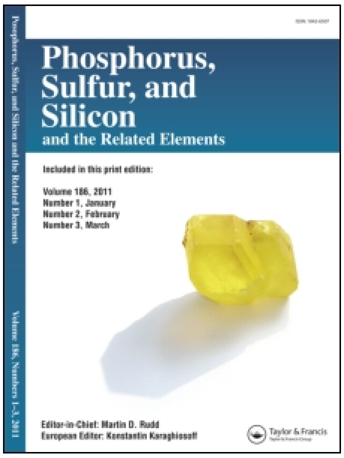

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# The Kinetics and Mechanism of the Reaction of Onium Cyclopentadienylides with Tetrahalo-p-Benzoquinones

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

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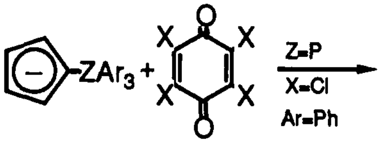
Abstract The reaction of triphenylphosphonium cyclopentadienylide (1) with halogen-substituted p-benzoquinones (4) is shown to give a new class of dipolar (zwitterionic) dyes (5) containing phosphorus. The general structure of these molecules has been investigated by a combination of mass spectrometry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

## INTRODUCTION

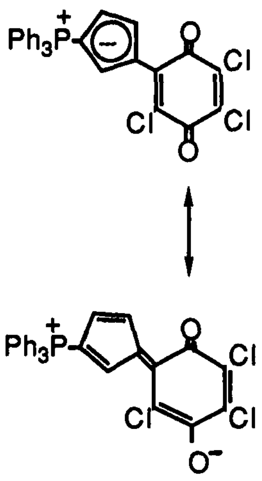
Several classes of dipolar (zwitterionic) dyes have been known for many years[1,2] but these compounds have recently received considerable attention as a result of their electrical properties and potential value as organic conductors or semiconductors.[3,4] Most of these dipolar species involve electron delocalisation 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 (1)[5], dialkyl 'onium ylids (2)[6] and the pyridinium cyclopentadienylide (3)[7] with tetrahalo-*p*-benzoquinones (4) in organic media ($CH_2Cl_2$ or PhMe ) gave intense blue solutions ($\lambda_{max}$, 650-700nm, $\varepsilon = 10^3$-$10^4$) which changed abruptly to yellow on protonation. 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 ir and nmr spectra of mixtures of 'onium ylids and *p*-benzoquinones were not typical of molecular complexes[8] but instead suggested σ-bond formation.The objective of this paper therefore, is to report the isolation and characterisation of the blue compounds formed from triphenylphosphonium cyclopentadienylide (1,Y=P) and the tetrahaloquinones (4) together with the kinetic data which defines the reaction mechanism.

## 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 x $10^{-2}$ M in (1) was complete within seconds and the mixture was subjected immediately to flash chromatography on silica using $CH_2Cl_2$ as eluant. A briliant blue band 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)*

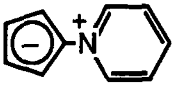


(1) Z=P,As (4) X=F,Cl,Br,I



(5)

(2) Y=S



(3)

The FAB mass spectrum in a glycerol matrix gave a parent peak at 537 ($M^+$ for $C_{29}H_{18}O_2Cl_3P$ at 535 plus two mass units due to the reduction of the quinone unit by glycerol) and 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 15.0 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 $\lambda_{max}$= 680 nm ( $\varepsilon$ = 4,550 l mol $^{-1}$ cm$^{-1}$) typical of a methionine-type dye.[1,2]

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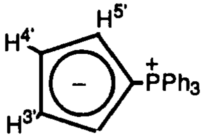
* Found: C, 64.45 ; H, 3.85 ; P, 5.48 ; Cl, 19.41 %

$C_{29}H_{18}O_2Cl_3P$ requires : C, 64.98 ; H, 3.39 ; P, 5.28 ; Cl, 19.86%

The structure of (5) however, was deduced from its high resolution $^1H$ (at 250 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 other two cyclopentadiene protons whereas the remaining two signals (at 7.05 and 6.36 ppm) each showed one strong and one weak coupling. 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).



(6)

The complete assignments of $^1H$ and $^{13}C$ signals for (5) derived from COSY, DEPT, and carbon-proton 2-D correlation spectra are shown in Table I.

Kinetic data derived from stopped flow techniques monitoring the appearance of (5) at 680nm 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 X=F (relative rate, 210) > Cl (6.6) > Br (6.0) > I (1) in $CH_2Cl_2$ at 25°. 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 in a pathway which is analogous to the mechanism governing nucleophilic 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.

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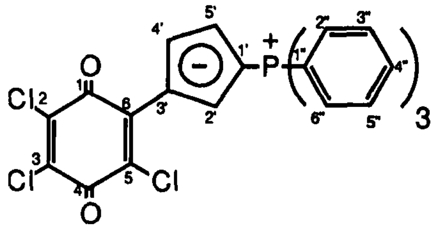
TABLE I $^{1}$H and $^{13}$C nmr data on (5) in $CD_2Cl_2$ at -30$^{o}$C



$^{1}$H nmr

| δ (ppm) | Integration | Assignment | J values (Hz) |
|---|---|---|---|
| *ca.* 7.6 (m) | 15 | 2"-6" | - |
| 7.05 (sextet) | 1 | 5' | $J_P = 4.9$ ; $J_{4'} = 4.7$ ; $J_{2'} = 2.1$ |
| 6.94 (sextet) | 1 | 2' | $J_P = 6.3$ ; $J_{4'} = 2.1$ |
| 6.36 (quintet) | 1 | 4' | $J_P = 2.5$ |

$^{13}$C nmr

| δ (ppm) | DEPT | Assignment | $J_P$ (Hz) |
|---|---|---|---|
| 181.1 | 0 | C-1 | 0 |
| 172.7 | 0 | C-4 | 0 |
| 143.0 | 0 | | |
| 141.2 | 0 | C-2, 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 |