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C. Dennis Hall^a; Peter Speers^a; Rosa Valero^b; Francisco Perez Pla^b; Donald B. Denney^c

^a Department of Chemistry, King's College, London ^b Department of Physical Chemistry, University of Valencia, Burjassot, Spain ^c Department of Chemistry, Rutgers, The State University of New Jersey, Piscataway, N.J., U.S.A.

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THE KINETICS AND MECHANISM OF THE REACTION OF ONIUM CYCLOPENTADIENYLIDES WITH TETRAHALO- *p*-BENZOQUINONES

C. DENNIS HALL* and PETER SPEERS

Department of Chemistry, King's College, Strand, London WC2R 2LS

ROSA VALERO and FRANCISCO PEREZ PLA

Department of Physical Chemistry, University of Valencia, Burjassot, Spain,

DONALD B. DENNEY

*Department of Chemistry, Rutgers, The State University of New Jersey,
Piscataway, N.J., 08903, U.S.A.*

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The reaction of triphenylphosphonium cyclopentadienylide (1) with halogen-substituted *p*-benzoquinones (4) is shown to give a new class of dipolar (zwitterionic) dyes (5) containing phosphorus. The general structure of these molecules has been investigated by a combination of mass spectrometry and multinuclear (^1H , ^{13}C and ^{31}P) nmr using the specialist techniques of DEPT spectroscopy, homonuclear (COSY) and heteronuclear 2-D nmr. In addition, stopped-flow (uv/visible) techniques have been used to study the kinetics of the reactions and hence demonstrate that the rate-limiting step is nucleophilic addition of the ylid nucleophile to the quinone, followed by a rapid loss of halide ion. This mechanism follows the classical pattern associated with nucleophilic aromatic substitution in activated aryl halides.

Key words: dipolar dyes containing phosphorus.

INTRODUCTION

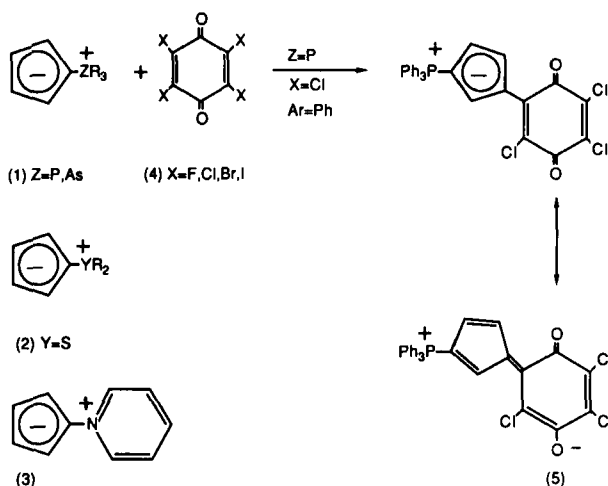
Several classes of dipolar (zwitterionic) dyes have been known for many years^{1,2} but these compounds have recently received considerable attention as a result of their electrical properties and potential value as organic conductors and/or semiconductors.^{3,4} Most of these dipolar species involve electron delocalization between N and O with the latter element as the negative end of the dipole. We were therefore intrigued to observe that the reaction of triaryl 'onium ylids,⁵ (1), dialkyl 'onium ylids (2)⁶ and the pyridinium cyclopentadienylide (3)⁷ with halogen-substituted *p*-benzoquinones (4) in organic medium (eg: CH_2Cl_2 or toluene) gave intense blue solutions (λ_{max} , 650–720 nm, $\epsilon = 10^3$ – 10^4) which changed abruptly to yellow on protonation with, for example, HClO_4 . The very broad visible absorption bands observed with these compounds suggested that they might be molecular complexes exhibiting a charge-transfer band. On the other hand, distinct changes in the i.r. and nmr spectra of mixtures of 'onium ylids and *p*-benzoquinones were not typical of molecular complexes⁸ but instead, suggested

* Author to whom correspondence should be addressed.

σ -bond formation. The objective of this paper therefore, is to report the isolation and characterisation of the blue compound formed from triphenylphosphonium cyclopentadienylide (1, Y = P) and chloranil (4, X = Cl) together with the kinetic data which defines the mechanism of the reaction.

RESULTS AND DISCUSSION

The reaction between (1, Y = P, 2 mole) and chloranil (4, X = Cl, 1 mole) in CH_2Cl_2 at 25° and at a concentration of $ca\ 1 \times 10^{-2}\text{ M}$ in (1) was complete within seconds and the mixture was subjected immediately to flash chromatography on silica using CH_2Cl_2 as eluant. The brilliant blue compound separated cleanly from a minor purple band (as yet, uncharacterised) and protonated (1) and after removing the solvent, the dark blue crystalline residue was rechromatographed, isolated and recrystallised to give dark blue lustrous crystals of the product (5).†



The FAB mass spectrum in a glycerol matrix gave a parent peak at 537 ($[M + 1]^+$ for $\text{C}_{29}\text{H}_{18}\text{O}_2\text{Cl}_3\text{P}$ at 535 + two mass units due to the reduction of the quinone unit by glycerol) plus peaks at 539, 541 and 543 in the ratio required (8:4:2:1) for the two isotopes of chlorine within the molecule. The ^{31}P nmr spectrum in CH_2Cl_2 at 101.4 MHz gave a single sharp peak at 15.03 ppm, very close to that of the parent ylid at 13.6 ppm. Titration with HClO_4 , in glacial acetic acid as solvent and using crystal violet as indicator gave an equivalent weight of $ca\ 530$ and clearly therefore, the compound is a phosphonium ylid rather than a phosphonium salt. The electronic spectrum (in CH_3CN) showed a very broad adsorption at $\lambda_{\text{max}} = 680\text{ nm}$ ($\epsilon = 4,550\text{ l mol}^{-1}\text{ cm}^{-1}$) typical of a methionine-type dye.^{1,2}

The structure of (5) however, was deduced from its high resolution ^1H (at 250 MHz and 360 MHz) and ^{13}C (at 90.6 MHz) nmr spectra. The COSY spectrum in CD_2Cl_2 at -30° showed three cyclopentadiene protons as multiplets at 7.05, 6.94, and 6.36 ppm and the signal at 6.94 showed two weak couplings with the

† Found: C, 64.45; H, 3.85; P, 5.18 and Cl, 19.41%

$\text{C}_{29}\text{H}_{18}\text{O}_2\text{Cl}_3\text{P}$ requires: C, 64.98; H, 3.39; P, 5.28; Cl, 19.86%

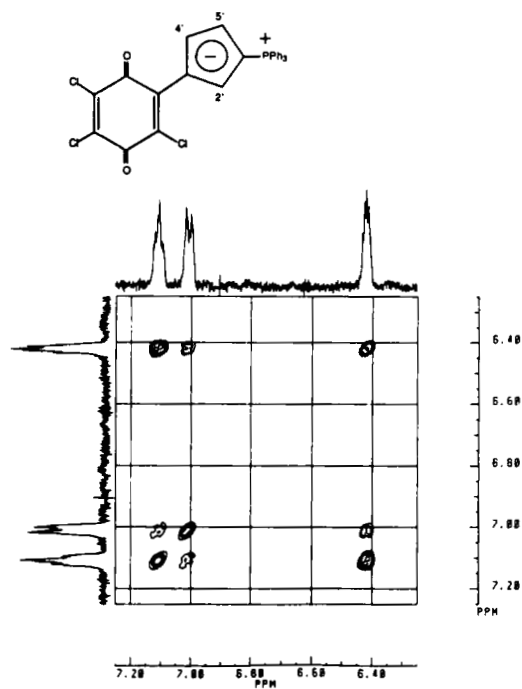


FIGURE 1 The COSY nmr spectrum of (5) in CD₂Cl₂ at -30°C showing the cyclopentadiene protons (2', 4', and 5') only; Bruker AM 360.

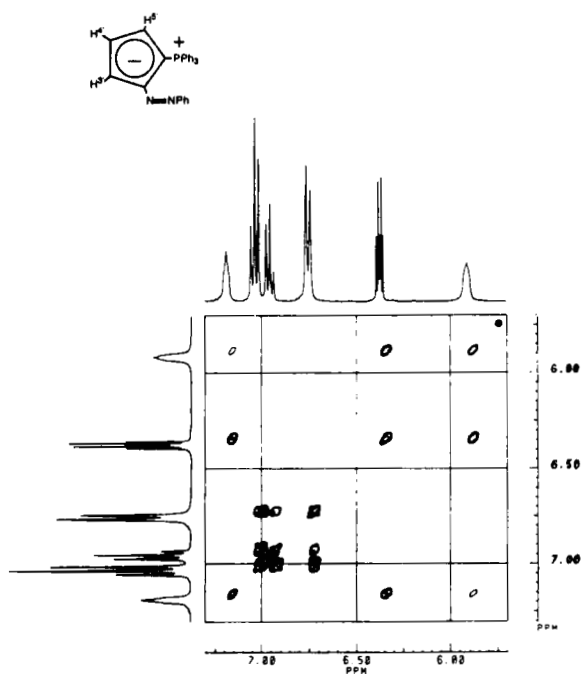
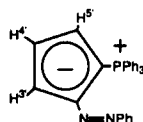


FIGURE 2 The COSY nmr spectrum of (6) in CD₂Cl₂ at ambient showing the cyclopentadiene protons (3', 4', and 5') and the aromatic region; Bruker AM 360.

other two cyclopentadiene protons whereas the remaining two signals (at 7.05 and 6.36 ppm) each showed one strong and one weak coupling (Fig. 1). This is only consistent with substitution in position 3 of the cyclopentadiene ring since substitution in position 2, as established chemically for (6)¹⁰, would give two strong couplings for H-4 (J_{34} and J_{45}); this coupling pattern is in fact found in the COSY spectrum of (6). (Fig. 2). The complete assignment of ^1H and ^{13}C signals for (5) derived from COSY, DEPT, and carbon-proton 2-D correlation spectra is shown in Table I.



(6)

Kinetic data derived from stopped flow techniques monitoring the appearance of (5) at 680 nm shows that the reaction is first-order in both (1) and (4) and that the rate of reaction for a range of (4) follows the sequence $\text{X} = \text{F} > \text{Cl} > \text{Br} > \text{I}$

TABLE I
 ^1H and ^{13}C n.m.r. data on (5) in CD_2Cl_2 at -30°C

^1H n.m.r. S (ppm)	Number of protons	Assignment	J Values (Hz)
ca 7.6 (mult)	15	2''-6''	—
7.05 (sextet)	1	5'	$J_p = 4.9$; $J_4 = 4.7$; $J_2 = 2.1$ $J_p = 6.3$; $J_4 = 2.1$ $J_p = 2.5$
6.94 (sextet)	1	2'	
6.36 (quintet)	1	4'	
^{13}C n.m.r. S (ppm)	Dept	Assignment	J_p (Hz)
181.1	0	C-1	0
172.7	0	C-4	0
143.0	0		
141.2	0	C2, 3, 5	0
140.3	0		
135.74	+	C-4''	0
135.69	+	C-2'', C-6''	10.0
133.1	+	C-2'	15.8
131.5	+	C-3'', C-5''	12.5
124.7	0	C-1''	90.6
123.90	0	C-6	0
123.98	0	C-3'	20.3
123.69	+	C-5'	13.6
121.4	+	C-4'	13.6
95.4	0	C-1'	110.0

TABLE II

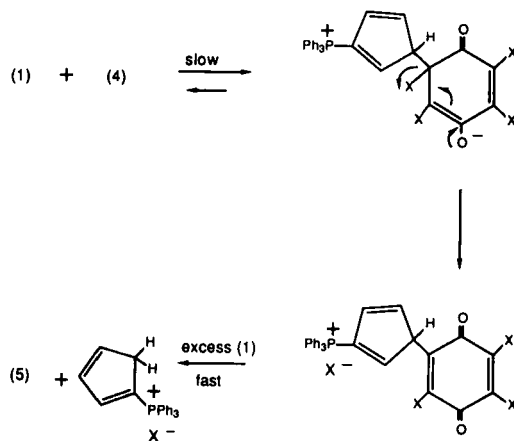
Second-order rate coefficients (k_2) for the reactions of (1, Z = P) with (4) in CH_2Cl_2 at 30°C ; [4] $7.5 \times 10^{-5} \text{ M}$

X	F	Cl	Br	I
$k_2(1 \text{ mol}^{-1} \text{ s}^{-1})$	*	1500	1400	248

* Too fast to measure precisely at 30°C .

(Table II). This shows conclusively that the mechanism involves rate-limiting addition of the ylid to the quinone ring followed by a rapid loss of the halide ion (Scheme 1) in a pathway which is analogous to the mechanism governing nucleophile substitution in activated aryl halides.¹¹

Work is in progress to examine the reaction with a range of ylids, (1)–(3) and further results in this area will be published in the full paper. We thank the SERC and the University of Valencia for financial support to P.S. and F.P.P. respectively.



SCHEME 1

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