

SPECTROSCOPIC STUDIES OF ORGANOPHOSPHORUS COMPOUNDS

Part V.—Ultraviolet Spectra of Phosphine-*p*-Benzoquinone Adducts

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The UV spectra of phosphine-*p*-benzoquinone adducts have been studied under acid and basic conditions. The position of the bands is susceptible to changes in pH. In the acid medium there is a decrease in intensity of the $n \rightarrow \pi$ transition, as in ionized carboxyls while in the basic medium, there is a red shift with an enhancement in intensity, which is characteristic of phenols. In the phosphonium dithioformates also similar variations are noted. These observations suggest that the betaine structure is favoured in the acid medium while the phosphinemethylene structure is dominant in the basic medium.

The compounds obtained on the admixture of phosphines and *p*-quinones have almost the same features in the IR region of the spectra, i.e. the quinone carbonyl frequency shifts considerably to lower frequencies. However, there is also the evidence of a P=C bond required for a phosphinemethylene structure.¹ The spectra in the visible and UV region also have typical features and it is found that the shifts occur with variation in the pH of the solution. This paper describes such variations and an attempt has been made here to interpret them in terms of their structure.

Like the IR, the characteristic features of the UV spectra of the quinones are well known² and it is possible to assign the band positions to the quinonoid or benzenoid absorptions. The spectrum of *p*-benzoquinone has three main maxima at (I) 240 m μ , (II) 280-320 m μ and (III) 420-500 m μ .² For monosubstituted quinones, band I is split into two and the position is shifted by about 10 m μ ; band II by 25 m μ and band III either does not appear or if it does so it is very weak with no change in position. These bands are, of diagnostic value and it is found that the maxima recorded here correspond to the substituted quinones extending the idea of Ramirez to phosphines in general, that they react with quinones having low oxidation potential by carbon attack.³

The substitution may give either a betaine or a phosphinemethylene. The latter would give an *o*-quinonoid effect in which case there would be a red shift by about 20 m μ with a decrease in intensity from 4.2 to 3.3. On the other hand, a dipolar ionic structure demands the normal position for a trisubstituted aromatic ring. In the present case it is found that the positions are shifted and the intensity is also lowered.

Band I occurs in these compounds at 257 ± 3 m μ . Another band occurs at 265 ± 2 and a third at 272 ± 1 m μ . This band system is absent in the trimethylphosphine analogue and since the aryl-

phosphonium compounds have a similar band pattern it should be safely assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic rings. Band II occurs at 320 m μ . While band III is located between 430 and 460 m μ . In the aromatic phosphines there is a tendency to shift this absorption to higher wavelengths. In most of the compounds, a weak IV band also occurs at 580 to 700 m μ .

The spectra of the present series of compounds have features similar to the other tautomeric mixtures like the pyridine carboxylic acids where the band position and intensity are dependent on the pH of the medium.⁴ Here it is observed that the spectra in the acid medium are similar to those of the neutral solutions and in the basic medium there is a considerable alteration in the shape and intensity of the bands.

Supposing that the phosphinemethylene structure is depicted by the neutral solution, the lower pH would have no effect on the phenolic —OH since the zwitterionic nature would be favoured by the acid medium and it will result in the ionization of the carbonyl group. The decrease in intensity in the case of pyridine carboxylic acids has been interpreted in terms of the removal of proton from the carboxyl group. Since we also observe a decrease in intensity of band III which is due to the $n \rightarrow \pi$ transition⁵ we can take it as an evidence of the formation of the betaine in the acidic media.

In the basic medium band II is totally absent and the absorption intensity is very much higher than in neutral solutions. The phenolic —OH ionizes in the basic medium and an increase in intensity with a red shift is characteristic of the spectra of the phenols, so that the spectra are those of the anion:

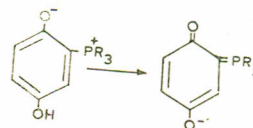


TABLE I.—UV SPECTRA

Phosphine		Band I				Band II		Band III			
		<i>Phosphine-p-Benzoquinone Adducts</i>									
Trimethyl phosphine	N μ	242	256				320	435	677		
	pH 6 ϵ	7500	4300				5850	420	100		
	A μ		260				312	421	700		
	pH 2 ϵ		800				7650	290	128		
	B μ		266	273	283		x	430	700		
	pH 8 ϵ		8280	7400	5700		x	438	130		
Phenyl dimethyl phosphine	N μ		256	263	271		320	460	580		
	pH 6 ϵ		3300	2400	2100		4860	350	140		
	A μ			265	272		317	470	540		
	pH 2 ϵ			5600	1650		5600	60	40		
	B μ		256	263	271	286		x	450	470	480
	pH 8 ϵ		8350	7900	6960	4850	x	360	240	200	
Triphenyl phosphine	N μ		260	266	272		329	360	415	690	
	pH 6 ϵ		5200	4930	1500		4650	2050	190	60	
	A μ		261	267	273		323		400	705	
	pH 2.5 ϵ		3850	4000	3700		6000		70	55	
	B μ			264	267			367	430	700	
	pH 8 ϵ			8800	8000			3100		50	
<i>p</i> -Tritolyl phosphine	N μ		257	264	272		320		432	455	675
	pH 6 ϵ		8500	7600	6850		6700		1627	1360	639
	A μ		257	264	273		320		430		675
	pH 3 ϵ		7500	6500	5100		5300		824		288
	B μ				272	290		x	430		655
	pH 8 ϵ				8150	6000	x		1351		433
		<i>p-Benzoquinone</i>									
	N μ	239	242	285		310	355		425	445	
	pH 6 ϵ	14700	15100	3150		800	44		31	27	
	A μ	239	242			310	355		425	445	
	pH 2 ϵ	14500	14600			700	63		33	28	
	B μ		255,	272,	298	315	357		420	525	
	pH 8 ϵ		8850	9400	5000	4000	113		59	14	
		<i>Hydroquinone</i>									
	N μ	224		291			x			x	
	pH 6 ϵ	6780		3520			x			x	
	A μ	224		291			x			x	
	pH 2 ϵ	6800		3570			x			x	
	B μ		240	270		300	307	315	395	420	
	pH 8 ϵ		8200	5050		2800	3000	2900	39	38	
		<i>Carbon Disulphide Adducts</i>									
Trimethyl phosphine	N μ			273	297		345	353		x	
	pH 6 ϵ			633	1016		275	285		x	
	A μ			265	271			353		x	
	pH 3 ϵ			58	17			145		x	
	B μ		258			299		353		x	
	pH 8 ϵ		810			810		200		x	
Phenyl dimethyl phosphine	N μ			263	270	285	310	353	370	380	x
	pH 6 ϵ			2166	1767	700	433	18	17	15	x
	A μ		252	257	263	269		x			x
	pH 3 ϵ		1000	1150	1157	800		x			x
	B μ		255	263	270	295			370		x
	pH 8 ϵ		5966	5700	5467	3095			35		x

A== acidic, B= basic, N= neutral

Since the spectra have been recorded in a polar medium it is natural to expect that the spectrum would be that of the dipolar form. The compounds being already in the dipolar form in the ground state a reorientation of the dipole moment would be favoured with a change in the media. This usually results in a blue shift as is observed from Table 1.

The 320 $m\mu$ band seems to be characteristic of the dipolar form. This appears in the phosphine-carbon disulfide adducts which have been shown to exist as the phosphonium dithioformates,⁶ and also in benzoyacetanilide where the band at 323 $m\mu$ has been assigned to the anion.⁷ The absence of this band possibly does indicate the favouring of the phosphinemethylene structure shown above.

Finally, a comparison of these spectra with that of the quinone and hydroquinone under similar set of conditions shows that in the basic medium the spectra of these compounds are quite similar but for the difference in intensity. However, in the neutral and acid media, differences are to be noted in that the intensity of the bands decreases by about 100 in the acidic medium, so that in *p*-benzoquinone also, the carboxyl group ionizes to a certain extent. This, however, is not the case in hydroquinone.

The spectra of quinone, hydroquinone and the phosphonium dithioformates serve to characterise the spectra of the phosphine-quinone adducts which are betaines in the methanol and acidic

methanol solutions but are phosphinemethylenes in the basic medium.

Experimental

The compounds were prepared as described earlier.

The spectra were run on a Beckman DK-2 spectrophotometer using alcoholic solutions. The acid and basic media were obtained by adding a drop of hydrochloric acid or sodium hydroxide to the neutral solution. The pH of the solution so obtained was measured by means of a pH meter.

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