to a solid foam. The product was cooled, transferred into drybox, and crushed mechanically. To force the reaction to completion, the material was again heated under vacuum at temperatures ranging from 217–245° for 2.5 hr. Imidazole continued to sublime from the system, and some sintering was observed at the highest temperature. The amount of imidazole obtained was 1.56 g. The weight of the brown polymer was 4.83 g. Based upon imidazole recovery, the average degree of polymerization (D.P.) was 4.19.

Anal. Calcd. (D.P. 4.19): C, 66.78; H, 3.78; N, 16.83; P, 8.31. Found: C, 64.47, 64.36; H, 4.05, 4.01; N, 16.70, 16.59; P, 8.32, 8.39.

The oligomer melts from 244–280°, it begins to decompose thermally at 360°. At room temperature the product is insoluble in toluene, dimethoxyethane, and methyl ethyl ketone; it is soluble in 2-benzoylpyridine.

The experiment was repeated, allowing the reaction to proceed for 5.5 hr. at 275–290°. Imidazole recovery and elemental analysis indicated an average degree of polymerization of 11.0. Again the product solidified at the reaction temperature.

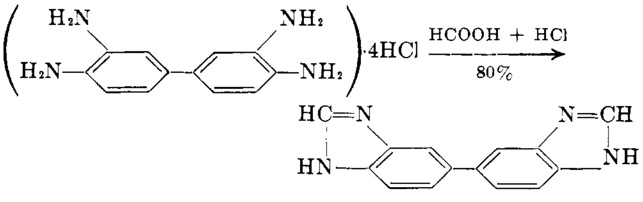
1,1′-(5,5′-Bibenzimidazolyl)phenylphosphine Oxide Oligomer, Prepared from Dipyrrol-1-ylphenylphosphine Oxide.—Compound V (5.12 g., 0.020 mole) and 5,5′-bibenzimidazole (4.68 g., 0.020 mole) were transferred into a 100-ml. flask in an inert atmosphere box. The flask was connected through a trap immersed in liquid nitrogen to a dry nitrogen by-pass line. Formation of liquid condensate was observed when the reaction temperature had been raised to 208°. The temperature was increased to 308° in order to melt the reactants and to obtain thorough mixing. Subsequently, the system was evacuated slowly to <1 mm., and heating was continued at 270–310° for 6 hr. The reaction mixture was converted to a dark brown solid product.

The liquid condensate, 2.08 g., was identified as pyrrole by its infrared spectrum. The infrared spectrum of the solid product (7.15 g.) is similar to that of poly[1,1′-(5,5′-bibenzimidazolyl)-phenylphosphine oxide] prepared from DIPPO. By elemental analysis of the solid product, the average degree of polymerization was 3.0 ± 0.3.

Anal. Calcd. (D.P. 3.0): C, 67.66; H, 3.90; N, 16.03; P, 8.18. Found: C, 66.41; H, 3.78; N, 15.49; P, 7.96.

Attempted Reaction of Dipyrrol-1-ylphenylphosphine Oxide with N,N′-Diphenyl-*p*-phenylenediamine.—Compound V (10.25 g., 0.04 mole) and pure N,N′-diphenyl-*p*-phenylenediamine (10.41 g., 0.04 mole) were heated in redistilled quinoline (40 ml.) solution at 220° for 15.5 hr. The system was evacuated at 80°. Gas chromatographic analysis of the collected quinoline indicated that it contained only 0.5% of the pyrrole expected from the desired polymerization. The nonvolatile solids were identical with starting materials by infrared spectra.

5,5′-Bibenzimidazole.—A mixture of 7.0 g. (0.021 mole) of 3,3′-diaminobenzidine tetrahydrochloride, 17.4 g. (0.378 mole) of formic acid, and 38 ml. of 5 *N* hydrochloric acid was heated at reflux for 0.5 hr. The reaction mixture was then poured into 55 ml. of concentrated ammonium hydroxide and 25 g. of ice. The brown solid was filtered off and dissolved in methanol. The solution, after filtration to clarify, was evaporated to dryness and the residue was washed with ether. The product weighed 4.0 g. (80%) and melted at 265–267°. Recrystallization from isopropyl alcohol yielded a 1:1 adduct which was decomposed at 190–200° to yield pure 5,5′-bibenzimidazole, melting at 292–293.5°. The X-ray diffraction pattern was unique.



Anal. Calcd. for $C_{14}H_{10}N_4$: C, 71.78; H, 4.30; N, 23.92. Found: C, 71.60; H, 4.18; N, 23.67.

5,5′-Bibenzimidazole is soluble in ethanol, formamide, ethylenediamine, dimethylformamide, pyridine, *m*-cresol, hot diglyme, and hot water. It is insoluble in acetone, ether, benzene, hexane, chloroform, dioxane, ethyl acetate, and tetrahydrofuran.

The neutralization equivalent, determined by titration with hydrochloric acid in glycol–isopropanol solution, was 119.6 (calcd. 117.1).

A sample that had been stirred in water and azeotroped with benzene to dry (m.p. 275–280°) gave a different X-ray diffraction pattern from the material above.

Anal. Calcd. for $C_{14}H_{10}N_4 \cdot H_2O$: C, 66.65; H, 4.79; N, 22.21. Found: C, 65.57; H, 4.28; N, 21.56.

This "monohydrate" was unchanged by recrystallization from methanol–benzene, according to the X-ray diffraction pattern. However, extraction with diethylamine converted it to the anhydrous bibenzimidazole as shown by X-ray diffraction.

As a means of identifying 5,5′-bibenzimidazole, the dihydrochloride was prepared for X-ray diffraction analysis. 5,5′-Bibenzimidazole was dissolved in dilute hydrochloric acid. On evaporating part of the water and adding acetone, a crystalline product was obtained, m.p. about 310°. Its X-ray diffraction pattern was unique.

Anal. Calcd. for $C_{14}H_{10}N_4 \cdot 2HCl \cdot 2H_2O$: Cl, 20.66; N, 16.32. Found: Cl, 20.57; N, 16.24.

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Phosphorus Compounds. V. Tautomerism in Phenylphosphinic Acid and Its Anion[1-3]

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Hydrogen isotope exchange in the P(O)H system in aqueous and deuterium oxide solutions of phenylphosphinic acid, its sodium salt, and the corresponding deuterated acid and salt, followed by infrared techniques, has shown the reaction to be both acid and base catalyzed. The almost total lack of exchange in buffered neutral solutions shows that a simultaneous attack by a nucleophile and an electrophile is not a significant factor in the exchange reaction. The proportion of "enol" in neutral phenylphosphinate solution probably does not exceed that found in aqueous acetone solutions.

A previous article[1] of this series reported both acid and base catalysis in the hydrogen isotope exchange reaction with dialkyl phosphonates. This finding is in marked contrast[4] to the same reaction with the parent acid, phosphorous acid, which is usually considered to have a structure somewhat similar to that

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(1) Previous paper in this series: W. J. Bailey and R. B. Fox, *J. Org. Chem.*, **28**, 531 (1963).

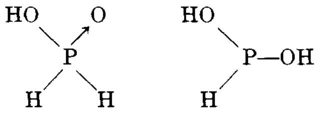
(2) Presented before the Division of Organic Chemistry at the 134th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1958.

(3) Abstracted from a thesis submitted to the Faculty of the Graduate School of the University of Maryland, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1959.

(4) A. I. Brodskii and L. V. Sulima, *Dokl. Akad. Nauk SSSR*, **85**, 1277 (1952).

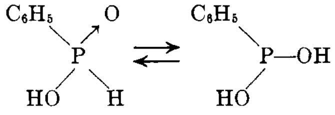
of its diesters. Although the parent acid undergoes exchange in acidic aqueous solution,[5,6] its anion has not been found to undergo hydrogen isotope exchange at the hydrogen atom bound to the phosphorus atom.[4,6] It has, therefore, been inferred that a prototropic equilibrium does not play a significant role in the reactions of the salts of this acid and that the possession of the P(O)H diadic system does not imply the existence of tautomers in a specific family of compounds.

Hypophosphorous acid, which also contains the P(O)H system, has often been designated as a tautomeric pair.



The reactions of the acid itself appear to substantiate the idea of a prototropic equilibrium preceding such reactions as hydrogen isotope exchange[4,5,7] and halogenation.[7] In neutral or basic solution, however, hydrogen isotope exchange in the anion is very slow[4,5,8,9] and, as in the case of phosphorous acid, tautomerism is not necessary to explain the observed reactions.

In view of these diverse results, it would be of interest to compare esters of hypophosphorous acid with those of phosphorous acid, but alkyl hypophosphites are, unfortunately, unknown. However, another family of compounds which may be related to hypophosphorous acid, is the phosphinic acids, and phenylphosphinic acid is readily available. This acid, as well as the parent acid, can be considered to exist as a tautomeric pair.



The phenyl group can, of course, be viewed as replacing an OH group on the phosphorus atom; in this sense phenylphosphinic acid might be thought of as a derivative of phosphorous acid. An investigation of prototropic equilibria in the P(O)H system of phenylphosphinic acid and its anion might be revealing in regard to the mechanism of the reactions of this derivative.

Experimental

Materials and Apparatus.—Stuart Oxygen Co. 99.8% deuterium oxide was employed in the exchange experiments. Phenylphosphinic acid, m.p. 84°, was a recrystallized commercial product. With the exception of the materials listed all other chemicals were C.P. reagent grade and used as received. The following compounds were prepared specifically for this work.

Phenylphosphinic acid-d_2, $C_6H_5P(O)D(OD)$, was obtained by the deuterolysis of phenylphosphonous dichloride with cold 99.8% deuterium oxide.

Sodium phenylphosphinate-*d*, $C_6H_5P(O)D(ONa)$, was prepared by the neuralization of the d_2-acid with a cold sodium deuteroxide solution. The salt also could be made by deuterolysis of phenylphosphonous dichloride with sodium deuteroxide solution, but the heat of reaction tended to produce disproportionation of the phosphine, and it was difficult to separate the phosphinate from sodium chloride. Both this deuterated salt and the corresponding undeuterated salt were readily separated from fairly concentrated aqueous solutions by precipitation with acetone or tetrahydrofuran.

Sodium phenylphosphinate, $C_6H_5P(O)H(ONa)$, was obtained by neutralization of the acid with sodium hydroxide, followed by precipitation with acetone. The salt prepared in this way invariably gave an aqueous solution which had a pH slightly below 7, although the break in the neutralization curve of the acid occurs slightly above pH 7.

In all infrared work, a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics was used. Solid samples were run as potassium bromide pellets.[10-13] Spectra of solutions were obtained with standard calcium fluoride absorption cells. The cell thicknesses, determined by measurement of interference fringes in the empty cells,[14] were 0.0982 and 0.109 mm.; the 0.0982-mm. cell was used for the compensating solution at all times. It was not felt necessary to make a correction for the difference in these path lengths, since the "blank" absorption in the reference cell was usually only a few per cent.

Hydrogen-Deuterium Exchange Experiments.—The infrared spectrum of phenylphosphinic acid[15] is generally unsuitable for following hydrogen-deuterium exchange in this molecule because of the greatly broadened bands and general absorption in the 2-6-μ range resulting from hydrogen bonding. In the sodium salt of phenylphosphinic acid, however, this broad absorption is absent. In Fig. 1, a comparison is made of the infrared spectra for the Na-H salt and its deuterated analog [$C_6H_5P(O)H(ONa)$ is designated the Na-H salt and $C_6H_5P(O)D(ONa)$ the Na-D salt]. Bands are very sharp, and although both the bands at the P-H stretching frequency (2280 cm.$^{-1}$) and the P-D stretching frequency (1650 cm.$^{-1}$) are fairly strong, there is some degree of interference in the 1650-cm.$^{-1}$ region which precludes the use of these bands in the quantitative analysis of this exchange. Fortunately, there is little absorption in either spectrum in the 3200-3600-cm.$^{-1}$ region where O-H stretching absorption would occur. This region has been used repeatedly in the analysis of water-heavy water mixtures.[16]

Preliminary Measurements on the P-H and P-D Bands.—Solutions of approximately 20% by weight of the Na-D salt in water were made acidic or basic by the addition of suitable amounts of hydrochloric acid or sodium hydroxide. At intervals, the solutions were neutralized and the salt precipitated by the addition of a large volume of tetrahydrofuran. No exchange was observed between tetrahydrofuran and the Na-D salt or deuterium oxide over a period of 24 hr. The precipitated salt was washed first with tetrahydrofuran and then with diethyl ether and dried by evacuation of the sample at 1-mm. pressure for 2 hr. at room temperature. The infrared spectrum was obtained with the sample in the form of a pressed potassium bromide pellet. Lack of significant absorption in the O-H stretching region was taken as evidence that the salt had been dried sufficiently. Transmittances (T) were measured for the absorption at 2280 (P-H), 1650 (P-D), and 1430 cm.$^{-1}$ (a phenyl ring-breathing absorption, assumed constant in both salts and, therefore, used as the reference band). Values of T were obtained by conventional base-line techniques.

Results

From the Beer-Lambert law, the absorbance from preliminary measurements on P-H and P-D bands is log $1/T = \alpha t x$, where α is the absorptivity (or extinction coefficient), t is the path length, and x is the mole fraction of the constituent responsible for the absorption. With the subscripts H, D, and R to refer to properties which are functions of the P-H, P-D, and reference portions of the molecules, one obtains the following ($x_R = 1$).

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(5) A. Simon and W. Schulze, *Z. Anorg. Allgem. Chem.*, **296**, 287 (1958).

(6) R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1574 (1959).

(7) W. A. Jenkins and D. M. Yost, *J. Chem. Phys.*, **20**, 538 (1952).

(8) H. Erlenmeyer and H. Gärtner, *Helv. Chim. Acta*, **17**, 970 (1934).

(9) H. Erlenmeyer, W. Schoenauer, and G. Schwarzenbach, *ibid.*, **20**, 726 (1937).

(10) A. W. Baker, *J. Phys. Chem.*, **61**, 450 (1957).

(11) U. Schiedt and H. Reinwein, *Z. Naturforsch.*, **7B**, 270 (1952).

(12) M. M. Stimson and M. J. O'Donnell, *J. Am. Chem. Soc.*, **74**, 1805 (1952).

(13) U. Schiedt, *Z. Naturforsch.*, **8B**, 66 (1953).

(14) D. C. Smith and E. C. Miller, *J. Opt. Soc. Am.*, **34**, 130 (1944).

(15) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

(16) J. Gaunt, *Spectrochim. Acta*, **8**, 57 (1956); *Analyst*, **79**, 580 (1954).

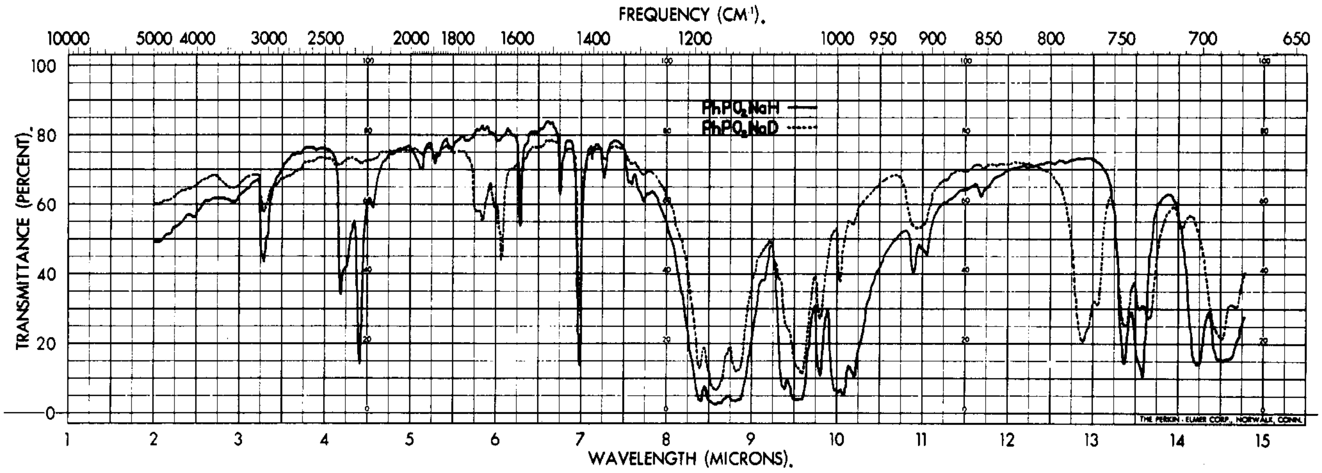

Fig. 1.—Infrared spectrum of the sodium–hydrogen and sodium–deuterium salts.

$$x_D = \frac{\alpha_R}{\alpha_D}\left(\frac{\log \frac{1}{T_D}}{\log \frac{1}{T_R}}\right)$$

The value of α_R/α_D is obtained from the spectrum of the pure Na–D salt, where $x_D = 1$; the best value was found to be 1.10. When a similar procedure was carried out to obtain x_H, α_R/α_H was found to be 1.02.

When these calculations were carried out with data such as that given in Table I, it was usually found that $x_H + x_D > 1$ (about 1.1 to 1.4). The reason for this is not known, but this discrepancy is possibly due to interference bands in the P–D region. A comparison of the spectra of the pure Na–H and Na–D salts in the 12–15-μ range (Fig. 1) shows changes in the position and intensities of the bands which indicate that some ring deuteration may have taken place during the preparation of salts. Since the degree to which this affects the intensity of the reference band is not known, a major source of error may reside in such changes. Therefore, for purposes of comparison, the figures were arbitrarily placed on a per cent basis by the following proportion.

Table I

Infrared Bands in Precipitated Sodium Salt of Phenylphosphinic Acid-d_2

Solution	Time, min.	Transmission,[a] %		
		T_D	T_H	T_R
pH 2 (HCl)	5	13.8	84.7	11.7
	60	35.9	86.0	30.5
	240	21.2	56.0	16.1
	1380	39.3	28.5	15.1
	2820	75.9	19.3	13.0
pH 4 (HCl)	5	13.3	87.5	12.6
	60	20.5	90.0	19.3
	240	21.7	89.2	18.4
	1380	37.9	94.1	33.2
	2820	48.1	94.5	38.8
pH 11.5 (NaOH)	1380	12.7	80.7	10.6
	6840	14.0	79.1	12.6
5% NaOH	120	27.3	85.0	23.7
	240	34.0	84.2	28.3
	1380	34.8	50.7	21.0

[a] T_D, T_H, and T_R are transmissions of the bands at 1650, 2280, and 1430 cm.$^{-1}$, respectively.

$$\%D = 100\,\frac{x_D}{x_D + x_H}$$

In Table II the per cents of deuterium remaining in the Na–D salt under various conditions are given as calculated from the data in Table I. In neutral solution and in a phosphate buffer at pH 6.8, no exchange whatever was detected in this way.

At least at high concentrations, deuterium oxide has little effect on the rate of exchange (Table II). The rate of exchange does increase with increasing acid concentration for deuterium oxide solutions (Table II). Similarly, the rate is dependent on the concentration of base for the Na–H salt in deuterium oxide solutions containing sodium deuteroxide (Table II).

Table II

Exchange Rates for Phenylphosphinic Acid-d_2

Solution	Time, min.	Deuterium remaining in precipitated Na–D salt, %
pH 2 (HCl)	0	95
	5	93
	60	89
	240	74
	1380	45
	2820	13
pH 4 (HCl)	0	95
	5	94
	60	94
	240	94
	1380	95
	2820	93
pH 11.5 (NaOH)	0	95
	1380	92
	6840	90
5% NaOH	0	95
	120	90
	240	87
	1380	63

Several attempts also were made to measure the exchange taking place in neutral aqueous solutions of the Na–D salt. In these runs, the pellet technique was used over a period of 6 weeks. During this time, only negligible exchange was detected by the appearance of absorption in the region of 2280 cm.$^{-1}$ (the P–H stretching absorption frequency) under the following conditions: (a) 1 M Na–D salt in water, pH 6.3;

(b) 1 *M* Na–D salt in water, pH 6.3, vessel filled with glass helices to give increased surface; (c) 1 *M* Na–D salt in a citric acid–phosphate buffer, pH 6.3; (d) 1 *M* Na–D salt in a phosphate buffer, pH 6.8. In addition, pyridine did not appear to catalyze the exchange significantly.

Exchange Rates in Deuterium Oxide Solutions.—The applicability of the Beer–Lambert law to the absorption at 3350 cm.$^{-1}$ (the O–H stretching vibration) was shown over the range of concentration from 0.1 equiv./l. to 0.6 equiv./l., from which it is found that $C_H = 1.24 \log 1/T$. Solutions of known water content were prepared by transfer of suitable weighted amounts of a solution of 1.1188 g. of water in 19.1198 g. of tetrahydrofuran (162.8 mg. of this solution contains 1 mequiv. of O–H hydrogen; this is approximately the equivalent weight of the Na–D salt), followed by dilution to 5.00 ± 0.03 ml. with deuterium oxide.

TABLE III

EXCHANGE OF PHENYLPHOSPHINIC ACID AND ITS SODIUM SALT WITH DEUTERIUM OXIDE

Time, hr.	Log $1/T$	C_{OH}, moles/l.	C_{OH}/C^0_{P-H}	$T_{0.25}$, hr.
$C_6H_5PO_2H_2$, 0.252 *M*; D_2O, 30.3 *M*; tetrahydrofuran, 406 mg./ml.				
0.15	0.156	0.193	0.77	2.1
0.40	0.174	0.216	0.86	
1.58	0.224	0.278	1.10	
3.82	0.280	0.347	1.38	
5.74	0.313	0.388	1.54	
23.9	0.393	0.487	1.93	
$C_6H_5PO_2H_2$, 0.253 *M*; D_2O, 40.6 *M*; tetrahydrofuran, 226 mg./ml.				
0.10	0.177	0.220	0.87	2.0
0.36	0.197	0.244	0.96	
1.67	0.252	0.312	1.23	
3.98	0.288	0.357	1.45	
5.90	0.318	0.394	1.56	
24.1	0.399	0.495	1.96	
$C_6H_5PO_2H_2$, 0.113 *M*; $C_6H_5PO_2HNa$, 0.97 *M*; D_2O, 49.9 *M*				
0.19	0.150	0.186	0.172	47
2.08	0.139	0.172	0.159	
4.57	0.139	0.172	0.159	
27.1	0.223	0.276	0.255	
51.7	0.337	0.418	0.386	
119.1	0.555	0.688	0.635	
$C_6H_5PO_2HNa$, 0.499 *M*; C_5H_5N, 5.85 *M*; D_2O, 30.2 *M*				
0.10	0.041	0.051	0.010	. . .
0.68	0.047	0.058	0.012	
18.5	0.064	0.079	0.016	
90.0	0.119	0.148	0.030	
138.0	0.137	0.170	0.034	
$C_6H_5PO_2HNa$, 0.975 *M*; OD^-, 0.022 *M*; D_2O solution				
2.80	0.018	0.022	0.023	190 (estd.)
19.7	0.051	0.063	0.065	
24.1	0.054	0.067	0.069	
93.6	0.119	0.147	0.151	
$C_6H_5PO_2HNa$, 0.929 *M*; OD^-, 0.105 *M*; D_2O solution				
0.16	0.044	0.055	0.059	67
2.35	0.061	0.077	0.083	
19.1	0.087	0.108	0.116	
23.6	0.094	0.117	0.126	
92.9	0.231	0.286	0.308	
$C_6H_5PO_2HNa$, 0.989 *M*; OD^-, 0.551 *M*; D_2O solution				
0.21	0.143	0.177	0.179	1
1.79	0.272	0.334	0.348	
18.6	0.367	0.455	0.450	
23.0	0.400	0.496	0.501	
92.3	0.796	0.997	1.008	

The rate of exchange was followed by changes in the transmittance in the 3350-cm.$^{-1}$ region—that is, by the rate of formation of OH in solutions of the Na–H salt or the H acid under various conditions of acidity. The results are presented in Table III. In the next to last column is given the amount of exchange taking place per initial mole of P–H in the solution. Where significant, the time in which one-fourth the initial P–H hydrogen atoms were exchanged is given in the last column. Approximately 1 *M* Na–H salt solutions in deuterium oxide were used in the compensating cells in these runs. Over a period of 6 weeks, no appreciable exchange took place in the solutions used in the compensating cell. As a matter of comparison, it also was found that no appreciable exchange took place in a 1 *M* solution of pure acetone in deuterium oxide over the same period.

Discussion

Deuterium exchange reactions have played leading roles in the elucidation of prototropic mechanisms in both carbon and phosphorus systems. These reactions, which have been utilized in the present and earlier[1] studies, are generally considered to be representative of reactions involving electrophilic attacks in so far as acid catalysis is concerned. It is this kind of attack which is of interest since the less stable tautomer in these systems contains a free electron pair on the phosphorus atom. The interpretation of hydrogen–deuterium exchange in this work is based on the assumption that the rates of exchange of hydrogen atoms bound to phosphorus and oxygen are different by many orders of magnitude. Justification for this assumption is found in a comparison of the exchange rates in neutral phosphites and hypophosphites with the very high rates of exchange observed in aliphatic alcohols.[17,18] Acidic hydrogen atoms in P–OH groups undergo extremely rapid exchange.[4] An exhaustive study of the kinetics of these reactions would be necessary to elucidate completely the details of the mechanism of the prototropic changes taking place in these systems. Consequently, only a qualitative picture of the mechanism of these changes is presented in this paper.

The extent of hydrogen–deuterium exchange can be followed by many methods: density measurements on the water removed from the reaction medium,[4] absorption at the P–D stretching frequency in the Raman spectra,[5,6] and, very recently, n.m.r. spectroscopy.[19,20] For accurate H/D ratios, mass spectrometry is often the method of choice. Less accurate, perhaps, but more informative in some respects, is infrared spectroscopy. This method not only allows one to measure the over-all extent of exchange through changes in band intensities, but also enables one to detect and, sometimes, to measure exchanges taking place simultaneously in various parts of the molecule. For example, phenylphosphinic acid contains at least three types of hydrogen atoms: O–H, P–H, and C–H. Each of these groups can be observed by means of the infrared

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(17) J. Hine and C. H. Thomas, *J. Am. Chem. Soc.*, **75**, 739 (1953).

(18) H. Kwart, L. P. Kuhn, and E. L. Bannister, *ibid.*, **76**, 5998 (1954).

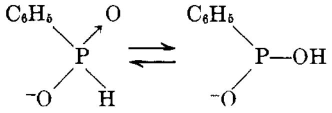
(19) Z. Luz and B. Silver, *ibid.*, **83**, 4518 (1961); **84**, 1095 (1962).

(20) P. R. Hammond, *J. Chem. Soc.*, 1365 (1962).

absorption bands at the appropriate frequencies. In this investigation, direct observation of the absorption at these P-H and P-D stretching frequencies in sodium phenylphosphinate was used as a qualitative measure of the exchange taking place in the phosphinic acid system. A more precise measure of the rate of exchange was obtained by following the increase in the intensity of the absorption at the O-H stretching frequency in deuterium oxide solutions containing the acid or its salt.

Since, in common with the majority of kinetic studies which have been made on hydrogen isotope exchange reactions, simultaneous exchange reactions can take place at points in the molecule which are not involved in the reaction of interest, the data are often at best interpreted on the basis of fractional exchange times, and only qualitative conclusions can be made regarding the mechanisms of the reactions involved.[21] This has been done in the present study. In place of more accurate assay methods, the use of the infrared spectrometer in this work not only has given information of sufficient accuracy but also has confirmed and, to a certain extent, identified the competing exchange reactions.

Aside from the interesting possibility of ring deuteration, several conclusions can be drawn from the results which are qualitatively in agreement with the previous work on the phosphonate.[1] There is the hint that perhaps the mechanisms suggested for the ester would also hold for the acid system. Two important points, however, are quite clear: (a) the exchange is catalyzed by both acids and bases, and (b) termolecular mechanisms involving both acids and bases are not important. The latter conclusion is established by the nearly complete absence of catalysis by the constituents of neutral buffers.[22] Since exchange is negligible over a period as long as 6 weeks in neutral or near-neutral aqueous solutions, it also may be concluded that the ionization constant for the P-H bond in this molecule must be exceedingly small. By the same token the postulation of an uncatalyzed equilibrium between the tautomers



does not appear to be well-founded. The findings that the amount of exchange in neutral solution is of the same order of magnitude as that found in acetone serves to place an upper limit on the rate of formation of enolic form in aqueous solutions of sodium phenylphosphinate. Schwarzenbach and Wittwer,[23] using a bromometric technique, found that a 10% aqueous solution of acetone contains about $10^{-4}\%$ enol, but did not estimate a rate of formation.

Earlier work[4-6,8,9] showed that hydrogen isotope exchange took place rapidly with hypophosphorous acid, slowly with phosphorous acid, and was absent in the salts of these acids. It was assumed, but not proved, that exchange was preceded by an acid-catalyzed prototropic transformation to the enolic forms. The independence of the rate of exchange on the concentration of the attacking reagent was not established in any of these reports, and in the present work there is only an indication of such independence. It is of interest, however, that exchange in the phenylphosphinic acid system more closely resembles that of hypophosphorous acid than it does phosphorous acid, and, in fact, most closely resembles that of the dialkyl phosphonates reported previously.[1]

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(21) S. Z. Roginsky, "Theoretical Principles of Isotope Methods for Investigation of Chemical Reactions," AEC Translation 2873, Academy of Sciences U.S.S.R. Press, Moscow, 1956, p. 191.

(22) C. G. Swain, *J. Am. Chem. Soc.*, **72**, 4578 (1950).

(23) G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 669 (1947).

Structure and Stereochemistry of Diels-Alder Adducts of Levopimaric Acid

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Levopimaric acid or rosin reacted with β-propiolactone and acrylic acid to form adducts, two of which have been isolated in pure form and are related to the adducts previously obtained with acrylonitrile. Structures of these substances and of the adducts formed with methyl acrylate and fumaric acid have been established.

Diene reactions of abietic-type resin acids with fumaric acid[6] and acrylonitrile[7] have been reported earlier from this laboratory, but structures of the products were left uncertain. In this paper we report the reaction of levopimaric acid or rosin with β-propiolactone, acrylic acid, and methyl acrylate. Structures of the major products as well as those of the adducts reported earlier[6,7] have been determined. In the special case of the adducts, levopimaric acid and acrylonitrile, our conclusions based on chemical evidence do not support the preference expressed by other workers on n.m.r. spectroscopic grounds.[8]

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(5) U. S. Public Health Predoctoral Fellow, 1962-1964.

(6) N. J. Halbrook and R. V. Lawrence, *J. Am. Chem. Soc.*, **80**, 368 (1958).

(7) N. J. Halbrook, J. A. Wells, and R. V. Lawrence, *J. Org. Chem.*, **26**, 2641 (1961).

(8) W. L. Meyer and R. W. Huffman, *Tetrahedron Letters*, **16**, 691 (1962).