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Structure and Reactivity in the Reaction of Diazoindanes and Diazoindanones with Triphenylphosphine: The Formation of Mono-, and Bisphosphazines and Hydrazone-Compounds

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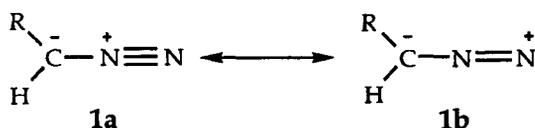
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The reactions of diazoindanes and diazoindanones with triphenylphosphine have been studied in acetonitrile. The diazoindanes and diazoindanones react with triphenylphosphine to give triphenylphosphazine. The reaction of 1,3-bis(diazo)indan-2-one with a tenfold excess of triphenylphosphine in dry acetonitrile gave the 1,3-bis(phosphazino)indan-2-one, however in acetonitrile containing below of 1% water, the 1,3-bis(hydrazone)indan-2-one was produced by hydrolysis. The phosphazine compound could be easily converted into bishydrazone by recrystallization, due to small amounts of water in the solvent. The reactivity of triphenylphosphine toward diazoindanes and diazoindanones depends on the structure of the diazo compounds.

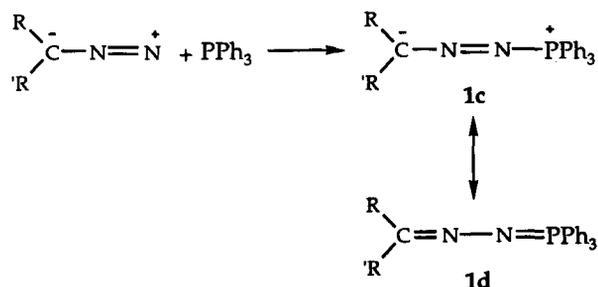
Introduction

Diazoalkanes provide a useful source of a wide variety of reactive intermediates such as, carbocations, radicals, carbenes and organometallic species.¹⁻⁵ Generally the reactivity of diazoalkanes towards nucleophiles increases with increasing contribution of limiting electron structures, **1a** and **1b**.⁶



Even though triphenylphosphine is more weak nucleophile than amine, it forms stable addition complexes through the reaction of diazoalkanes unlike amines.⁷ This

unique reaction results in the ability of phosphorus to stabilize the phosphazine which is formed by π -acceptance into its empty d orbitals.⁸



In general diazo compounds react with triphenylphosphine to give the adduct (**1d**), which is formed easily in a

biphilic process.⁹

A biphilic process results in the formation of two new covalent bonds, that is, one is placed at the σ -bond and the other at the π -bond in the case of phosphazines.¹⁰ It is proposed that the lone pair of phosphorus is involved in the formation of the σ -bond, while the electron cloud moves backward from the diazo moiety into the vacant 3d orbitals on phosphorus.¹¹ This situation is analogous to the classical synergistic bonding in phosphine complexes of transition metals.

The reactivity of triphenylphosphine toward diazo compounds depends on the structure of the diazo compounds.¹² Aromatic α -diazo ketones like diazoindanes and diazoindanones (Scheme 1) have a different reactivity among the diazo compounds.¹³

The reactions of diazoindanes and diazoindanones with triphenylphosphine would show a different mechanism by structural change of aromatic α -diazo ketones and electronic effect.

This research is focused on unusual findings for the reaction mechanism of a reaction series of diazoindanes and diazoindanones towards triphenylphosphine and to elucidate the mechanisms involved.

Experimental

Instrumentation. ¹H NMR spectra were recorded on a Bruker WM-200 (200 MHz) spectrometer as solutions in deuteriochloroform (CDCl₃), unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to CDCl₃ (7.24 ppm) as internal standard. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants are given in hertz (Hz). ¹³C NMR were recorded on a Bruker WM-200 (75 MHz) spectrometer as solutions in CDCl₃ unless otherwise indicated. Chemical shifts are expressed in parts per million (ppm, δ) downfield from TMS and are referenced to the center line of CDCl₃ (77.0 ppm) of the solvent peaks as internal standard. Infra-red spectra were recorded either neat on KBr discs or as nujol mulls as indicated using a Perkin-Elmer 1320 or 1720 FT-IR spectrometer and are reported in wavenumber (cm⁻¹). Ultra violet-visible spectra were recorded on a Hewlett-Packard HP 8452A diode array spec-

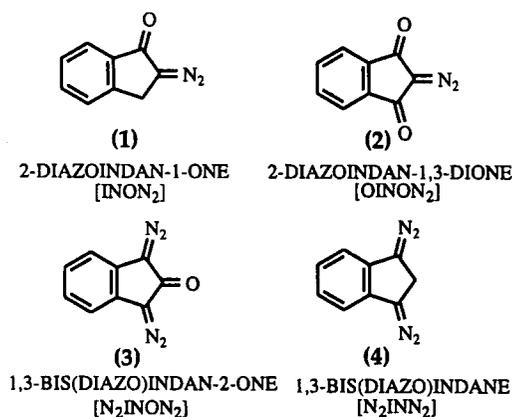
trophotometer. Mass spectra were obtained on a VG 7070E Double Focusing or a Fisons Instruments Trio 1000 mass spectrometers. The purity of samples was checked by microanalysis and high pressure liquid chromatography. Melting points were determined on a Kofler hot stage apparatus. Thin layer chromatography was performed using Merck 5554 pre-coated silica plates. Flash column chromatography was performed using Merck silica gel 60.

Preparation and purification of materials. All chemicals were obtained from Aldrich Chemicals Ltd: (i) Indan-1,3-dione (Aldrich, 97%) was commercial sample and used without further purification. (ii) Indan-2-one (Aldrich, 98%) was purified by recrystallization from ethanol or diethyl ether (needles, mp, 60 °C, lit.,¹⁴ 59 °C). (iii) Indan-1-one (Aldrich, 99%) was purified by recrystallization from petroleum ether (plates, mp 42 °C). The hydrazones were prepared by refluxing the corresponding ketones with hydrazine hydrate in ethanol. Full details are given only for the preparation of new compounds. The compounds prepared in this way were characterized as follows:

1,3-Bis(hydrazono)indane. Indan-1,3-dione (7.31 g; 50 mmol) was weighed into a flask containing 250 mL of ethanol. Hydrazine hydrate (48.5 mL; a tenfold excess) was added to this and the flask fitted with a reflux condenser. The reactants were heated under reflux for 3 hours, the reaction being monitored by tlc. The reaction mixture was slowly cooled to room temperature and pale off-yellow crystals formed on standing overnight. The solution was filtered and the crystals dried. A portion of the solvent (*ca.* 50 mL) was removed *in-vacuo* and the solution left to stand overnight. More pale off-yellow crystals formed and, after filtration, were dried. The combined solid was recrystallized from absolute ethanol to yield pale yellow crystals (7.37 g, 85%); mp 188-190 °C (with decomposition); ν_{\max} 3380, 3210, 1620, 1240, 1200, 1090, 1010, 925, 830, 790, 725, 660 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 3.3 (s) and 3.5 (s) (2H; CH₂), δ 6.4 (4H, s; NH₂), δ 7.3-7.4 (2H, m; ArH), δ 7.6-7.7 (2H, m; ArH); Mass spec. (EI) $m/z=174$ (M⁺ and base), 157, 145, 128, 102, 89, 77; C₉H₁₀N₄ requires; C, 62.05; H, 5.79; N, 32.17; Found: C, 62.12; H, 5.77; N, 32.28%. This compound was also prepared by hydrolysis of the bisphosphazine.

1,3-Bis(oximino)indan-2-one has previously been reported by Regitz and Heck¹⁵ who generated bis(tosylhydrazono)indan-2-one from ninhydrin, but the synthesis was inefficient and the final product difficult to purify. Therefore, we used an adaptation of the method described by Lee *et al.*¹⁶ using *n*-butyl nitrite in place of isoamyl nitrite with concentrated hydrochloric acid. It was recrystallized from methanol/ether; pale-yellow crystals (Yield=90%); mp 230 °C (lit., 225-226 °C); ν_{\max} 3300, 1760, 1655, 1625, 1595, 1570, 1425, 1320, 1225, 1200, 1095, 1020, 1010, 850, 840, 795 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ 3.3 (2H, bs; NOH), δ 7.3-7.7 (2H, m; ArH), δ 8.2-8.4 (2H, m; ArH); Mass spec. (EI) $m/z=190$ (M⁺), 144, 128 (base), 117, 102, 90, 75; C₉H₈N₂O₃ requires; C, 56.84; H, 3.18; N, 14.73; Found: C, 56.79; H, 3.17; N, 14.70%.

2-Oximinoindan-1-one¹⁷ was prepared by reaction of indan-1-one and isoamyl nitrite with concentrated hydrochloric acid in ethanol. It was recrystallized from ethanol; pale-yellow crystals; (Yield=93%); mp 200-201 °C (lit., 200



Scheme 1.

$^{\circ}\text{C}$); ν_{max} 3250, 3100, 1715, 1645, 1595, 1320, 1290, 1250, 1015, 895, 790, 765 cm^{-1} ; Mass spec. (EI) $m/z=161$ (M^+), 144 (base), 116, 89, 63; $\text{C}_9\text{H}_7\text{NO}_2$ requires; C, 67.07; H, 4.38; N, 8.69; Found: C, 67.29; H, 4.36; N, 8.70%.

1,3-Bis(diazo)indan-2-one(3)¹⁶ was prepared by reaction of a cold alkaline solution of 1,3-bis(oximino)indan-2-one with chloramine solution. It was recrystallized from methylene chloride/petroleum ether (60-80 $^{\circ}\text{C}$); red crystals (Yield=54%); mp 124-125 $^{\circ}\text{C}$ (lit., 126-127 $^{\circ}\text{C}$); ν_{max} 2110, 2080, 1645, 1465, 1375, 1365, 1320, 1305, 1185, 750 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.1-7.3 (2H, m; ArH), δ 7.3-7.5 (2H, m; ArH); ^{13}C NMR (CDCl_3) 209.43 (CO), 183.63 (CN_2), 126.54, 121.86, 119.46 (ArH); Mass spec. (EI) $m/z=184$ (M^+), 156, 128, 100, 74 (base); $\text{C}_9\text{H}_4\text{N}_4\text{O}$ requires; C, 58.70; H, 2.19; N, 30.42; Found: C, 58.66; H, 2.18; N, 30.49%. The diazo transfer method was also tried for the synthesis of the bis(diazo)-compound by treating indan-2-one with potassium ethoxide and *p*-tosyl azide, but the resultant product was a black, high molecular weight compound (M.W.>3,000 by mass spectrometry).

2-Diazoindan-1-one(1)¹⁸ was prepared by reaction of 1,3-bis(oximino)indan-2-one with chloramine solution. It was recrystallized from petroleum ether (40-60 $^{\circ}\text{C}$); yellow crystals (Yield=55%); mp 88-89 $^{\circ}\text{C}$ (lit., 89 $^{\circ}\text{C}$); ν_{max} 2090, 1690, 1660, 1610, 1345, 1325, 1295, 1255, 1165, 1150, 1110, 1080, 935, 780 cm^{-1} ; Mass spec. (EI) $m/z=158$ (M^+), 130, 102 (base), 76; $\text{C}_9\text{H}_6\text{N}_2\text{O}$ requires; C, 68.35; H, 3.82; N, 17.71; Found: C, 68.46; H, 3.82; N, 17.79%.

1,3-Bis(diazo)indane (4). 1,3-Bis(hydrazono)indane (3.0 g; 17.2 mmol) was ground up in a mortar together with yellow mercuric oxide (18.63 g; 86 mmol) and of sodium sulphate (*ca.* 5 g). The mixture was introduced into a 250 mL round bottomed flask surrounded with aluminium foil. Dried ether (100 mL) was then added, followed by 4-5 drops of cold saturated ethanolic potassium hydroxide solution. The flask was stoppered and the contents were stirred at room temperature for 3 hours. The progress of the reaction was monitored by infra-red spectroscopy looking for the appearance of the diazo peak, and concurrent disappearance of the hydrazone peaks. When the reaction was completed the mixture was filtered and the residue was washed twice with dry ether. The solvent was removed *in-vacuo* (at 35 $^{\circ}\text{C}$) to yield a dark red oil (1.38 g, 47%) which did not crystallize on standing at -20 $^{\circ}\text{C}$. However kinetic experiments were still carried out with this compound.; ν_{max} 2075, 1430, 1350, 1300, 1210, 1115, 1065, 750 cm^{-1} ; Mass spec. (EI) $m/z=170$ (M^+), 142, 114 (base), 88, 63. This compound was decomposed within 2 hours at room temperature yielding an oily solid. The products of thermal decomposition were appeared on the basis of mass spectrometric investigation to consist of two isomeric dimer, bis diazo compounds.; *cis*- and *trans*-1,1'-bis(diazo)-3,3'-biindanylidene isomers.; (a) Mass spec. (EI) $m/z=284$ (M^+), 242, 215, 156, 142, 114 (base), 88 and (b) Mass spec. (EI) $m/z=284$ (M^+), 242, 215, 156 (base), 142, 114, 88.

2-Diazoindan-1,3-dione (2). was prepared, as a useful reference diazo-compound, by the method suggested by Regitz and Heck (diazo transfer reaction).¹⁵ The diazo compound was obtained by reacting potassium ethoxide and *p*-tosyl azide with indan-1,3-dione and was isolated in 21% yield. It was recrystallized from ethanol; yellow crystals;

mp 148-150 $^{\circ}\text{C}$ (lit., 149 $^{\circ}\text{C}$); ν_{max} 2110, 1680, 1602, 1355, 1330, 1190, 1140, 955, 870, 800 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.4-7.7 (4H, m; ArH); ^{13}C NMR (CDCl_3) 182.77 (CN_2), 137.76, 135.50, 123.36 (ArH); Mass spec. (EI) $m/z=172$ (M^+), 88 (base); $\text{C}_9\text{H}_4\text{N}_2\text{O}_2$ requires; C, 62.80; H, 2.34; N, 16.27; Found: C, 62.76; H, 2.31; N, 16.32%.

1-Diazoindane¹⁹ was prepared by the oxidation of the indan-1-one hydrazone with silver oxide in dry ether with saturated methanolic potassium hydroxide solution under at -15 $^{\circ}\text{C}$. The progress of the reaction was monitored by infra-red spectroscopy checking for the presence of the diazo peak. The reaction mixture was then filtered and the residue was washed twice with dry ether. The solvent was removed *in-vacuo* (at -15 $^{\circ}\text{C}$) to yield a red oil which did not crystallize; ν_{max} 2020 cm^{-1} ; This diazo compound was decomposed within 10 minutes at room temperature and the colour was changed from red to yellow. Flash column chromatography (methylene chloride eluent) was permitted isolation of two compounds; 1,1'-biindanylidene (minor) and indan-1-one azine (major) products. (1) 1,1'-biindanylidene was obtained as yellow crystals by recrystallization from methylene chloride.; mp 85 $^{\circ}\text{C}$; yield=13%; Mass spec. (EI) $m/z=232$ (M^+), 217, 202, 117 (base), 101 (Accurate mass required $m/z=232.1252$; Found: $m/z=232.1251$); $\text{C}_{18}\text{H}_{16}$ requires; C, 93.06; H, 6.94; Found: C, 92.56; H, 7.08%. (2) Indan-1-one azine was obtained as brown crystals by recrystallization from acetonitrile; mp 154-155 $^{\circ}\text{C}$; yield=87%; Mass spec. (EI) $m/z=260$ (M^+), 130 (base), 115, 103, 77 (Accurate mass required $m/z=260.1313$; Found: $m/z=260.1312$); $\text{C}_{18}\text{H}_{16}\text{N}_2$ requires; C, 83.04; H, 6.19; N, 10.76; Found: C, 82.91; H, 6.24; N, 10.64%.

***p*-Toluenesulfonyl chloride**. A commercial sample was dissolved in the minimum amount of chloroform (2.5 mL/g) and diluted with five volumes of petroleum ether (bp 40-60 $^{\circ}\text{C}$). It was recrystallized²⁰ from petroleum ether (bp 60-80 $^{\circ}\text{C}$); white crystals; mp 68-69 $^{\circ}\text{C}$ (lit., 68 $^{\circ}\text{C}$).

***p*-Toluenesulfonyl azide**²¹ was prepared by a modification of the procedure of Curtius and Kraemer²¹ by adding with sodium azide in water to freshly distilled *p*-toluenesulfonyl chloride in 95% ethanol.

Triphenylphosphine. A commercial sample was recrystallized²² from ethanol.; mp 80-82 $^{\circ}\text{C}$ (lit., 80 $^{\circ}\text{C}$).

Solvents. Dichloromethane was distilled from calcium hydride, under nitrogen and stored over activated molecular sieves. Chloroform was distilled, under nitrogen, from phosphorus pentoxide. Acetonitrile (hplc grade) was also dried and fractionally distilled over calcium hydride or phosphorus pentoxide,²³ bp 81.6 $^{\circ}\text{C}$ and stored in the same way. It was also purified by passage through a column of activated alumina (type 507C) immediately prior to use in kinetic experiment.

1,3-Bis(phosphazino)indan-2-one (5). 1,3-Bis(diazo)indan-2-one (0.184 g, 1.0 mmol) and triphenylphosphine (2.623 g, 10 mmol) in 20 mL of a freshly distilled acetonitrile were stirred together at 30 $^{\circ}\text{C}$ for 30 min., the reaction being monitored by tlc. A dark brown precipitate was formed and the reaction was stirred for a further 30 minutes. The reaction mixture was flash filtered off, collected and the crystals dried *in-vacuo*. A portion of the solvent (*ca.* 10 mL) was removed at reduced pressure and the solution was left to stand 1 hour. More pale off brown

crystals were formed and, after filtration, were dried. The combined solid was characterized; brown crystals (0.59 g, 83%); mp 145-147 °C; v_{\max} 1690, 1595, 1510, 1200, 1120, 960, 865, 760, 740, 700 cm^{-1} ; $^1\text{H NMR}$ (Acetone- d_6) δ 7.2-8.0 (34H, m, ArH); Mass spec. (EI) $m/z=709$ (M^+), 557, 449, 414, 279 (base), 262, 201, 183, 154, 136, 107, 89, 77; $\text{C}_{45}\text{H}_{34}\text{N}_4\text{P}_2\text{O}$ requires; C, 76.26; H, 4.83; N, 7.91; Found: C, 76.02; H, 4.81; N, 7.89%. The brown solid product was washed with methanol and recrystallized from petroleum ether (60-80 °C). It was converted to 1,3-bis(hydrazono)indan-2-one to give yellow crystals (0.15 g, 80%); mp 185 °C; (EI) $m/z=188$ (M^+ and base), 160, 144, 128, 115, 102, 88; $\text{C}_9\text{H}_8\text{N}_4\text{O}$ requires; C, 57.44; H, 4.29; N, 29.77; Found: C, 57.33; H, 4.26; N, 29.83%. The triphenylphosphine oxide was separated by flash column chromatography (acetonitrile eluent) to give white crystals (0.37 g, 67%) and recrystallized from petroleum ether (60-80 °C); mp 152-154 °C, (Aldrich Chemical Co., mp 153-155 °C); Mass spec. (EI) $m/z=278$ (M^+), 277 (base), 201, 183, 152, 77; $\text{C}_{18}\text{H}_{15}\text{PO}$ requires; C, 77.67; H, 5.43; Found: C, 77.51; H, 5.45%.

1,3-Bis(hydrazono)indan-2-one (6). 1,3-Bis(diazo)indan-2-one (5.0 g, 27.2 mmol) and triphenylphosphine (14.25 g, 54.4 mmol) and a distilled water (0.01 g, 0.56 mmol) in acetonitrile (200 mL) were stirred together at 30 °C for 20 hours, the reaction being monitored by tlc. The solvent was removed at reduced pressure and dried. The product was separated by flash column chromatography in acetonitrile to give 1,3-bis(hydrazono)indan-2-one as yellow crystals (4.55 g, 89%) and triphenylphosphine oxide as white crystals (10.4 g, 69%). 1,3-Bis(hydrazono)indan-2-one was recrystallized from ethanol; mp 187 °C; v_{\max} 3390, 3230, 3160, 1670, 1600, 1575, 1560, 1535, 1260, 1190, 1090, 1035, 940, 745 cm^{-1} ; Mass spec. (EI) $m/z=188$ (M^+ and base), 160, 144, 128, 115, 102, 88; $\text{C}_9\text{H}_8\text{N}_4\text{O}$ requires; C, 57.44; H, 4.29; N, 29.77; Found: C, 57.30; H, 4.28; N, 29.72%. Triphenylphosphine oxide was recrystallized from petroleum ether (60-80 °C); mp 153-156 °C, (lit., 153-155 °C); v_{\max} 1590, 1315, 1190, 1120, 760, 730, 700 cm^{-1} ; Mass spec. (EI) $m/z=278$ (M^+), 277 (base), 201, 183, 152, 77; $\text{C}_{18}\text{H}_{15}\text{PO}$ requires; C, 77.69; H, 5.43; Found: C, 77.76; H, 5.42%.

2-Phosphazinoindan-1-one. 2-Diazoindan-1-one (0.5 g, 3.16 mmol) and triphenylphosphine (0.83 g, 3.16 mmol) in 30 mL of a freshly distilled acetonitrile were stirred together at 30 °C for 10 min., the reaction being monitored by tlc. The solvent was removed at reduced pressure and dried. The product was characterized; orange crystals (1.25 g, 94%); mp 165-167 °C; v_{\max} 1670, 1580, 1180, 1145, 1105, 1060, 930, 700 cm^{-1} ; $\text{C}_{27}\text{H}_{21}\text{N}_2\text{PO}$ requires; C, 77.13; H, 5.03; N, 6.61; Found: C, 76.85; H, 5.03; N, 6.63%. It was recrystallized from acetonitrile and converted to 2-hydrazonoindan-1-one to give yellow crystals (0.36 g, 71%); mp 181 °C; Mass spec. (EI) $m/z=160$ (M^+ and base), 144, 131, 116, 89, 77, 63; $\text{C}_9\text{H}_8\text{N}_2\text{O}$ requires; C, 67.48; H, 5.03; N, 17.49; Found: C, 67.47; H, 5.03; N, 17.67%. The triphenylphosphine oxide was separated by flash column chromatography (acetonitrile eluent) to give white crystals and recrystallized from petroleum ether (60-80 °C); mp 153 °C, (lit., 153-155 °C); Mass spec. (EI) $m/z=278$ (M^+), 277 (base), 201, 199, 183, 152, 77, 51; $\text{C}_{18}\text{H}_{15}\text{PO}$ requires; C, 77.67; H, 5.43; Found: C, 77.40; H, 5.41%.

2-Hydrazonoindan-1-one. 2-Diazoindan-1-one (0.5

g, 3.16 mmol) and triphenylphosphine (0.83 g, 3.16 mmol) and a distilled water (0.06 g, 3.33 mmol) in acetonitrile (30 mL) were stirred together at 30 °C for 6 hours, the reaction being monitored by tlc. The solvent was removed at reduced pressure and dried *in-vacuo*. The product was separated by flash column chromatography in acetonitrile to give 2-hydrazonoindan-1-one as yellow crystals (0.45 g, 89%) and triphenylphosphine oxide as white crystals (0.69 g, 79%). 2-Hydrazonoindan-1-one was recrystallized from acetonitrile; mp 180-182 °C; v_{\max} 3380, 3300, 3210, 1670, 1580, 1550, 1300, 1200, 1150, 1080, 935 cm^{-1} ; Mass spec. (EI) $m/z=160$ (M^+ and base), 144, 131, 116, 89, 77, 63; $\text{C}_9\text{H}_8\text{N}_2\text{O}$ requires; C, 67.48; H, 5.03; N, 17.49; Found: C, 67.47; H, 5.02; N, 17.66%. Triphenylphosphine oxide was recrystallized from petroleum ether (60-80 °C); mp 151-152 °C, (lit., 153-155 °C); v_{\max} 1590, 1315, 1190, 1120, 760, 730, 700 cm^{-1} ; Mass spec. (EI) $m/z=278$ (M^+), 277 (base), 201, 199, 183, 152, 77, 51; $\text{C}_{18}\text{H}_{15}\text{PO}$ requires; C, 77.67; H, 5.43; Found: C, 76.52; H, 5.51%.

2-Phosphazinoindan-1,3-dione. 2-Diazoindan-1,3-dione (0.43 g, 2.5 mmol) and triphenylphosphine (0.66 g, 2.5 mmol) in 30 mL of a freshly distilled acetonitrile were stirred together at room temperature for 10 min., the reaction being monitored by tlc. The solvent was removed at reduced pressure and dried. The product was characterized; red crystals (1.01 g, 93%); mp 97-98 °C; $\text{C}_{27}\text{H}_{19}\text{N}_2\text{PO}_2$ requires; C, 74.65; H, 4.41; N, 6.45; Found: C, 74.30; H, 4.38; N, 6.46%. It was recrystallized from acetonitrile and converted to 2-hydrazonoindan-1,3-dione to give yellow crystals (0.36 g, 83%); mp 185 °C; Mass spec. (EI) $m/z=174$ (M^+), 158, 146 (base), 118, 105, 89, 76; $\text{C}_9\text{H}_6\text{N}_2\text{O}_2$ requires; C, 62.07; H, 3.47; N, 16.09; Found: C, 62.18; H, 3.70; N, 15.59%. The triphenylphosphine oxide was separated by flash column chromatography (acetonitrile eluent) to give white crystals (0.45 g, 65%) and recrystallized from petroleum ether (60-80 °C); mp 151 °C, (lit., 153-155 °C); Mass spec. (EI) $m/z=278$ (M^+), 277 (base), 199, 183, 152, 115, 77, 51; $\text{C}_{18}\text{H}_{15}\text{PO}$ requires; C, 77.67; H, 5.43; Found: C, 77.71; H, 5.41%.

2-Hydrazonoindan-1,3-dione. 2-Diazoindan-1,3-dione (0.43 g, 2.5 mmol) and triphenylphosphine (0.66 g, 2.5 mmol) and a distilled water (0.05 g, 2.78 mmol) in acetonitrile (30 mL) were stirred together at room temperature for 12 hours, the reaction being monitored by tlc. The solvent was removed at reduced pressure and dried *in-vacuo*. The product was separated by flash column chromatography in acetonitrile to give 2-hydrazonoindan-1,3-dione as yellow crystals (0.37 g, 85%) and triphenylphosphine oxide as white crystals (0.56 g, 81%). 2-Hydrazonoindan-1,3-dione was recrystallized from acetonitrile; mp 181 °C; v_{\max} 3300, 3150, 1700, 1655, 1575, 1185, 1140, 965, 880 cm^{-1} ; Mass spec. (EI) $m/z=174$ (M^+), 172, 158, 146 (base), 118, 105, 89, 76; $\text{C}_9\text{H}_6\text{N}_2\text{O}_2$ requires; C, 62.07; H, 3.47; N, 16.09; Found: C, 62.00; H, 3.44; N, 16.38%. Triphenylphosphine oxide was recrystallized from petroleum ether (60-80 °C); mp 151-152 °C, (lit., 153-155 °C); v_{\max} 1580, 1300, 1175, 1100, 740, 690 cm^{-1} ; Mass spec. (EI) $m/z=278$ (M^+), 277 (base), 199, 183, 152, 115, 107, 95, 77; $\text{C}_{18}\text{H}_{15}\text{PO}$ requires; C, 77.67; H, 5.43; Found: C, 77.74; H, 5.42%.

2-Phosphoranoindan-1,3-dione. 2-Diazoindan-1,3-

dione (0.43 g, 2.5 mmol) and triphenylphosphine (0.66 g, 2.5 mmol) in 30 mL of a freshly distilled acetonitrile were stirred together at 50 °C for 5 hours, the reaction being monitored by tlc. The solvent was removed at reduced pressure and dried. The product was isolated and characterized. It was recrystallized from dichloromethane/petroleum ether (60-80 °C) and found by microanalysis and infra-red spectroscopy; red-orange crystals (0.73 g, 72%); mp 185-187 °C; ν_{\max} 1630, 1585, 1480, 1190, 1120, 1025, 1000, 920, 750, 690 cm^{-1} ; Mass spec. (EI) $m/z=406$ (M^+ and base), 377, 281, 260, 203, 185, 165, 152, 129, 107, 77; (CI) $m/z=407$ ($M+H$), 279, 263 (base), 187, 165, 150, 133, 94, 80; $C_{27}H_{19}PO_2$ requires; C, 79.79; H, 4.71; Found: C, 77.71; H, 4.69; N, 1.37%.

1,3-Bis(phosphazino)indane. 1,3-Bis(diazo)indane (0.17 g, 1.0 mmol) and triphenylphosphine (2.623 g, 10 mmol) in 30 mL of a freshly distilled acetonitrile were stirred together at 30 °C for 30 min., the reaction being monitored by tlc. A brown precipitate was formed and the reaction was stirred for a further 30 minutes. The reaction mixture was flash filtered off, washed with methanol and the crystals were dried *in-vacuo*. A portion of the solvent (*ca.* 10 mL) was removed at reduced pressure and the solution left to stand 1 hour. More pale off brown crystals were formed and, after filtration, were dried. The combined solid was characterized; brown crystals (0.48 g, 69%); mp 40-42 °C; Mass spec. (EI) $m/z=557$ (M^+), 279 (base), 171; $C_{45}H_{36}N_4P_2$ requires; C, 77.80; H, 5.22; N, 8.06; Found: C, 75.67; H, 5.40; N, 4.60% (For example, 1-phosphazino-3-diazoindane; $C_{27}H_{21}N_4PO$ requires; C, 72.31; H, 4.70; N, 12.49).

1,3-Bis(hydrazono)indane. 1,3-Bis(diazo)indane (0.17 g, 1.0 mmol) and triphenylphosphine (0.52 g, 2.0 mmol) and a distilled water (0.04 g, 2.2 mmol) in acetonitrile (50 mL) were stirred together at 30 °C for 20 hours, the reaction being monitored by tlc. The solvent was removed at reduced pressure and dried. The product was separated by flash column chromatography in acetonitrile to give 1,3-bis(hydrazono)indane as yellow crystals (0.15 g, 86%) and triphenylphosphine oxide as white crystals (0.35 g, 63%). 1,3-Bis(hydrazono)indane was recrystallized from ethanol; mp 184-185 °C; Mass spec. (EI) $m/z=174$ (M^+ and base), 157, 128, 115, 102, 89, 77; $C_9H_8N_4O$ requires; C, 62.05; H, 5.79; N, 32.17; Found: C, 61.84; H, 5.75; N, 32.37%. Triphenylphosphine oxide was recrystallized from petroleum ether (60-80 °C); mp 152-153 °C, (lit., 153-155 °C); ν_{\max} 1590, 1315, 1190, 1120, 760, 730, 700 cm^{-1} ; Mass spec. (EI) $m/z=278$ (M^+), 277 (base), 201, 183, 152, 77; $C_{18}H_{15}PO$ requires; C, 77.69; H, 5.43; Found: C, 77.55; H, 5.44%.

Kinetic Method. The reactions were carried out in a two-legged glass vessel (one leg capacity *ca.* 1 mL) which was connected to a 1mm quartz UV cell and a tap for introducing reaction solutions and for degassing. The reaction vessel is degassed through tubing, then the tap closed to seal the reagents from the external atmosphere. The reactants are mixed by the inverting apparatus. The solution of substrate under study (usually 1.0×10^{-3} M) and base solution (1.0×10^{-3} - 8.0×10^{-3} M) were pipetted into separate legs of the reaction vessel and degassed. The solutions were equilibrated at a suitable temperature before being thoroughly mixed at the temperature and transferred to the UV cell which was placed in the cell holder of the spectrometer at

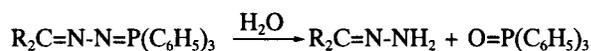
the same temperature. The starting time was measured at the moment of mixing of the reactants. The appearance of the coloured species in the reaction mixture was measured by the increase in optical density at suitable time intervals.

Results and Discussion

1,3-Bis(diazo)indan-2-one (N_2INON_2) (3) and triphenylphosphine were reacted together in acetonitrile by standing overnight at room temperature. After purification a yellow crystalline solid was obtained which was identified as 1,3-bis(hydrazono)indan-2-one (6). Simultaneously with the product (6), triphenylphosphine oxide (7) was produced as shown in Scheme 2.

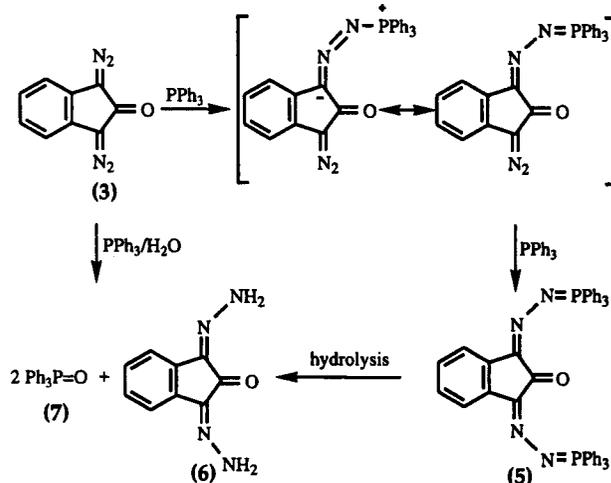
The triphenylphosphine oxide (7) was isolated in high yield, as white crystals, by flash column chromatography (methylene chloride/acetonitrile eluent). These results could be explained briefly by the reaction mechanism as shown in Scheme 2. Firstly diazo compound (3) reacts with triphenylphosphine to give the adduct, triphenylphosphazine (5). However triphenylphosphazines in general are unstable in the presence of a small amount of moisture.

It is known that phosphazines can react with water to produce hydrazones,²⁴ and this result is observed in the electrochemical reaction.



The reaction of N_2INON_2 (3) with a tenfold excess of triphenylphosphine in dry acetonitrile gave the 1,3-bis(phosphazino)-indan-2-one (5), however with acetonitrile containing 1% water, 1,3-bis(hydrazono)indan-2-one (6) was produced through hydrolysis as shown in Scheme 2. The bisphosphazine compound (5) could be easily converted into bis-hydrazone due to a small amount of water in the solvent.

This hydrolysis can be demonstrated on the basis of the ultraviolet spectra of the reaction mixture as an increase in the absorbance at 384 nm which occurs initially due to formation of bisphosphazine (5) and the subsequent decrease in the absorbance which occurs as it is slowly hydrolyzed as shown in Figure 1. Other mono-, and bis(phosphazino)-



Scheme 2.

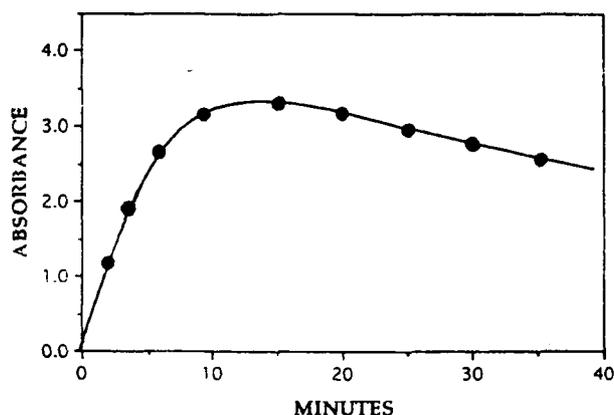


Figure 1. Variation of intensity of absorbance vs. reaction time for the reaction of 1,3-bis(diazo)indan-2-one (1.00×10^{-3} M) and triphenylphosphine (2.50×10^{-2} M) in acetonitrile at room temperature at $\lambda=384$ nm.

compounds were also prepared in pure acetonitrile solvent from the mono-, and bis(diazo) compounds with equimolar and excess amounts of triphenylphosphine.

When the colour of the diazo compound was totally discharged, the phosphazine crystallized out. However the product was converted into the hydrazone and triphenylphosphine oxide due to a small amount of water. Through these reactions, phosphazines and hydrazones were crys-

tallized out and were characterized. On the other hand 1,3-bis(phosphazino)indane was not isolated. In contrast to these results 1,3-bis(diazo)indane and triphenylphosphine in the presence of water gave a 1,3-bis(hydrazono)indane as pale yellow crystals. The products are summarized in Table 1. The molar extinction coefficients and λ_{\max} of the diazo compounds, phosphazines and hydrazones are collected in Table 2.

The absorption peaks of mono- and bisphosphazines are appeared at between 360 and 380 nm. Among others, 1,3-bis(phosphazino)indan-2-one ($\lambda_{\max}=384$ nm) shows the highest wavelength absorption among the phosphazines produced from this study.

Infra-red spectroscopy was investigated to see if it would be observable through the following the reaction kinetics. In principle the rate of disappearance of the diazo peak at ca. 2100 cm^{-1} could be monitored. The infra-red absorbance at various time intervals throughout the reaction was determined by measuring the transmittance of the diazo peak and the transmittance of the background noise either side of this peak. This kinetic observance was not proved as an accurate enough method. However, a satisfactory method for the kinetics of these reactions was given a viable means by UV spectrophotometry as shown in Figure 2 as a typical run. The UV/visible spectrum of dilute solutions shows only phosphazine formation but in the case of 2-diazoindan-1,3-dione in pure solvent, only the phosphorane arises.

The second-order rate constants (k_2) for the reactions of

Table 1. Characterization of Phosphazines and Hydrazones after Conversion from Various Diazo compounds

Diazo Compounds	Phosphazines					Hydrazones					m/z (M ⁺ /base)
	Yield (%)	mp/°C	Analysis			Yield (%)	mp/°C	Analysis			
			Theory	Found				Theory	Found		
INON ₂ (1)	94	165-167	%C	77.13	76.85	89	180-182	%C	67.48	67.47	160 (160)
			%H	5.03	5.03			%H	5.03	5.02	
			%N	6.61	6.63			%N	17.49	17.66	
			%C	74.65	74.30			%C	62.07	62.00	174 (146)
OINON ₂ (2)	93	97-98	%H	4.41	4.38	85	181	%H	3.47	3.44	
			%N	6.45	6.46			%N	16.09	16.38	
			%C	76.26	76.02			%C	57.44	57.30	188 (188)
N ₂ INON ₂ (3)	83	145-147	%H	4.83	4.81	89	187	%H	4.29	4.28	
			%N	7.91	7.89			%N	29.77	29.72	
								%C	62.05	61.96	174 (174)
N ₂ INN ₂ (4)	-	-				86	184-185	%H	5.79	5.77	
								%N	32.17	32.27	

Table 2. The Molar Extinction Coefficients and λ_{\max} for Mono-, and Bis(diazo) compounds, Phosphazines and Hydrazones^a

Diazo Compounds	Mono-, and bis(diazo)		Phosphazine		Hydrazone	
	λ_{\max}/nm	$\epsilon/1 \text{ mol}^{-1} \text{ cm}^{-1}$	λ_{\max}/nm	$\epsilon/1 \text{ mol}^{-1} \text{ cm}^{-1}$	λ_{\max}/nm	$\epsilon/1 \text{ mol}^{-1} \text{ cm}^{-1}$
INON ₂ (1)	258	17200	364	43300	264	12200
	324	10900			310	22100
OINON ₂ (2)	246	41500	374	19000	328	21600
N ₂ INON ₂ (3)	300	11600	384	30800	374	8200
N ₂ INN ₂ (4)	266	11300	378	-	-	-
	332	7800				

^aThe solvent was acetonitrile.

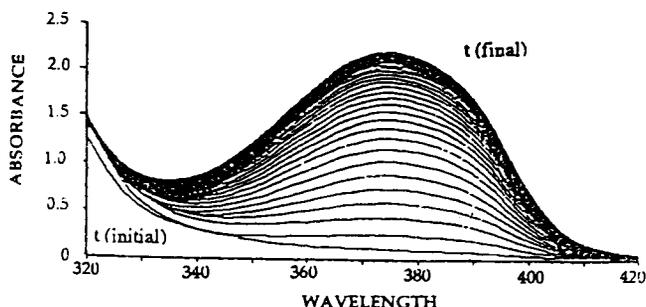


Figure 2. Time-resolved UV/vis spectra variation for the formation of 2-phosphazino-indan-1,3-dione in acetonitrile at 50 °C ($\lambda_{\text{max}} = 374$ nm); solution of 2-diazoindan-1-one (3.10×10^{-3} M) and triphenylphosphine (2.50×10^{-2} M), time interval=20 sec.

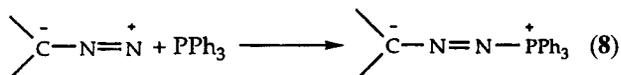
mono-, and bis(diazo) compounds with triphenylphosphine at 30, 40 and 50 °C are summarized in Table 3. The second-order rate constants (k_2) are obtained from the following relationship in Table 3,

$$k_2 = k_{\text{obs}} / [\text{PPh}_3] \quad (1)$$

where k_{obs} is the pseudo first order rate constant, which is determined by the time-resolved UV/vis spectra variation. $[\text{PPh}_3]$ refers the concentration of triphenylphosphine.

The plot of k_{obs} vs different concentrations of triphenylphosphine gave a good linearity to show the small standard deviations.

The order of magnitude of the rate constants reveals $[\text{OINON}_2] > [\text{N}_2\text{INON}_2] > [\text{N}_2\text{INN}_2] > [\text{INON}_2]$ at the same reaction condition in Table 3. This result is basically caused by increasing the ability of diazo group²⁵ to stabilize the betaine intermediate (8).



The ability to form betaine intermediate increases with increasing the π -electron localization of the diazo group.²⁶ That is, $[\text{OINON}_2]$ might more stabilize the π -electron localization by the neighbored oxygen compared with other di-

Table 3. The Second-Order Rate Constants ($k_2 \times 10^2$ L.mol⁻¹.sec⁻¹) of the Reactions of Mono-, and Bis(diazo) compounds with Triphenylphosphine at 30, 40 and 50 °C

Diazo Compounds	Temp. (°C)	k_2 ($\times 10^2$ L.mol ⁻¹ .sec ⁻¹)	Correlation Coefficient
[INON ₂]	30	3.26	0.9889
	40	4.23	0.9769
	50	5.89	0.9993
[OINON ₂]	30	19.6	0.9997
	40	36.7	0.9933
	50	66.0	0.9979
[N ₂ INON ₂]	30	12.5	0.9982
	40	20.0	0.9985
	50	26.2	0.9850
[N ₂ INN ₂]	30	3.97	0.9913
	40	5.65	0.9999
	50	7.14	0.9997

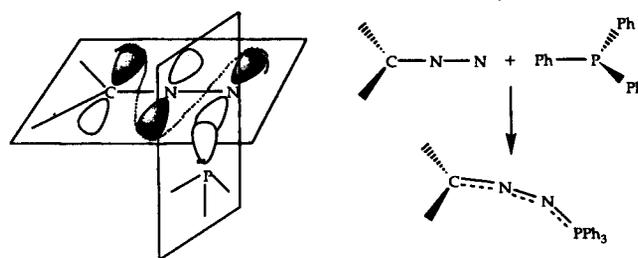


Figure 3. The interaction of HOMO(P_p) and LUMO (π^*_{NN}).

azo compounds. On the other hand $[\text{INON}_2]$ might less stabilize the π -electron localization.

The π -electron participation pattern can be interpreted in terms of the interaction of the frontier orbitals²⁷ of the reactants, considering both HOMO(P_p)-LUMO(ArCN_2) and HOMO(ArCN_2)-LUMO(P_p).

There are two ways by which the interactions between the frontier orbitals of the diazo compounds and PPh_3 can be formulated. In the first one HOMO(P_p)-LUMO(π^*_{NN}) and LUMO(P_d)-HOMO(π_2) are involved in the primary and secondary interactions, respectively. In these orbitals, only the HOMO(π_2) is strongly dependent on diazo structure as shown in Figure 3.

In Figure 3, the approach of phosphazine toward the diazo group conforms to the principle²⁸ of least nuclear motion (PLNM). The process of forming phosphazine would be controlled kinetically and the *anti*-isomer of phosphazine the thermodynamically controlled along with the stabilization of diazonium cation based on the theory of PLNM.

In the other possibility of interaction of the frontier orbitals, the primary and secondary interactions are HOMO(P_p)-LUMO(π_3^*) and LUMO(P_d)-HOMO(π_{NN}) respectively as shown in Figure 4.

In this case the P_d orbital interacts with π_{NN} in the nuclear plane. This second possibility seems less likely, since it does not appear to conform to theory of PLNM. It is suggested that in the series of diazoalkanes,²⁵ the first kind of interaction exists in which the HOMO(π_2)-LUMO(P_d) interactions. However, it seems that the interactions in diazoketones are favorable to HOMO(π_{NN})-LUMO(P_d) and HOMO(P_p)-LUMO(π^*_{NN}) instead of HOMO(P_p)-LUMO(π^*_{NN}) in which both interactions are structure-dependent.

In conclusion, the reactivity of diazoindanes and diazoindanones toward triphenylphosphine is much more structure-dependent compared with other diazoalkanes. This means that the reactivity of diazoindanes and diazoindanones should be related to the stability of the analogous carbanion and diazonium ion unless there is developing the negative charge as a

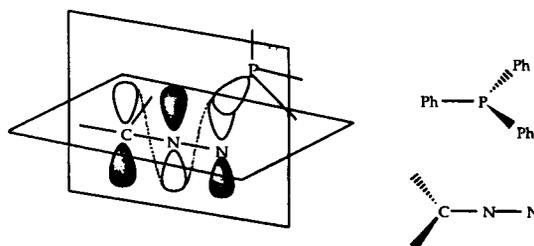


Figure 4. The interaction of HOMO(P_p)-LUMO(π_3^*).

result of nucleophilic attack by triphenylphosphine.

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Copper Oxide-Modified Polymeric Composite Electrodes for Amperometric Detection of Carbohydrates in LCEC Analysis

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Modified polymeric composite electrodes having highly dispersed CuO particles through the electrode matrix were prepared for LCEC or flow injection analysis of carbohydrates. The composite electrodes were prepared by incorporating carbon black and highly dispersed copper oxide particles in polystyrene matrix cross-linked with divinylbenzene. The analytical characteristics of the electrodes for LCEC and flow injection analysis of carbohydrates were evaluated. Improved performance in LCEC and flow injection analysis of carbohydrates is demonstrated in terms of sensitivity, reproducibility, stability and surface renewability. It was possible to get improved performance of the electrodes as well as adaptability of the electrodes for practical applications by employing highly dispersed catalyst particles through the electrode matrix and robust polymeric electrode matrix.

Introduction

Detection of carbohydrates after HPLC separation has

been of great research interest to analytical chemists because of their importance in physiological, clinical, medicinal, food and nutritional aspects. Due to the lack of a functional group absorbing light in most carbohydrates cumbersome pre- or post-column derivatizations are required in

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