

## CYCLOPENTADIENYLIDENEPHOSPHINAZINES

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(Received in the UK 31 August 1973; Accepted for publication 20 September 1973)

**Abstract**—Diazocyclopentadienes which are not alkyl- or aryl-substituted at both the 2- and 5-positions react readily with triphenylphosphine to form cyclopentadienylidenephosphinazines. If both of these positions are so substituted phosphinazines are not formed. A phosphinazine was obtained from 2-chloro-3,4,5-triphenyldiazocyclopentadiene while its 2-nitro-analogue apparently formed a readily hydrolysed phosphinazine. Diazotetraphenylcyclopentadiene formed a phosphinazine with tri-*n*-butylphosphine. The reasons for these differences in reactivity are discussed.

When heated to higher temperatures some of the phosphinazines decomposed with loss of nitrogen to give phosphonium cyclopentadienylides.

Electron-withdrawing substituents in the five-membered ring make the phosphinazines susceptible to ready hydrolysis to cyclopentadienone hydrazones. Cyclopentadienylidenephosphinazines are protonated by mineral acids on nitrogen rather than on the cyclopentadiene ring.

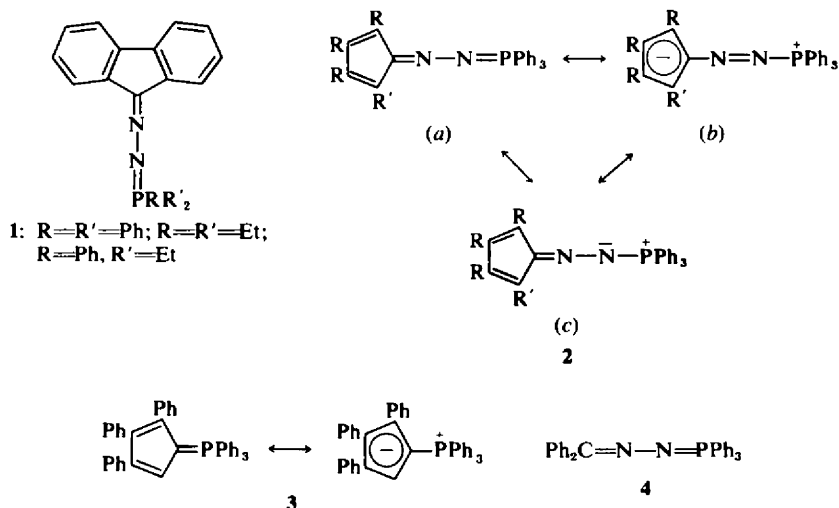
Phosphines react with diazo-compounds, by what has been described as a biphilic process,<sup>1</sup> to form phosphinazines.<sup>2</sup> Among the first examples of phosphinazines to be reported were cyclopentadienylidenephosphinazines, namely the fluorenylidene compounds(1);<sup>3</sup> more recently the preparation of cyclopentadienylidene-triphenylphosphinazine itself (2, R = R' = H)<sup>4,5</sup> and some phenyl-substituted derivatives<sup>6,7</sup> have been recorded but the reactions between diazocyclopentadienes and phosphines have not been extensively studied.

When triphenylphosphine and diazo-2, 3, 4-triphenylcyclopentadiene were dissolved in benzene or when they were melted together at 100° the phosphinazine (2, R = Ph, R' = H) was formed in

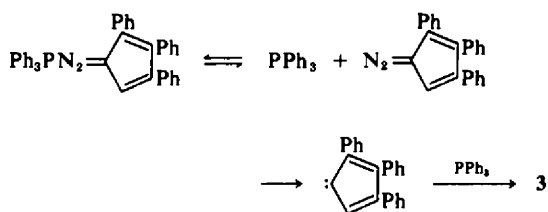
high yield. If however these reactants were melted together for 1 h at temperatures exceeding 140° the product was the cyclopentadienylide (3).

It had been noted<sup>3</sup> that diphenylmethylenetriphenylphosphinazine (4) decomposed on heating to give nitrogen and triphenylphosphonium diphenylmethylide but this reaction appears not to be a general one;<sup>8</sup> for example it does not proceed in the case of the parent cyclopentadienylidene-triphenylphosphinazine (2, R = R' = H).

In the present case, at the higher temperatures used the diazo-compound may decompose directly into a carbene which reacts with triphenylphosphine to give the resultant ylide 3 (*cf* Refs 6, 7). Alternatively, and more probably since a longer reaction time is required than is usual in direct



formation of ylides from carbenes, the phosphinazine may be formed first but slowly decomposes again at the high temperature to regenerate diazo-compound which itself at once decomposes:



In accord with this suggestion, a similar yield of the ylide (3) could be obtained by heating a mixture of the phosphinazine and triphenylphosphine at temperatures above 140°. This ylide (3) had previously only been prepared by the salt method from bromotriphenylcyclopentadiene<sup>9</sup> and had not been obtained by carbenic decomposition of the diazo-compound in triphenylphosphine.<sup>6,7</sup>

Similarly diazo-2,4-diphenylcyclopentadiene formed a phosphinazine at lower temperatures, but when melted with triphenylphosphine at 150° gave the corresponding phosphonium cyclopentadienylide, which also formed when the phosphinazine was heated with excess triphenylphosphine at 150°.

In contrast, diazocyclopentadienes with two alkyl or phenyl groups at the 2,5-positions did not react with triphenylphosphine to form phosphinazines. Tetraphenyl-, 2,3,4-triphenyl-5-*p*-tolyl-, 2-benzyl-3,4,5-triphenyl-, 2-methyl-3,4,5-triphenyl-, 2,3,5-triphenyl- and 2,5-diphenyl-diazocyclopentadienes did not react with triphenylphosphine either in solution or when melted together at 100°, but in melts at higher temperatures formed the corresponding cyclopentadienylides. 2,5-Dimethyl-3,4-diphenyl-diazocyclopentadiene formed a mixture of presently unidentified products apparently (mass spectrum) containing small amounts of the ylide, but again no phosphinazine.

2-Chloro-diazo-3,4,5-triphenylcyclopentadiene did not form a phosphinazine in solution, but when the reactants were melted together at 130°, and ethanolic perchloric acid was added to the cooled residue, the phosphinazinium perchlorate crystallised. A similar reaction appeared to take place when 2-bromo-diazo-3,4,5-triphenylcyclopentadiene and triphenylphosphine were melted together but no tractable product could be isolated.

The 2-bromodiazotriphenylcyclopentadiene was obtained in a much improved yield (90%) by a modification of the method used previously,<sup>13</sup> which involves the reaction of diazo-2,3,4-triphenylcyclopentadiene with *N*-bromosuccinimide. The hitherto unreported chloro-analogue

was obtained similarly in high yield using *N*-chlorosuccinimide as chlorinating agent.

Tetrachlorodiazocyclopentadiene had been previously reported to give the phosphinazine (2; R = R' = Cl) by reaction with triphenylphosphine in solution.<sup>10</sup> This phosphinazine was also readily obtained by heating the neat reactants together at 90°, but if this temperature was exceeded a violent reaction ensued with evolution of nitrogen and formation of a black tar. If this phosphinazine was heated at 110° in a vacuum, some nitrogen was evolved gently but among the reaction products was tetrachlorodiazocyclopentadiene. This must have been formed by cleavage of the phosphinazine and provides further evidence for the suggested mode of conversion of phosphinazines into phosphonium ylides. At 130° or above vigorous evolution of nitrogen took place and no tractable products could be isolated. Other phosphinazines have been shown to dissociate thermally in the same fashion.<sup>11,12</sup>

Diazo-2-nitro-3,4,5-triphenylcyclopentadiene, obtained impure and in poor yield by nitration of diazo-2,3,4-triphenylcyclopentadiene with benzoyl nitrate in acetonitrile, reacted with triphenylphosphine in solution. The product isolated was the hydrazone of 2-nitro-3,4,5-triphenylcyclopentadienone, which presumably arose by hydrolysis of the first-formed phosphinazine, as discussed below.

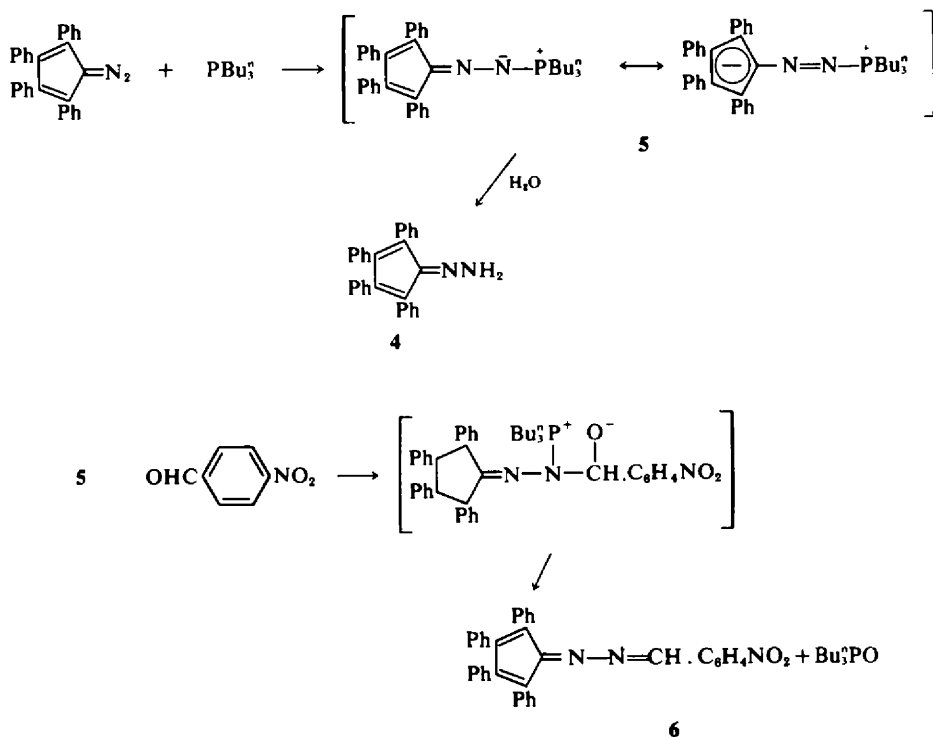
Although diazotetraphenylcyclopentadiene did not react with triphenylphosphine to give a phosphinazine under any conditions which were tried, it reacted with tri-*n*-butylphosphine in ether-light petroleum at room temperature. The isolated product was the hydrazone of tetraphenylcyclopentadienone (4), again presumably the hydrolysis product of an initially formed phosphinazine (5).

In order to provide evidence for the formation of the phosphinazine (5) as an intermediate in this reaction, a solution of diazotetraphenylcyclopentadiene, tri-*n*-butylphosphine, and *p*-nitrobenzaldehyde in dry benzene was heated under reflux. A good yield of the azine (6) resulted, which could have been formed from (5) by a mechanism analogous to the Wittig reaction; other examples of reactions between phosphinazines and aldehydes to give azines have been reported.<sup>14</sup>

It was shown that the hydrazone (4) also reacted with *p*-nitrobenzaldehyde to give the azine (6). Since, however, the reaction involving the diazo-compound, tri-*n*-butylphosphine and *p*-nitrobenzaldehyde was carried out under anhydrous conditions, it seems reasonable to assume that the azine was formed directly from the phosphinazine (5) and not from the hydrazone, whose intermediacy would require a hydrolytic step.

The hydrazone (4) had not been described previously. It is readily oxidised to diazotetraphenylcyclopentadiene by means of mercuric oxide.

The differences in reactivity of different diazo-



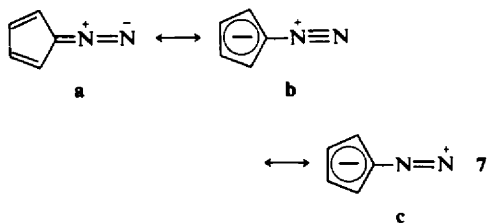
cyclopentadienes with phosphines may be associated with both electronic and steric factors. Thus the greater reactivity of tri-*n*-butylphosphine towards diazotetraphenylcyclopentadiene may be due both to the facts that it is a better nucleophile than triphenylphosphine and that it can take up a less sterically hindering conformation.

The failure of 2,5-dialkyl-, -diaryl- or -alkylaryl-substituted diazocyclopentadienes to react with triphenylphosphine may be due to steric hindrance but electronic factors may additionally be involved since a 2-nitro-5-phenyl-substituted diazocyclopentadiene did react.

Mesomeric forms (7 a-c) contribute to the structures of diazocyclopentadienes. Electron-withdrawing substituents in the ring may be expected to lead to relatively greater contributions from forms (b) and (c) whereas electron-donating substituents will favour the contribution of form (a). Thus in turn electron-withdrawing substituents should increase the reactivity of diazocyclopentadienes towards phosphines whereas electron-donating substituents should decrease the reactivity.

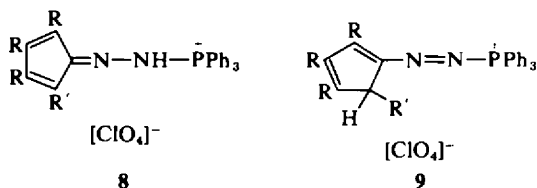
At first sight this may appear to conflict with the finding that the cleavage of phosphinazines by methyl iodide, which is shown to proceed *via* the prior dissociation of the phosphinazine into a diazo-compound and a phosphine, is assisted by electron-withdrawing substituents in the diazo-moiety.<sup>12</sup> However the controlling factor here is the diminished nucleophilic reactivity of phosphinazines with electron-withdrawing substituents. In consequence phosphinazines without electron-withdrawing substituents themselves react with methyl iodide without dissociation, whereas those with electron-withdrawing substituents are insufficiently reactive to compete for the methyl iodide with triphenylphosphine, formed by partial dissociation of the phosphinazine. Methylation of the triphenylphosphine in turn prevents its recombination with the diazo-moiety to reform phosphinazine.

The presence of electron-withdrawing substituents on the cyclopentadiene ring appears also to facilitate the hydrolysis of these phosphinazines, presumably by causing a greater contribution of the dipolar form (2b) to the overall structure, which assists nucleophilic attack at the phosphorus atom. Thus, whereas the parent cyclopentadienyldenetriphenylphosphinazine (2, R = R' = H) was reported<sup>4</sup> to resist all attempts at its hydrolysis, exposure of its tetrachloro-derivative (2, R = R' = Cl) to the at-



mosphere for 24 h resulted in its complete conversion into tetrachlorocyclopentadienone hydrazone and triphenylphosphine oxide. Similarly 2-nitro-3, 4, 5-triphenylcyclopentadienyldenetriphenylphosphinazine was very easily hydrolysed.

Like other phosphinazines, cyclopentadienyldenenephosphinazines are basic and dissolve in mineral acids to form salts. In some cases crystalline perchlorates were obtained on addition of perchloric acid followed by ether to ethanolic solutions of the phosphinazines. It has been shown<sup>12</sup> that phosphinazines are usually protonated on nitrogen rather than on carbon but cyclopentadienyldene derivatives are frequently protonated at the 5-position of the ring.<sup>13,15</sup> Thus the salts might have either of the structures (8) or (9).



The NMR spectrum of the perchlorate of (2, R = Ph, R' = H) had no peak due to a methylene group which would be present if protonation took place at the 5-position of the ring. Furthermore the IR spectra of this salt and of the salt of (2, R = Ph, R' = Cl) showed typical N-H absorption at 3200 cm<sup>-1</sup>. Thus formula (8) rather than formula (9) represents the structure of these cyclopentadienyldenenephosphinazinium salts.

#### EXPERIMENTAL

Light petroleum had a boiling range 40–60°.

2, 3, 4 - Triphenylcyclopentadienyldenetriphenylphosphinazine. (2, R = Ph, R' = H).

(a) *In melt* < 140°. Diazo-2, 3, 4-triphenylcyclopentadiene (0.64 g, 2 mmoles) and triphenylphosphine (0.786 g, 3 mmoles) were ground up together and heated in a bath just below 140° for 10 min. The mixture was cooled, and ether (5 ml) and light petroleum (15 ml) were added. An orange ppt was filtered off and recrystallised from chloroform, with the addition of a small amount of ether to initiate crystallisation, to provide the phosphinazine (1.0 g, 70%) as orange needles, m.p. 165° (lit.<sup>7</sup> 166°),  $\lambda_{\max}$  (EtOH) 220, 265, 362 nm (log  $\epsilon$  = 3.82, 3.64, 3.50),  $\lambda_{\max}$  [EtOH + HClO<sub>4</sub> (70%)(99:1)] 228, 263, 341 nm (log  $\epsilon$  = 3.68, 3.56).

(b) *In solvent*. The diazo-compound (0.64 g) was dissolved in light petroleum (15 ml) and benzene (5 ml). Triphenylphosphine (0.524 g, 2 mmoles) was added. The mixture was heated at 40° for 5 min and then kept at room temp for 2 h. The phosphinazine crystallised out (1.02 g, 90%).

2, 3, 4 - Triphenylcyclopentadienyldenetriphenylphosphinazinium perchlorate

Perchloric acid (60%, 0.2 ml) was added to a suspension

of (2, R = Ph, R' = H; 0.58 g) in MeCN (10 ml). On addition of ether pale red crystals separated out and were filtered off and washed with ether to give the perchlorate (0.55 g, 80%), red prisms (from MeOH), m.p. 222–225° (dec) (Found: C, 71.6; H, 4.6; N, 4.2. C<sub>41</sub>H<sub>32</sub>ClN<sub>2</sub>O<sub>4</sub>P requires: C, 71.8; H, 4.7; N, 4.1%).

Triphenylphosphonium 2, 3, 4 - triphenylcyclopentadienylyde (3)

(a) Diazo-2, 3, 4-triphenylcyclopentadiene (0.64 g, 2 mmoles) and triphenylphosphine (1.05 g, 4 mmoles) were ground together and put into a flask which was flushed with oxygen-free nitrogen and then plunged into a bath at 160° and kept at 160° for 1 h. The mixture was cooled and ether was added to it, whereat the ylide separated as a green-yellow solid (0.310 g, 28%), m.p. and mixed m.p. with an authentic sample<sup>9</sup> 242–245° (from MeCN) (lit.<sup>9</sup> 240–243°).

(b) This ylide was also obtained in similar yield by heating triphenylphosphine and 2, 3, 4-triphenylcyclopentadienyldenetriphenylphosphinazine together under the same conditions.

Triphenylphosphonium 2, 4 - diphenylcyclopentadienylyde

(a) Prepared like its 2, 3, 4-triphenyl-analogue, but from diazo-2, 4-diphenylcyclopentadiene and triphenylphosphine and with a reaction time and temperature of 15 min and 150–155°, this greenish-yellow ylide (0.249 g, 26%) had m.p. 224–226° (from n-butanol),  $\lambda_{\max}$  (CH<sub>2</sub>Cl<sub>2</sub>) 223, 291 nm (log  $\epsilon$  = 4.38, 4.40) (Found: C, 87.6; H, 5.8, C<sub>15</sub>H<sub>17</sub>P requires: C, 87.9; H, 5.7%).

(b) The ylide was obtained in similar yield by heating triphenylphosphine and 2, 4-diphenylcyclopentadienyldenetriphenylphosphinazine together under the same conditions.

2 - Chloro - 3, 4, 5 - triphenylcyclopentadienyldenetriphenylphosphinazinium perchlorate

2 - Chloro - 3, 4, 5 - triphenyldiazocyclopentadiene (0.355 g, 1 mmole) and triphenylphosphine (0.524 g, 2 mmole) were heated together at 130° for 5 min. The mixture was cooled and EtOH (5 ml) and perchloric acid (60%, 0.1 ml) were added. Addition of ether then precipitated red crystals which were filtered off, washed with ether and recrystallised from MeOH, crystallisation being initiated by an added drop of ether. The perchlorate then formed orange prisms (0.39 g, 55%), m.p. 243–245°,  $\lambda_{\max}$  (EtOH) 250 sh, 373 nm (log  $\epsilon$  = 4.42, 4.32),  $\lambda_{\max}$  [EtOH-M-KOH (100:1)] 258, 382 nm (log  $\epsilon$  = 4.39, 3.98) (Found: N, 4.1. C<sub>41</sub>H<sub>31</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>P requires: N, 3.9%).

2-Chloro-3,4,5-triphenyldiazocyclopentadiene

N-chlorosuccinimide (0.5 g, 3.3 mmole) was added to a soln of 2, 3, 4-triphenyldiazocyclopentadiene (0.96 g, 3 mmole) in chloroform (20 ml). The soln was heated at 60° for 30 min, cooled, and the solvent was evaporated. The residue was dissolved in ether (50 ml). The soln was thoroughly washed with water and dried (Na<sub>2</sub>SO<sub>4</sub>), and solvent was removed. The orange residue was chromatographed (alumina-benzene). The first yellow band was eluted as an orange solution. Removal of solvent left the chlorotriphenyldiazocyclopentadiene (0.85 g, 85%), golden needles, m.p. 143–145° (dec) from nitromethane (Found: C, 78.0; H, 3.85. C<sub>23</sub>H<sub>15</sub>ClN<sub>2</sub> requires: C, 77.9; H, 4.25%).

**2-Bromo-3,4,5-triphenyldiazocyclopentadiene**

N-bromosuccinimide (1.2 g, 7 mmole) was added to a soln of 2, 3, 4 - triphenyldiazocyclopentadiene (2.24 g, 7 mmole) in chloroform (20 ml) and the mixture was heated at 50° for 30 min. It was then cooled and the volume was reduced by evaporation to 5 ml. Ether (25 ml) was added and the soln was washed thoroughly with water and dried (Na<sub>2</sub>SO<sub>4</sub>). Solvent was removed and the orange residue was dissolved in a minimal volume of benzene and chromatographed (alumina-benzene). Removal of solvent from the first yellow fraction gave the bromotriphenyldiazocyclopentadiene as yellow needles (2.5 g, 90%), m.p. 130–131° from nitromethane (lit.<sup>13</sup> m.p. 128–130°).

**Tetrachlorocyclopentadienyldienetriphenylphosphinazine (2, R = R' = Cl)**

(a) A soln of tetrachlorodiazocyclopentadiene (0.85 g, 5 mmoles) in light petroleum (15 ml) was added to triphenylphosphine (1.31 g, 5 mmoles) and the mixture was kept at room temp for 3 h. The dark red ppt of the phosphinazine (1.96 g, 91%) was filtered off and had m.p. 131° (dec) from cyclohexane (lit.<sup>10</sup> m.p. 132°).

(b) The diazo-compound (0.85 g) and triphenylphosphine (2.1 g, 8 mmoles) were ground well together and heated gently to 90°. If this temp was exceeded a violent reaction ensued with evolution of N<sub>2</sub> and formation of a black tar. After 5 min at 90° the mixture was cooled, dissolved in the minimum amount of benzene and chromatographed on alumina. Benzene-light petroleum (1:1) eluted triphenylphosphine; benzene then eluted the phosphinazine, m.p. 130–132° (dec), red prisms from cyclohexane,  $\lambda_{\max}$  (EtOH) 261, 268, 275 sh, 366 (log  $\epsilon$  = 2.91, 2.90, 2.80, 3.72),  $\lambda_{\max}$  [EtOH + HClO<sub>4</sub> (70%) (99:1)] 223, 260, 261, 273, 338 (log  $\epsilon$  = 3.65, 2.83, 2.91, 2.87, 3.59) (Found: C, 56.3; H, 3.2; N, 5.8; Cl, 28.4. Calc. for C<sub>23</sub>H<sub>13</sub>Cl<sub>4</sub>N<sub>2</sub>P: C, 57.0; H, 3.1; N, 5.7; Cl, 28.9%).

**2-Nitro-3,4,5-triphenyldiazocyclopentadiene and its reaction with triphenylphosphine**

2, 3, 4 - Triphenyldiazocyclopentadiene (3.82 g) was added to a cooled soln of AgNO<sub>3</sub> (2.04 g) in MeCN (40 ml). A cooled soln of benzoyl chloride (1.69 g) in MeCN (10 ml) was then added slowly while the temp was kept below 5°. The soln was stirred at 0–5° for 2 h, filtered, diluted with water and extracted with ether (3 × 30 ml). The ether extract was washed with water, dil Na<sub>2</sub>CO<sub>3</sub> aq, water and then dried (Na<sub>2</sub>SO<sub>4</sub>). The ether was evaporated and the residue was dissolved in the minimal amount of benzene and chromatographed on alumina. Elution with benzene and removal of the solvent gave a residue which, when triturated with MeOH, gave the nitro compound (0.10 g, 2.3%) as a brown solid, m.p. 152–154°,  $\nu_{\max}$  2120 cm<sup>-1</sup> (N<sub>2</sub>). Without further purification this product (0.040 g) was dissolved with triphenylphosphine (0.030 g) in MeCN (2 ml). The soln was warmed for 5 min and the solvent was then removed. The residue was chromatographed (silica-benzene). A red band was eluted which, after removal of solvent, consisted of red crystals of 2 - nitro - 3, 4, 5 - triphenylcyclopentadienone hydrazone (0.025 g, 62%), m.p. 168–170° from nitromethane (M 367.133. C<sub>23</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub> requires M 367.132).

**Reaction of diazotetraphenylcyclopentadiene with tri - n - butylphosphine.**

Tri - n - butylphosphine (0.202 g, 1 mmole) was added to

a soln of diazotetraphenylcyclopentadiene (0.396 g, 1 mmole) in light petroleum (15 ml) and ether (5 ml). The mixture was kept at room temp for 3 h. The orange ppt was filtered off and recrystallised from nitromethane to give tetraphenylcyclopentadienone hydrazone (4) (0.24 g, 60%), scarlet needles, m.p. 240–242° (dec),  $\lambda_{\max}$  (CHCl<sub>3</sub>) 263, 346 nm (log  $\epsilon$  = 3.58, 3.51) (Found: C, 87.1; H, 5.6; N, 7.35. C<sub>20</sub>H<sub>22</sub>N<sub>2</sub> requires: C, 87.3; H, 5.5, N, 7.0%).

**Reaction of diazotetraphenylcyclopentadiene with tri - n - butylphosphine in the presence of p - nitrobenzaldehyde**

A soln of diazotetraphenylcyclopentadiene (0.396 g, 1 mmole), tri - n - butylphosphine (0.202 g, 1 mmole) and p-nitrobenzaldehyde (0.151 g, 1 mmole) in dry benzene (15 ml) was heated under reflux for 4 h. The volume of soln was reduced to 5 ml and the residue was chromatographed on alumina. Light petroleum-benzene (1:1) eluted unreacted diazo-compound (0.06 g); benzene eluted a product which after removal of solvent and trituration with nitromethane gave 1 - p - nitro - benzylidene - 2 - tetraphenylcyclopentadienyldiene azine (6) (0.30 g, 55%), deep maroon needles, m.p. 245–246° from nitromethane,  $\lambda_{\max}$  (CHCl<sub>3</sub>) 265, 349 nm (log  $\epsilon$  = 3.63, 3.77) (Found: C, 81.3; H, 4.7; N, 8.0. C<sub>30</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> requires: C, 81.4; H, 4.7; N, 7.9%). Chloroform eluted tetraphenylcyclopentadienone hydrazone (0.12 g).

**Reaction of tetraphenylcyclopentadienone hydrazone with p - nitrobenzaldehyde**

A soln of tetraphenylcyclopentadienone hydrazone (0.28 g, 1 mmole) and p - nitrobenzaldehyde (0.151 g, 1 mmole) in chloroform was heated under reflux for 3 h. Solvent was removed and the residue was triturated with warm benzene (5 ml). MeOH (5 ml) was added to complete the precipitation of the product, which was filtered off, washed with ether and recrystallised from nitromethane to give the azine (6), (0.37 g, 85%) m.p. 246°.

**Oxidation of tetraphenylcyclopentadienone hydrazone**

Tetraphenylcyclopentadienone hydrazone (0.28 g), mercuric oxide (0.3 g) and anhyd Na<sub>2</sub>SO<sub>4</sub> (0.1 g) were ground together well. Dry ether (10 ml), followed by conc ethanolic KOH (0.1 ml), were added and the mixture was shaken for 5 min. The soln was filtered and the solid residue was washed with ether. The combined ethereal soln and washings were evaporated and the orange residue was triturated with EtOH to provide diazotetraphenylcyclopentadiene (0.25 g, 90%), m.p. 148° (dec).

**Hydrolysis of tetrachlorocyclopentadienyldienetriphenylphosphinazine**

When this phosphinazine (0.432 g, 1 mmole) was kept in air for 24 h it lost its crystalline form and became sticky. Recrystallisation from light petroleum-methylene chloride provided tetrachlorocyclopentadienone hydrazone (0.11 g, 65%) as scarlet needles, m.p. 174–176° (lit.<sup>10</sup> 176°). The mother liquors were evaporated and the residue was boiled with water which was decanted while hot and allowed to cool. Triphenylphosphine oxide (0.12 g, 45%), m.p. 150°, crystallised out.

**Acknowledgements**—We gratefully acknowledge the award of research scholarships by the S.R.C. (to B. H. F.) and by the University of St. Andrews (to M. I. C. S.).

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