrochemical experiments with a platinum electrode in deoxygenated nonaqueous solvents.² Chandross and Sonntag have recently shown that chemiluminescence occurs when 9,10-diphenylanthracene anion radical (DPA^-) is treated with the 9,10-dichloride of DPA or a variety of oxidizing agents.³ They proposed that oxidation of DPA^- produces DPA in an excited state (DPA^*) which emits light in returning to the ground state. These results suggest two possible mechanisms for the chemiluminescent reaction occurring during electrolysis of aromatic hydrocarbons. The radical anion R^- formed at the cathode is oxidized directly to an excited state R^* at the anode surface, or an oxidant is produced at the anode which reacts with R^- to form R^* . Either of these mechanisms could occur depending upon the potential of the anode.

To elucidate the mechanism of the chemiluminescent process during electrolysis, the electrochemistry of DPA in deoxygenated dimethylformamide (DMF) solutions of several supporting electrolytes at a hanging mercury drop and a platinum wire electrode was investigated. Typical results of cyclic voltammetric experiments of a 0.1 *M* tetra-*n*-butylammonium perchlorate (TBAP) solution in the presence and absence of DPA are shown in Figure 1. At mercury the reduction of DPA to DPA^- and DPA^{2-} occurs well before discharge of the supporting electrolyte and follows the usual mode of electroreduction of aromatic hydrocarbons in aprotic solvents.⁴ At a platinum electrode only the wave for the reduction to DPA^- occurs before the final current rise. With both electrodes no separate wave for the oxidation of DPA is observed. The luminescence

(1) This research was supported by the Robert A. Welch Foundation.

(2) D. M. Hercules, *Science*, **145**, 808 (1964).

(3) E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

(4) "Advances in Polarography," I. S. Longmuir, Ed., Pergamon Press, New York N. Y., 1960: (a) P. H. Given and M. E. Peover, p. 948; (b) A. C. Aten and G. J. Hoijtink, p. 777, and references contained therein.

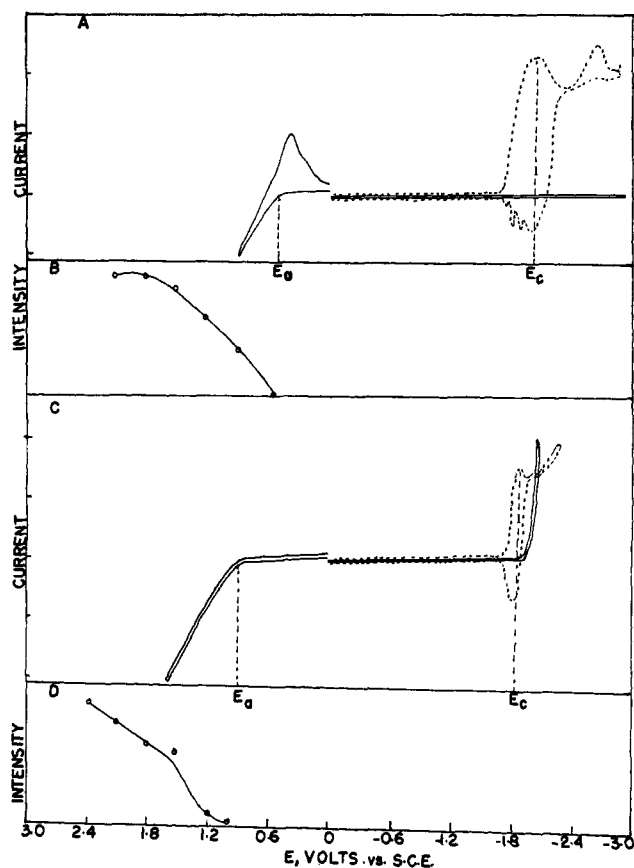


Figure 1. Cyclic voltammetric curves and light emission during electrolysis of 9,10-diphenylanthracene. A and C: the dimethylformamide solutions were 0.1 *M* in tetra-*n*-butylammonium perchlorate, without (solid lines) and with (dashed lines) 3 *mM* DPA at hanging mercury drop (A) or platinum wire electrode (C). B and D: light emission upon holding electrode potential at E_c for 1–2 sec. and then switching to various positive potentials, using hanging mercury drop (B) or platinum wire electrode (D).

reaction was studied by holding the potential of the working electrode at a potential, E_c , where reduction to DPA^- occurs, for several seconds, and then switching the potential to various more positive values and observing the occurrence and intensity of light emission. The potentials were controlled with an electronic potentiostat; a platinum auxiliary electrode in a separate chamber and an aqueous saturated calomel electrode (s.c.e.) were used. Emitted light was measured using a Dumont 6467 photomultiplier tube with an output to either a sensitive galvanometer (0.003 μ a./mm.) or an oscilloscope.⁵ Typical results are shown in Figure 1. No emission results until the potential of the working electrode is switched to a threshold potential, E_a , at which oxidation of the supporting electrolyte or electrode occurs, 0.51 v. vs. s.c.e. with the mercury electrode and 1.00 v. with the platinum electrode in TBAP. Beyond E_a the intensity of the emitted light increases with increasing potential. Upon switching back to E_c , light emission is again observed, as Hercules reported.² The light emission, when observed on an oscilloscope, is in the form of a single sharp pulse on

(5) (a) The technique of monitoring emitted light during electrolysis has been described by T. Kuwana, B. Epstein, and E. Seo, *J. Phys. Chem.*, **67**, 2243 (1963); *J. Electroanal. Chem.*, **6**, 164 (1963). (b) We are indebted to Professor W. C. Gardiner for assistance in the design of these experiments.