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SPECTROSCOPIC STUDIES OF ORGANOPHOSPHORUS COMPOUNDS—III

THE CONSTITUTION OF THE PHOSPHINE-QUINONE ADDUCTS

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Abstract—The IR spectra of trimethylphosphine, phenyldimethylphosphine, triphenylphosphine and tri-*p*-tolylphosphine adducts of *p*-benzoquinone, toluquinone and 1,4-naphtho-quinone have been studied. On the basis of the absorption pattern corresponding to the out-of-plane bending of the hydrogens in the ring, the quinone adducts are shown to be ring-substituted compounds. The substitution has been shown to occur in the quinone ring of the naphthoquinone. The enhanced intensity absorptions in the 1400–1500 and 1220–1250 cm^{-1} regions and the colour of the compounds suggest that they are resonance hybrids of the phosphinmethylene and zwitterionic structures.

IN A previous paper it was shown that in the spectra of the addition compounds of alkylphosphines with carbon disluphide, the characteristic frequencies of the acceptor molecules are lost and a new absorption related to the new bond is present.[1] A similar phenomenon occurs in the quinone adducts of the alkyl and arylphosphines the constitution of which has not been determined although evidence[2–4] has been put forward in support of various structures which may be either ring-substituted or have a P—O—C linkage. More recently, however, the ylid structure, $R_3P{=}C{\cdot}CH{=}C(OH){\cdot}CH{:}CHC{=}O$, has been favoured.[5,6]

A distinction between the various structures is possible by means of IR spectroscopy and the spectra of the adducts of *p*-benzoquinone, 1,4-naphthoquinone and toluquinone with trimethylphosphine, phenyldimethylphosphine, triphenylphosphine and tri-*p*-tolylphosphine are reported. The compounds with trimethylphosphine, phenyldimethylphosphine and tri-*p*-tolylphosphine and all compounds with toluquinone are reported for the first time.

DISCUSSION

The characteristic spectral features of all the adducts are: (1) the shift of the P—C (aliphatic) stretching frequency to lower wavelengths, (2) the conspicuous absence of the strong absorptions corresponding to the carbonyl groups of the quinones at 1680 cm^{-1}, (3) the appearance of strong bands at 1420–1450 cm^{-1} and 1380–1400 cm^{-1} and (4) the appearance of a systematic change in the absorption pattern associated with various types of aromatic substitution in the 1600 to 1400 cm^{-1} and 1000 to 700 cm^{-1} regions.

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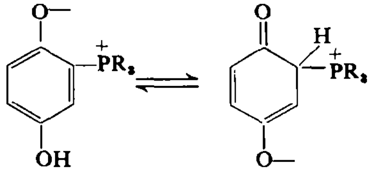
[1] M. A. A. Beg and M. S. Siddiqui, *Canad. J. Chem.* **43**, 608 (1965).
[2] A. Shönberg and A. F. A. Ismail, *J. Chem. Soc.* 1374 (1940).
[3] F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.* **78**, 5614 (1956).
[4] H. Hoffmann, L. Horner and G. Hassel, *Chem. Ber.* **91**, 58 (1958).
[5] C. Osuch, J. E. Franz and F. B. Zienty, *J. Org. Chem.* **29**, 3721 (1964).
[6] G. Aksnes, *Acta Chem. Scand.* **15**, 692 (1961).

The trimethylphosphine and phenyldimethylphosphine adducts are useful in the elucidation of their structure since it is possible to establish quaternization of the phosphorus atom by: (1) the shift of the P—C stretching frequency to lower wavelengths and (2) the splitting of the methyl rocking band, as observed previously.[1] The *p*-benzoquinone adducts of the phosphines absorb strongly at 1450–1420 cm^{-1} and also at 1380–1400 cm^{-1}. Those with toluquinone absorb at 1455–1445 cm^{-1} and also at 1370–1380 cm^{-1}. The *p*-napthoquinone adducts absorb at 1545–1540 cm^{-1} and also at 1400 cm^{-1}. Similarly triphenylphosphine and tri-*p*-tolyphosphine record strong absorptions at 1465–1450 cm^{-1} and at 1380–1400 cm^{-1} for adducts with I, at 1430–1450 cm^{-1} and also at 1405 cm^{-1} with II and at 1415–1460 cm^{-1} and at 1380 cm^{-1} for compounds with III.

These absorptions are more intense than expected for the various modes of ring stretching vibrations absorbing in this region and they may be assigned to C=O stretching vibration for the following reasons: According to our own observations with other addition compounds, there is usually a shift in the characteristic frequencies of the acceptor molecules to higher wavelengths. Because of the change in the symmetry of the quinone moiety, the degeneracy in the C=O absorption would be removed and a spliting with a large shift would be observed. It might be noted that in all the compounds there is splitting in the bands and, therefore, the formation of an addition compound is supported.

As metal chelates of *β*-diketones[7] and the ionized fatty acids exhibit similar phenomena, it is possible that the structure of the quinone compounds involves a resonance between forms I and II.



I II

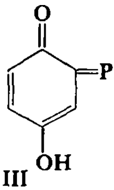
A reduced double bond character is indicated in the overall structure which also involves an ionic C—O. The degeneracy in the C=O character has been removed with a change in the ionic radius of the ionized oxygen. The resonance form would modify the character of the C=O and C—O bonds and would behave similarly to the ionized carboxylic acids. The split bands may be assigned to the C=O and $C—O^-$ stretching vibrations. Because of the quaternization of the phosphorus atom, as seen earlier, it may be suggested that this $C—O^-$ is possibly due to the zwitterionic nature of the addition compound.

In all cases another strong band occurs at 1220–1250 cm^{-1} and in the carboxylic acids, a medium intensity absorption is at 1320 cm^{-1}. It is suggested that the strong bands in the 1230–1180 cm^{-1} region are due to P=C in the phosphinmethylenes[8] and that the highly coloured nature of the compounds may be interpreted in terms of an ylid structure (III.)

In each case, a systematic change occurs in the pattern of absorption with respect

[7] K. Nakanishi, *Infra-Red Absorption Spectroscopy*. Holden-Day, U.S.A. (1963).

[8] M. A. A. Beg and Samiuzzaman, *Canad. J. Chem.* in press.



III

to the parent quinone. The spectrum of the addition compound of trimethylphosphine and *p*-benzoquinone listed in Table 1 has strong bands at 3450 and 3225 cm^{-1} corresponding to the hydroxyl group. Absorptions characteristic of a 1,2,4-substitution are noted in the 1600–1400 cm^{-1} region. As there is another set of strong absorptions at 1215–1255 cm^{-1} and at 1060 cm^{-1} which are not present in either phosphine or quinone, it has been suggested that these absorptions are due to the C—O stretching and O—H deformation vibrations.[9] Strong absorptions, due to CH_3 rocking, occur at 975, 960 and 955 cm^{-1}. This splitting of the CH_3 rocking mode, as pointed out earlier,[1] is characteristic of a reduced symmetry. The medium intensity sharp band at 868 cm^{-1} and a strong band at 800 cm^{-1} are characteristic of a 1,2,4-substitution[9] indicating that substitution in the aromatic ring has taken place. The bands at 770 and 735 cm^{-1} are assigned to P—C antisymmetric stretching and the band at 710 cm^{-1} to the C—H out-of-plane or ring deformation modes.

The spectrum of the compound formed by trimethylphosphine and toluquinone listed in Table 3, is similar to that of the *p*-benzoquinone derivative. Substitution possibly occurs at position 5 since the pattern corresponding to a 1,2,4,5-substitution ring is noted. The absorption due to the out-of-plane bending of two isolated hydrogens occurs as an intense band at 872 cm^{-1}. The CH_3 rocking, the C—O and O—H stretching and the P—C antisymmetric stretching vibrations occur at almost the same wavelengths as in the benzoquinone adducts discussed above.

The IR spectrum of the 1,4-naphthoquinone addition compound is in agreement with substitution in the aromatic ring system. The band at 772 cm^{-1} in naphthoquinone is not shifted in the addition compound. Since this absorption corresponds to a four adjacent hydrogen system, substitution must occur in the ring which has the carbonyls. A medium intensity band at 865 cm^{-1} probably corresponds to the absorption of an isolated hydrogen. There are a few extra bands in the spectrum of this compound and these are listed with tentative assignments in Table 5.

In order to characterize the absorptions of the arylphosphine adducts, the discussion of the spectra of the compounds with phenyldimethylphosphine may be helpful. In the latter group of compounds, the methyl rocking vibrations are split into two groups: one between 950 and 900 and the other between 1050 and 980 cm^{-1}. It is also found that the 750 cm^{-1} band corresponding to the out-of-plane bending of five adjacent hydrogen atoms of the phenyl group in phenyldimethylphosphine is split into two bands at 700 and 735 cm^{-1}. Furthermore, the X-sensitive vibration (mode q according to Whiffen) is shifted to 1120 cm^{-1}. These phenomena were also noted in the phenyldimethylphosphonium[1] dithioformate and the phosphonium compounds.[1,10] The medium intensity absorption at 770 cm^{-1} due to the P—C antisymmetric stretching further supports the structural similarity of these with the phosphonium compounds.

The characteristic feature of the compounds with triphenyl and tri-*p*-tolylphosphines

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[9] L. Horner and H. Oediger, *Liebigs Ann.* **627**, 142 (1959).

[10] L. J. Bellamy and R. F. Branch, *J. Chem. Soc.* 4491 (1954).

is a series of split bands in the 800–700 cm^{-1} region in addition to the bands mentioned earlier. Splitting of the bands in the above region is known to be due to quaternization.[10] In the case of the *p*-tolylphosphine compounds, the intensity and shape of the 1615 cm^{-1} band is similar to that of the corresponding phosphonium compounds in which the absorption due to the out-of-plane bending of an isolated hydrogen in the quinone ring is a medium intensity band at 860 cm^{-1}. In the methylphosphines this could be confused with the CH$_3$ rocking mode. The absorption at 860 cm^{-1} is therefore easily assigned. The other bands and their assignments are listed in Tables 2, 4 and 6.

On the basis of the pattern and characteristics of the various absorptions it may be assumed that the structure of the addition compound formed with the quinones is such that there is substitution in the quinone ring and that there is quaternization of the phosphorus atom. The structure of the compound formed may be either zwitterionic or of the ylid type. A distinction between the two types might be quite difficult. From the evidence available it may be concluded that there is a good deal of charge delocalization and it is quite likely that these addition compounds are the resonance hybrids of the zwitterionic phosphonium compound and the phosphinemethylene, having a larger contribution of the former.

TABLE 1. VIBRATIONAL FREQUENCIES OF THE *p*-BENZOQUINONE ADDUCTS OF Me$_3$P AND PhMe$_2$P

	Me$_3$P	PhMe$_2$P
O—H Stretch	3450 m	3450 m
	3225 m	
C—H Aromatic stretch	2995 m	3030 m
		2940 m
C—H Aliphatic stretch	2880 m	2900 m
Ring stretching skeletal vibrations	1590 w	1587 w
	1565 w	1560 w
	1515 w	1515 w
C—H Antisymmetric bending + C=O stretch	1456 s	1445 s
	1410 vs	1420 vs
	1380 s	1400 vs
C—H Symmetric bending and/or C—C skeletal	1310 m	1310 s
	1290 m	1295 m
		1285 m
C—O Stretch, P=C stretch or O—H deformation	1255 s	1255 vs
	1240 s	1240 vs
In-plane hydrogen deformation modes	1215 s	1215 s
	1115 s	1135 s
		1125 s
O—H Deformation	1060 s	1055 s
Ring breathing		1003 w
CH$_3$ Rock	975 s	955 s
	960 s	945 m
	955 s	930 vs
	905 w	905 m
Out-of-plane bending of isolated hydrogen	868 m	870 s
Out-of-plane bending of two adjacent hydrogens	835 w	840 s
	815 m	805 vs
	800 vs	
P—C Antisymmetric stretch	770 m	770 s
Out-of-plane bending of five hydrogens	735 w	732 s
Out-of-plane ring deformation	710 m	701 s
		672 m

TABLE 2. VIBRATIONAL FREQUENCIES OF THE *p*-BENZOQUINONE ADDUCTS OF Ph_3P AND $(p\text{-tol})_3P$

	Ph_3P	$(p\text{-tol})_3P$
O—H Stretch	3135 m	3450 m
C—H Aromatic stretch	3135 m	3030 m
	3015 m	3000 s
	2950 m	2940 m
		2860 m
Ring stretching vibrations	1600 m	1615 s
	1585 w	1560 w
	1565 w	1550 w
	1545 s	1540 m
	1520 m	1505 m
	1496 s	1480 s
	1480 s	
Ring stretching +C═O stretch	1450 vs	1465 vs
	1405 s	1400 vs
		1380 vs
Ring stretching	1320 m	1325 m
		1315 m
		1300 w
C—O Stretch P═C stretch or O—H deformation	1265 s	1275 sh
	1240 s	1250 vs
	1235 s	1240 s
In-plane hydrogen deformation	1215 s	1215 m
	1195 s	1195 s
	1165 m	1155 w
X-Sensitive vibration	1110 vs	1110 vs
In-plane hydrogen deformation	1070 w	1095 vs
O—H Deformation	1050 m	1070 w
In-plane hydrogen deformation	1030 w	1040 s
		1020 m
Ring breathing	1005 m	
	910 m	910 m
Out-of-plane bending of isolated hydrogen	865 m	855 m
Out-of-plane bending of two adjacent hydrogens	833 m	827 s
	806 m	810 vs
		800 s
Out-of-plane deformation of five hydrogens	752 s	730 w
	730 m	725 w
	720 vs	715 m
X-Sensitive vibration	710 vs	710 m
		700 s
Out-of-plane ring deformation	689 vs	687 w

TABLE 3. VIBRATIONAL FREQUENCIES OF THE TOLUQUINONE ADDUCTS OF Me_3P AND $PhMe_2P$

	Me_3P	$PhMe_2P$
O—H Stretch	3450 m	3425 m
	3165 m	
C—H Aromatic stretch	3015 m	3005 m
C—H Aliphatic stretch	2925 m	2907 m
Ring stretching vibrations	1605 w	1610 w
	1550 w	1590 w
	1500 w	1560 w
	1455 vs	1510 w
		1445 s
C—H Antisymmetric bending +C=O stretch	1430 vs	
	1412 s	1420 s
C—H Symmetric bending +C—O^- stretch	1387 vs	1380 vs
	1370 vs	1345 msh
	1315 m	
	1290 m	
C—O Stretch or P=C stretch or O—H deformation	1250 vs	1250 vs
		1235 vs
C—H In-plane vibrations *gem*-dimethyl	1212 vs	1193 vs
	1153 m	1170 s
	1140 m	1143 m
X-Sensitive		1120 m
O—H Deformation	1050 m	1042 m
C—H In-plane vibrations		1031 m
Ring breathing		1000 w
CH_3 Rock	1005 m	943 m
	972 s	930 m
	965 m	918 m
	958 s	
Out-of-plane bending of isolated hydrogen	872 s	868 m
	820 m	830 m
		806 w
P—C Antisymmetric stretch	772 m	760 m
	740 m	
C—H Out-of-plane deformation of five hydrogens		730 s
Out-of-plane ring deformation	694 m	692 s

TABLE 4. VIBRATIONAL FREQUENCIES OF TOLUQUINONE ADDUCTS OF Ph_3P AND $(p\text{-tol})_3P$

	Ph_3P	$(p\text{-tol})_3P$
O—H Stretch	3333 m	3390 s
C—H Aromatic stretch	3135 m	3135 vs
	3040 vs	3035 vs
	2940 vs	2960 vs
Ring stretching	1600 m	1610 s
	1582 w	1580 w
	1560 w	1563 w
	1500 m	1510 m
	1475 s	1500 m
		1480 w
Ring stretching +C=O and C—O$^-$ stretch	1440 msh	1450 s
	1430 vs	1435 s
	1405 vs	1405 vs
Ring stretching	1370 m	1375 m
	1333 w	1335 w
	1310 w	1340 w
	1280 w	1312 w
		1282 w
C—O Stretch or P=C stretch or O—H deformation	1225 s	1225 s
In-plane hydrogen deformation	1198 vs	1205 vs
	1160 w	1198 vs
	1150 w	1150 w
X-Sensitive	1110 vs	1110 vs
In-plane hydrogen deformation	1035 m	1040 m
	1025 m	1020 w
	1015 w	
Ring breathing	996 m	
Out-of-plane bending of isolated hydrogen	885 m	880 m
	880 m	870 m
Out-of-plane bending of two adjacent hydrogens		827 w
		807 vs
Out-of-plane C—H deformations	755 vs	755 s
	745 vs	750 s
		745 s
Out-of-plane deformation of five hydrogens	730 vs	
	720 vs	
X-Sensitive		708 m
Out-of-plane ring deformation	695 vs	670 vs
	690 vs	

Table 5. Vibrational frequencies of the 1,4-naphthoquinone adducts of Me$_3$P and PhMe$_2$P

	Me$_3$P	PhMe$_2$P
O—H Stretch	3450 s	3450 m
	3205 s	
C—H Aromatic stretch	3070 s	3070 m
		3033 m
C—H Aliphatic stretch	2985 s	2941 m
	2900 w	
Ring stretching vibrations	1615 m	1615 m
	1592 s	1540 s
	1545 vs	1510 m
	1475 w	
	1460 w	
C—H Antisymmetric bending +C=O and C—O$^-$ stretch	1430 s	1440 s
	1400 vs	1420 s
		1400 s
C—H Symmetric bending	1340 s	1325 s
	1315 m	1290 s
	1290 w	
	1270 m	
C—O Stretch or P=C stretch or O—H deformation	1240 s	1245 s
	1215 w	1205 m
C—H In-plane vibration	1156 m	1155 m
		1150 m
X-Sensitive vibration		1120 m
C—H In-plane vibration	1085 w	1080 w
O—H Deformation	1070 m	1070 m
CH$_3$ Rock	1025 m	1025 m
	970 s	940 m
	962 s	930 s
	977 w	
Out-of-plane bending of isolated hydrogen	860 m	872 m
		858 m
Out-of-plane bending of four adjacent hydrogens	840 m	840 m
	813 s	815 m
P—C Antisymmetric stretch	772 s	766 s
C—H Out-of-plane deformation of five adjacent hydrogens		755 s
C—H Out-of-plane deformation of four adjacent hydrogens	727 m	732 s
		725 s
Out-of-plane ring deformation	688 m	697 m
		685 s

Table 6. Vibrational frequencies of the 1,4-naphthoquinone adducts of Ph$_3$P and (p-tol)$_3$P

	Ph$_3$P	(p-tol)$_3$P
O—H Stretch	3390 m	3450 m
C—H Aromatic stretch	3030 m	3075 m
	2950 m	3000 m
	2850 m	2940 m
		2850 s
Ring stretching	1610 w	1610 s
	1595 w	1570 w
	1580 vw	1540 s
	1540 s	
	1505 w	1505 m
	1487 w	1460 s

TABLE 6 (*Cont.*)

Ring stretching +C=O stretch	1465 vs	
	1445 vs	1450 vs
	1430 vs	
C—H Symmetric bending +C—O$^-$ stretch	1418 vs	1415 vs
	1380 s	1380 s
Ring stretching or C—H symmetric bending	1325 s	1340 s
	1320 s	1320 s
C—O Stretch or P=C stretch or O—H deformation	1255 m	1255 s
C—H In-plane vibrations	1245 m	1245 s
	1220 m	1212 m
	1185 m	1196 s
	1156 w	
	1147 m	1150 s
X-Sensitive	1105 vs	1105 vs
C—H In-plane vibration	1080 m	1087 m
O—H Deformation	1070 s	1070 s
In-plane C—H deformation	1020 m	1020 s
Ring breathing	1000 m	
Out-of-plane bending of isolated hydrogen	870 s	875 m
		840 w
Out-of-plane bending of two adjacent hydrogens	817 m	807 vs
Out-of-plane bending of four adjacent hydrogens	770 m	
	775 m	767 vs
	750 m	
Out-of-plane bending of five hydrogens	745 m	
	725 vs	725 s
X-Sensitive	712 vs	709 m
	690 s	
Out-of-plane ring deformation	685 vs	692 s

EXPERIMENTAL

The phosphines were prepared by the Grignard method and their quinone adducts obtained by mixing ethereal solutions of the reactants in 1:1 molar proportions. The 1:1 adducts crystallized on standing for 1–3 hr and were purified after washing with ether by recrystallization from a MeOH–ether mixture. The purity of the products was checked from their m.ps and analyses were carried out by Alfred Barnhardt. The trimethylphosphine adducts of *p*-benzoquinone (I) toluquinone (II) and *p*-naphthoquinone (III) are all yellowish brown amorphous solids which melt with dec at 280–283°, 175–178° and 220–225° respectively. The compound of phenyldimethylphosphine with I is yellow, m.p. 270–273° (dec), with II it is pale yellow, m.p. 234–236° (dec) and with III it is dark yellow, m.p. 135° (dec). The derivative of triphenylphosphine with I is yellow, m.p. 250–253° (dec), with II it is yellowish red, m.p. 159–161° (dec) and with III it is yellow, m.p. 161–163° (dec). The compound of tri-*p*-tolylphosphine with I is yellow, m.p. 200–205° (dec), with II it is yellowish red, m.p. 255–260° (dec) and with III it is yellowish brown, m.p. 187–190° (dec).

The IR spectra were recorded on a Beckman model IR-5 and Perkin-Elmer model 234 Spectrophotometer, using both nujol mulls and KBr pellets. The absorptions are listed in Tables 1–6.