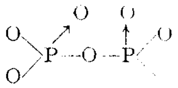
also account for some of the discrepancies in analytical results mentioned above.

The nuclear magnetic resonance spectrum of P^{31} observed in a dimethylformamide solution of the cyclohexene product[9] partially substantiates this formulation. At 17 megacycles/sec. using H_3PO_4 as standard a strong signal was obtained at +26.3 ± 0.3 p.p.m., attributed to a



structure. A second signal at +12.75 ± 0.25 p.p.m. of approximately 1/3–1/5 the intensity of the first was attributed to terminal phosphorus atoms in the chain. The failure of any trivalent phosphorus to show up in the spectrum may be due to further atmospheric oxidation of the solution as observed with the benzene-soluble products noted above.

Experimental

Cyclohexene. Typical Preparation Using Oxygen.—White phosphorus (10.0 g., 0.32 g. atom) was dissolved in 500 ml. of dry, thiophene-free benzene under nitrogen in a flask equipped with a magnetic stirrer and placed in a thermostated water-bath at 40°. Cyclohexene (14.5 g., 0.18 mole) was added, the system swept out with a liter of oxygen and connected to a large oxygen-filled gas buret. Stirring was commenced, and the oxygen pressure maintained at approximately 810 mm. Oxygen absorption and product precipitation began immediately. After 10 hours, 6.4 liters (0.285 mole at S.T.P.) of oxygen had been taken up and the reaction mixture was filtered on a sintered glass filter, washed with 500 ml. of petroleum ether, and dried under vacuum on the filter. The yield was 30 g., 100% of theory based on oxygen consumed.

Preparation using Air.—Cyclohexene (50 g., 0.61 mole) was added to 30 g. (0.97 mole) of phosphorus dissolved in dry benzene in a stirred flask and a slow stream of dry air drawn through the mixture for 48 hours. At the end of this time no phosphorus was present, as shown by the absence of white fumes on allowing a few drops of solution to evaporate on a watchglass. On isolation as previously described the phosphorate was obtained in 86% yield based on phosphorus.

Phosphorates of Other Olefins.—Products from other liquid olefins were prepared essentially as described above except that 0.1–0.5% azobisisobutyronitrile was added as initiator. Typical times required for absorption of the calculated amount of oxygen are indicated in Fig. 1. The soluble reaction products were isolated by evaporating off the benzene *in vacuo*, washing the residue with petroleum ether, and drying *in vacuo*. A Rast molecular weight determination on the 1-hexadecene phosphorate gave a value of 1521.

Gaseous olefins (ethylene and isobutylene) required a somewhat different apparatus. Thus in the preparation of ethylene phosphorate a solution of 10.4 g. of phosphorus (0.325 gram atom) in 600 ml. of benzene containing 0.2 g. of azobisisobutyronitrile was prepared and maintained at 40°. A 4:1 mixture of ethylene and oxygen contained in a reservoir system consisting of a gas buret and a 5-liter flask was circulated through the solution by means of a small diaphragm pump. As oxygen and ethylene were consumed they were replenished, maintaining the mixture below the explosive limit. After four days, the product was separated, washed with petroleum ether and dried. The yield was 22 g., 95% based upon phosphorus.

Determination of Oxygen–Phosphorus Ratio during Reaction.—The relative rates of consumption of oxygen and phosphorus in their reaction with cyclohexene were followed by periodically removing aliquots from a typical run, filtering off the product, evaporating benzene and cyclohexene from the filtrate, and determining residual phosphorus by titration with acidified bromide–bromate, a technique which gave good results in blank experiments with known amounts of phosphorus. Results have been plotted in Fig. 2 and indicate that the precipitate has the composition RP_2O_4 from the beginning of the reaction. Additional evidence was obtained by interrupting two experiments before oxygen absorption was complete, separating the residual olefin and benzene from product and phosphorus by filtration and vacuum distillation, and determining the unreacted cyclohexene by catalytic hydrogenation. Results are summarized in Table II, and while not entirely quantitative, indicate considerable unreacted cyclohexene with no evidence for any intermediate compound RP_2O_3.

TABLE II

PARTIAL OXIDATION EXPERIMENTS

Run[a]	1	2
C_6H_{10} taken	0.0177	0.0165
P_4 taken	.0342	.0320
O_2 absorbed	.0492	.050
RP_2O_4 formed	.0110	.0114
C_6H_{10} remaining	.008	.009

[a] All quantities in gram atoms.

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(9) The n.m.r. measurements and their analysis were obtained through the coöperation of the Chemical Warfare Laboratories, Army Chemical Center, Md.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY]

Chemical Properties of the Reaction Product of Cyclohexene with Phosphorus and Oxygen[1]

BY CHEVES WALLING, FRANK R. STACEY, SAUNDERS E. JAMISON AND EARL S. HUYSER

RECEIVED MARCH 24, 1958

Reactions of the product $C_6H_{10}P_2O_4$, obtained from cyclohexene, white phosphorus and oxygen, are described consistent with a polymeric anhydride structure. In water the product apparently is hydrolyzed immediately to β-phosphitocyclohexanephosphonic acid, which in turn undergoes rapid β-elimination of phosphorous acid and polymerization. In alcohols it is converted to a complex mixture of phosphorus esters, the structures of which have been only partially established.

Our preceding paper[2] described the reaction of a series of olefins with oxygen and white phosphorus in benzene solution to give white solid products of the approximate composition RP_2O_4 (or RP_2O_5) which reacted vigorously with water and alcohols and were suggested as having a polymeric anhydride structure, *e. g.*, for that from cyclohexene

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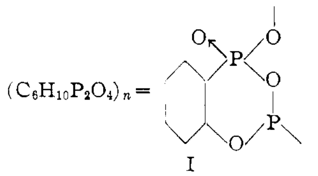
(1) Work supported by the Chemical Corps, U. S. Army.

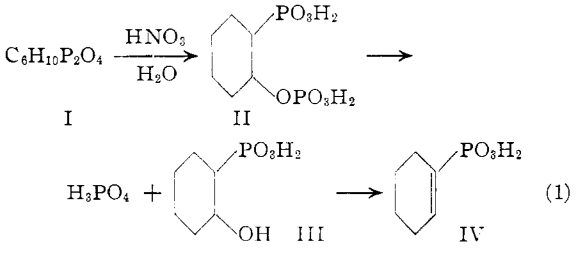
(2) C. Walling, F. R. Stacey, S. E. Jamison and E. S. Huyser, THIS JOURNAL, **80**, 4543 (1958).



A polymeric structure appears plausible because of the insoluble nature of the product, and the apparent molecular weight of the product from 1-hexadecene (1521).

This paper presents our evidence for the particular formulation chosen.

Derivatives.—Willstätter and Sonnenfeld,[3] who first described the cyclohexene product, suggested that oxidative hydrolysis with 45% nitric acid followed the path



(1)

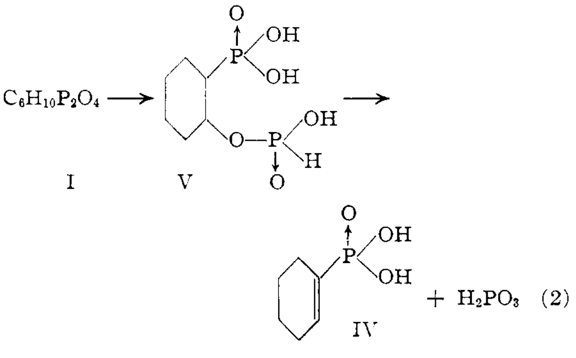
identifying the phosphoric acid and obtaining a lead salt with a lead content corresponding to $C_6H_9PO_3Pb$. We confirm their observations, obtaining a salt with approximately the proper analysis for lead and phosphorus. On oxidative hydrolysis with potassium bromate a mole of phosphoric acid is also liberated, and on prolonged ether extraction a small amount of organophosphorus acid was isolated, yielding an aniline salt, m.p. 190-191°, with the proper neutralization equivalent for IV. These observations indicate the existence of one C–P bond, and the ease of elimination certainly suggests that the second substituent is attached in the β-position. Ether extraction of a nitric acid hydrolyzate also yielded a mixture of organophosphorus acids from which a tetracyclohexylamine salt was isolated corresponding to II.

Although we have obtained no derivative corresponding to III from cyclohexene, nitric acid hydrolysis of the isobutylene–phosphorus–oxygen product yielded a lead salt of composition corresponding to a hydroxyphosphonic acid. Since no elimination occurred in this case, it presumably has the structure $HOCH_2C(CH_3)_2PO_3Pb$. As indicated in our previous paper, this suggests that initial attack on the olefin during oxidation involves a radical with the partial structure P–O·

The stoichiometry of the cyclohexene—oxygen–phosphorus reaction requires that half the phosphorus in the product be at the phosphate level of oxidation and half at the phosphite level. When products were allowed to react with ethanol and 1-butanol and the reaction mixture distilled *in vacuo* diethyl- and di-*n*-butyl phosphites were obtained in 29 and 28% yield, respectively, indication that it is the non-carbon-bonded phosphorus which is in the phosphite state.

While the foregoing observations are consistent with the structure I, it must be stated that we have been consistently unsuccessful in obtaining good yields of any identifiable derivative except the lead salt containing the cyclohexene portion of our reaction products. Attempts to distil hydrolysis or alcoholysis products invariably produced large quantities of non-volatile resinous residues. Similar residues also resulted when alcoholysis products were esterified by reaction with triethyl phosphite or diazomethane before distillation. We suspect that our failure is due to the ready (perhaps acid-catalyzed) vinyl polymerization of the Δ^2-cyclohexenephosphonic acid which (as is shown below) is formed rapidly in the presence of water. It is, in fact, very likely that the lead salt described above is actually a derivative of such a polymeric product. An attempt to prepare dimethyl Δ^2-cyclohexenephosphonate from sodium diethyl phosphite and cyclohexene oxide followed by dehydration yielded a similar resin with an infrared spectrum essentially identical with an alcoholysis product methylated with diazomethane. Such products are of high molecular weight (>400) and show no evidence of double bonds since they fail to react with bromine and show no vinyl hydrogen in their n.m.r. spectra.

Hydrolysis and Alcoholysis Studies.—On the basis of our formulation of the cyclohexene–phosphorus–oxygen product, non-oxidative hydrolysis might be expected to take course (2) and could be



(2)

followed by potentiometric titration since V possesses two strongly acidic and one weakly acidic hydrogen, and conversion to IV plus phosphorous acid produces an additional weakly acidic hydrogen (for convenience these two types will be differentiated as *primary* and *secondary* hydrogens). Figure 1 substantiates this picture, and, taking

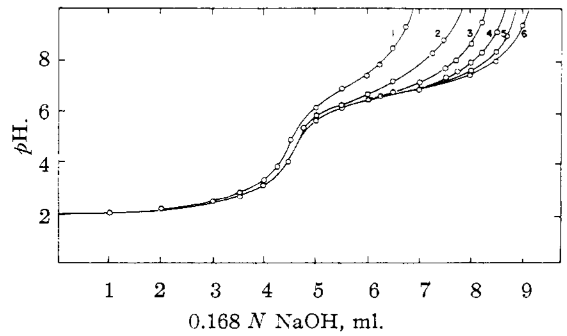


Fig. 1.—Titration of 0.39 millimole of cyclohexene hydrolysis product: curve 1, initial titration; curve 2, heated to reflux; curve 3, refluxed 20 min.; curve 4, 60 min.; curve 5, 90 min.; curve 6, 225 min.

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[3] R. Willstätter and E. Sonnenfeld, *Ber.*, **47**, 2801 (1914).

titration end-points at *p*H 4.5 and 8.5, respectively, indicates the initial presence of 2.07 primary and 1.03 secondary hydrogens. On refluxing the solution an additional secondary hydrogen appears, the elimination reaction being approximately a first-order reaction with a half-life (at reflux) of about 35 minutes. This appearance of an additional secondary hydrogen, incidentally, confirms our assignment of the ester phosphorus as phosphite, for the alternate formulation of V as a 2-phosphatocyclohexanephosphinic acid would yield phosphoric acid, the tertiary hydrogen of which does not titrate in this *p*H range.

If the cyclohexene–phosphorus–oxygen reaction product is dissolved in absolute ethanol and the resulting solution diluted with water and titrated, results are obtained of which Fig. 2 is typical.

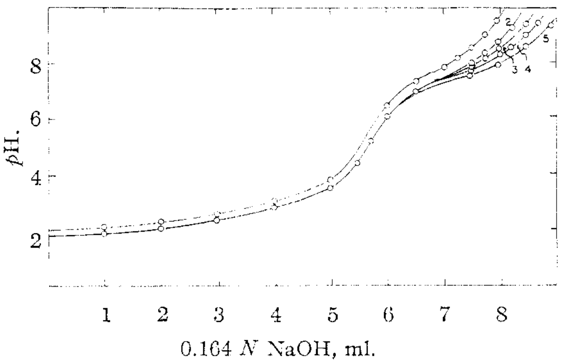
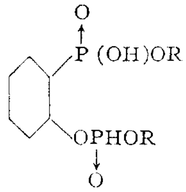
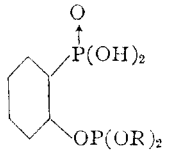
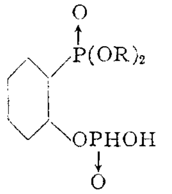
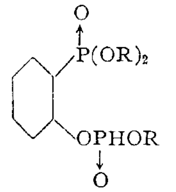
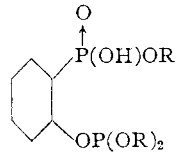
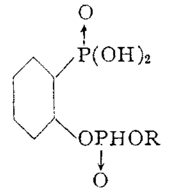
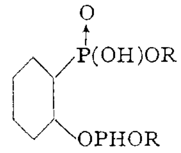


Fig. 2.—Titration of 0.675 millimole of cyclohexene alcoholysis product: curve 1, initial titration; curve 2, after 30 min. at 25°; curve 3, 90 min.; curve 4, 150 min. at 40°; curve 5, 240 min.

TABLE I

POSSIBLE ALCOHOLYSIS PRODUCTS OF $C_6H_{10}P_2O_4$

		Hydrogens, initial	After elimination
VI		1 primary	2 primary
VII		1 primary 1 secondary	1 primary 1 secondary
VIII		1 primary	1 primary 1 secondary
IX		None	1 primary
X		1 primary	1 primary
XI		1 primary 1 secondary	2 primary 1 secondary
XII		2 primary	2 primary 1 secondary

Again primary hydrogen is almost constant, but secondary hydrogen increases rapidly on standing, the final titration corresponding closely to two equivalents of hydrogen ion per $C_6H_{10}P_2O_4$ unit with primary and secondary hydrogens in a ratio of 2:1. We assume that the reaction with alcohol involves the opening of anhydride linkages to form phosphorus esters, and the increase in titer again represents an elimination reaction, in this case so rapid that it is significant in even our initial titration. The possible products which might arise from alcoholysis of the anhydride structure I are listed in Table I. Products VI–VIII are those which might arise from symmetric cleavage (*i. e.*, the opening of anhydride linkages in all RP_2O_4 units in the same manner) while IX–XII represent additional products which might be formed if opening were essentially random. If these latter products are important, the over-all stoichiometry requires that for every mole of IX or X produced an equivalent of XI or XII is formed as well. With this last fact in mind it is evident that any combination of products should lead to the eventual production of two equivalents of hydrogen ion as observed. However, it is also clear that alcoholysis does not lead to a single product as no compound in Table I should give the observed 2:1 ratio of primary to secondary hydrogen on hydrolysis. Noting next that VI gives no secondary hydrogen and any combination of random products (IX–XII) should give a 3:1 ratio, it appears that the mixture contains at least 50% of either (or both) VII and VIII. Since approximately 30% dialkyl phosphite actually was isolated on attempting to distil an alcoholysis product, much of this is presumably VII. Again, inspection of Fig. 2 indicates the rapid appearance, on adding an alcoholysis solution to water, of 1.33 equivalents of primary and 0.33 equivalent of secondary hydrogen, followed by the slow liberation of an additional 0.33 equivalent. While these observations are not sufficient to identify other components in the system, the excess of primary hydrogen over one equivalent must arise from VI, XI or XII, and the increase in secondary hydrogen from slow elimination from VIII or XII. Since the initial secondary hydrogen presumably arises from VII, these results can be accommodated by either approximately equal quantities of VI–VIII or a more complex mixture including unsymmetric products as well.

Experimental

Cyclohexene–phosphorus–oxygen reaction products were prepared as previously described, separated by filtration under moisture-free conditions, and stored in closed containers.

Lead Salts of Oxidative Hydrolysis Products.—A sample of cyclohexene reaction product (0.92 g., 0.0044 mole) was added to 5 cc. of 45% HNO$_3$ in a small flask and placed on a steam-bath. In a few seconds a vigorous reaction occurred and the flask was set aside for 10 min., then diluted with 35 cc. of water and heated for an hour at 85°. On addition of 0.013 mole of Ba(OH)$_2$ solution and enough NH$_4$OH to render the mixture basic, Ba$_3$(PO$_4$)$_2$ was precipitated, 1.15 g., theory 1.3 g. Treatment of the filtrate with lead nitrate (0.0048 mole) gave 1.6 g. of pale yellow lead salt which was slurried with 95% ethanol, filtered and dried. *Anal.* Found: Pb, 57.43, 57.55; P, 7.74. Calcd. for C$_6$H$_9$PO$_3$Pb: Pb, 56.4; P, 8.42. Similar treatment of an isobutylene reaction product, 1.8 g., gave the calculated yield of barium phosphate and 2.5 g. (theory 3.6 g.) of lead salt. *Anal.* Found: Pb, 57.87; P, 8.41. Calcd. for (C$_4$H$_8$(OH)PO$_3$Pb): Pb, 57.6; P, 8.64. Calcd. for (C$_4$H$_7$PO$_3$Pb): Pb, 60.7; P, 10.0.

Amine Salts of Hydrolysis Products.—A 5-g. sample of the cyclohexene product was hydrolyzed with nitric acid, the solvent removed *in vacuo*, and the residue taken up in 95% ethanol. Addition of cyclohexylamine precipitated a mixture of salts. Fractional crystallization from alcohol and then aqueous acetone removed amine phosphate as the more soluble component leaving finally 1 g. of material, m.p. 220–228°. *Anal.* Found: N, 7.77; P, 11.26. Calcd. for the tricyclohexylamine salt of β-phosphatocyclohexane phosphonic acid: N, 7.53; P, 11.1. By continuous ether extraction of a similar hydrolysis mixture and evaporation of the ether, a viscous residue was obtained which, on treatment with cyclohexylamine and recrystallization, gave a small amount of salt, m.p. 246–250°. *Anal.* Found: N, 8.28; P, 9.30. Calcd. for tetracyclohexylamine salt of the same acid: N, 8.55; P, 9.45. Refluxing a sample of cyclohexene product for two hours with potassium bromate solution followed by continuous ether extraction again yielded a residue which on treatment with aniline and recrystallization from methanol gave what was evidently the aniline salt of cyclohexenephosphonic acid or its polymer since it had the correct neutralization equivalent (129, calcd. 128). Here elimination was complete since the extracted aqueous solution gave the calculated yield of magnesium ammonium phosphate on treatment with magnesium and ammonium ions.

Potentiometric Titrations.—Weighed samples of cyclohexene reaction products were dissolved in water and aliquots titrated with standard NaOH solution using a glass electrode in the conventional manner. In the case of alcoholysis products the weighed samples were dissolved in absolute methanol and aliquots titrated after dilution with water. In order to establish that hydrolysis of intermediate esters was negligible during the titration, diethyl phosphite was added to one of these diluted samples without significant effect on the titration curve.

Isolation of Dialkyl Phosphites from Alcoholysis Products.—A sample of cyclohexene reaction product, 20.8 g., was dissolved in 100 cc. of absolute ethanol and refluxed for 5 hours. A small amount of yellow precipitate was removed by filtration, and the filtrate distilled *in vacuo*. In addition to the excess alcohol, only 4 g. of volatile material was obtained, b.p. on redistillation 62° (6 mm.), n^{25}D 1.4052, with an infrared spectrum identical with diethyl phosphite. The light brown viscous residue remaining yielded no further product, but darkened and decomposed on further heating. A similar alcoholysis using n-butyl alcohol yielded dibutyl phosphite, b.p. 101° (4 mm.), n^{25}D 1.4243, with the correct infrared spectrum.

Esterification of Alcoholysis Products.—A methanol solution of the cyclohexene product was treated with an ether solution of excess diazomethane which reacted immediately with evolution of nitrogen. Methanol was removed and the residue taken up in benzene in which it was now soluble. The remaining methanol was removed by azeotropic distillation and the solution treated with additional portions of diazomethane until the yellow color of the latter persisted. After the reaction mixture had stood overnight an attempt was made to distil it *in vacuo*. No volatile material other than a small amount of dimethyl phosphite and trimethyl phosphate could be obtained and the viscous residue was evidently polymeric since it had a Rast molecular weight of 410. Its analysis C, 41.85; H, 6.76; P, 18.60, corresponded to no obvious composition. Another experiment in which an ethanol alcoholysis product was heated with triethyl phosphite similarly gave no distillable product containing the cyclohexene ring, but only a viscous residue. The method, incidentally, appears to be a good one for further esterifying phosphate esters. Thus a mixture of triethyl phosphite and mixed mono- and diethyl phosphates gives diethyl phosphite and triethyl phosphate in good yield.

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[CONTRIBUTION FROM WASHINGTON UNIVERSITY AND THE CHEMICAL LABORATORY, THE FREE UNIVERSITY, AMSTERDAM]

Electron Spin Resonance Spectra of Aromatic Mononegative and Monopositive Ions[1]

BY E. DE BOER AND S. I. WEISSMAN

RECEIVED MARCH 17, 1958

The electron spin resonance (E.S.R.) spectra of the mononegative ions of anthracene, tetracene, phenanthrene, biphenyl, terphenyl, perylene, pyrene, triphenylene, coronene, fluoranthene, acenaphthylene, acepleiadylene, acenaphthene and acepleiadiene are reported. In addition, the E.S.R. spectra of the positive ions of perylene, tetracene, anthracene, acepleiadylene and acepleiadiene have been measured. The spectra are compared with those calculated on the assumption of a linear relationship between hyperfine coupling constant with a proton and the π-spin density on the adjacent carbon. The latter were calculated by a single configuration Hückel molecular orbital treatment. The spectra of the negative ions of all the alternant hydrocarbons except pyrene are in satisfactory agreement with the calculations. The spectra of the negative ions of the non-alternant hydrocarbons fluoranthene and acenaphthylene agree with the calculations, while the spectrum of acepleiadylene ion does not. Among the positive ions, the spectra of the ions of perylene, tetracene and anthracene agree with the calculations; the spectrum of the positive ion of acepleiadiene does not. The ions of the partially saturated hydrocarbons acepleiadiene and acenaphthene have high coupling constants with the methylene protons and are not satisfactorily treated by simple molecular orbital theory.

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