Structure and Reactivity in the Reaction of Diazoinanes and Diazoinadanones with Triphenylphosphine: The Formation of Mono-, and Bisphosphazenes and Hydrazone-Compounds

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

Introduction

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

Even though triphenylphosphine is more weak nucleophile than amine, it forms stable addition complexes through the reaction of diazooalkanes unlike amines. This unique reaction results in the ability of phosphorus to stabilize the phosphazene which is formed by π-acceptance into its empty d orbitals.

In general diazo compounds react with triphenylphosphine to give the adduct (1d), which is formed easily in a
biphilic process. 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 phosphazenes. 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. This situation is analogous to the classical synergistic bonding in phosphate complexes of transition metals.

The reactivity of triphenylphosphine toward diazo compounds depends on the structure of the diazo compounds. Aromatic α-diazo ketones like diazodienes and diazooindanes (Scheme 1) have a different reactivity among the diazo compounds. The reactions of diazoindanes and diazoindanes 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 diazoindanes towards triphenylphosphine and to elucidate the mechanisms involved.

**Experimental**

**Instrumentation.** 1H NMR spectra were recorded on a Brucker WM-200 (200 MHz) spectrometer in deuteriochloroform (CDCl3), unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ) downfield from trimethylsilylane (TMS) and are referenced to CDCl3 (7.24 ppm) as internal standard. Splitting patterns are designated as singlet, s; doublet, d; triplet, t; quartet, q; multiplet, m; br, broad. Coupling constants are given in hertz (Hz). 13C NMR were recorded on a Brucker WM-200 (75 MHz) spectrometer as solutions in CDCl3 unless otherwise mentioned. Chemical shifts are expressed in parts per million (ppm, δ) downfield from TMS and 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 spectrophotometer. 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. Melt-}

ing 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., 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 mixture was allowed to cool, the crystals dried. A portion of the solvent (ca. 50 mL) was removed in vacuo and the solution left to stand overnight. More pale 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); νmax 3380, 2100, 1620, 1240, 1200, 1090, 1010, 925, 830, 790, 725, 660 cm⁻¹; 1H NMR (DMSO-d₆) 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); Full spec. (El) m/z=174 (M⁺ and base), 157, 145, 128, 102, 89, 77; C₇H₁₇N₂ requires; C, 62.65; H, 5.79; N, 32.17; Found: C, 62.2; 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 Heck who generated bis(tosylhydrato)indan-2-one from mihydrin, 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. using n-butyl nitrite in place of isonoyl nitrite with concentrated hydrochloric acid. It was recrystallized from methanol/ether; pale-yellow crystals (Yield=90%); mp 230 °C (lit., 225-226 °C); νmax 3300, 1760, 1655, 1525, 1595, 1570, 1425, 1320, 1225, 1200, 1095, 1020, 1010, 850, 840, 795 cm⁻¹; 1H NMR (DMSO-d₆) δ 3.3 (2H, bs; NOH), δ 7.3-7.7 (2H, m; ArH), δ 8.2-8.4 (2H, m; ArH); Mass spec. (El) m/z=190 (M⁺); 144, 128 (base), 117, 102, 90, 75; C₇H₇N₂O requires; C, 56.84; H, 3.18; N, 14.73; Found: C, 56.79; H, 3.17; N, 14.70%.

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

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1.3-Bis(diazo)indan-2-one (3) 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 °C); red crystals (Yield=54%); mp 124-125 °C (lit., 126-127 °C); νmax 2110, 2080, 1645, 1645, 1735, 1635, 1230, 1105, 1185, 750 cm⁻¹; ¹H NMR (CDCl₃) δ 7.1-7.3 (2H, m; ArH), δ 7.3-7.5 (2H, m; ArH); ¹³C NMR (CDCl₃) 209.43 (CO), 183.63 (C₆), 126.54, 121.86, 119.46 (ArH); Mass spec. (EI) m/z=184 (M⁺), 156, 128, 100, 74 (base); C₁₃H₁₄N₂O 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).

Diazoinadan-1-one (1) was prepared by reaction of 1,3-bis(oximino)indan-2-one with chloramine solution. It was recrystallized from petroleum ether (40-60 °C); yellow crystals (Yield=55%); mp 88-89 °C (lit., 89 °C); νmax 2090, 1690, 1660, 1635, 1325, 1295, 1255, 1150, 1110, 1080, 935, 780 cm⁻¹; Mass spec. (EI) m/z=158 (M⁺), 130, 102 (base); 76; C₁₀H₉N₂O requires; C, 68.35; H, 3.82; N, 17.71; Found: C, 68.46; H, 3.82; N, 17.70.

1,3-Bis(diazo)indane (4). 1,3-Bis(hydrazino)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 °C) to yield a dark red oil (1.38 g, 47%) which did not crystallize on standing at −20 °C. However kinetic experiments were still carried out with this compound; νmax 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 identified 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'-binindanylidene 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-Diazoinadan-1,3-dione (2), was prepared as a useful reference diazo-compound, by the method suggested by Regitz and Heck (diazo transfer reaction). 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 °C (lit., 149 °C); νmax 2110, 1680, 1602, 1355, 1330, 1190, 1140, 955, 870, 800 cm⁻¹; ¹H NMR (CDCl₃) δ 7.4-7.7 (4H, m; ArH); ¹³C NMR (CDCl₃) 182.77 (CN₂), 137.76, 135.50, 123.36 (ArH); Mass spec. (EI) m/z=172 (M⁺), 88 (base); C₁₁H₉N₂O requires; C, 62.80; H, 2.34; N, 16.27; Found: C, 62.76; H, 2.31; N, 16.52%.

1-Diazoindanone was prepared by the oxidation of the indan-1-one hydrazonate with silver oxide in dry ether with saturated methanolic potassium hydroxide solution under at −15 °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 °C) to yield a red oil which did not crystallize; νmax 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:ethyl acetate 95:5) isolated two compounds; 1,1'-binindanylidene (minor) and indan-1-one azine (major) products. (1) 1,1'-binindanylidene was obtained as yellow crystals by recrystallization from methylene chloride: mp 85 °C; yield=13%; Mass spec. (EI) m/z=252 (M⁺), 217, 202, 117 (base). (2) Accurate mass required m/z=232.1252; Found: m/z=232.1251; C₁₂H₁₂N₂ 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 °C; yield=8%; Mass spec. (EI) m/z=260 (M⁺), 130 (base), 115, 103, 77 (Accurate mass required m/z=260.1313; Found: m/z=260.1312; C₁₂H₁₂N₂ 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 °C). It was recrystallized from petroleum ether (bp 60-80 °C); white crystals; mp 68-69 °C (lit., 68 °C).

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

**Triphenylphosphine.** A commercial sample was recrystallized from ethanol; mp 80-82 °C (lit., 80 °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, bp 81.6 °C and stored in the same way. It was also purified by passage through a column of activated alumina (type 50/70) immediately prior to use in kinetic experiment.

1,3-Bis(phosphazo)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 °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; 38, max 1690, 1595, 1510, 1200, 1120, 960, 865, 760, 740, 700 cm⁻¹; 1H NMR (Acetone-d_j): 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; C₈H₂₆N₄P₂O 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(hydroazido)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; C₈H₂₆N₄O 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, 142, 77; C₈H₂₆PO requires; C, 77.67; H, 5.43; Found: C, 77.51; H, 5.45%.

1,3-Bis(hydroazido)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(hydroazido)indan-2-one as yellow crystals (4.55 g, 89%) and triphenylphosphine oxide as white crystals (10.4 g, 69%). 1,3-Bis(hydrazone)indan-2-one was recrystallized from ethanol; mp 187 °C; 230, 3230, 3160, 1670, 1600, 1570, 1560, 1535, 1260, 1190, 1095, 940, 745 cm⁻¹; Mass Spec. (EI) m/z=188 (M⁺ and base), 160, 144, 128, 115, 102, 88; C₈H₂₆N₄O 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); 38, max 1590, 1315, 1190, 1120, 760, 730, 700 cm⁻¹; Mass Spec. (EI) m/z=278 (M⁺), 277 (base), 201, 183, 152, 77; C₈H₂₆PO requires; C, 77.69; H, 5.43; Found: C, 77.76; H, 5.42%.

2-Phosphazinoindan-1,3-dione. 2-Diazoindin-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; C₈H₂₆N₄PO 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-hydrazoneindan-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; C₈H₂₆N₄O requires; C, 62.07 H, 3.47; N, 16.69; 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, 77, 51; C₈H₂₆PO requires; C, 77.67; H, 5.43; Found: C, 77.71; H, 5.41%.

2-Hydrazoneindan-1,3-dione. 2-Diazoindin-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-hydrazoneindan-1,3-dione as yellow crystals (0.37 g, 85%) and triphenylphosphine oxide as white crystals (0.56 g, 81%). 2-Hydrazoneindan-1,3-dione was recrystallized from acetonitrile; mp 181 °C; 38, 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; C₈H₂₆N₄O 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); 38, 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; C₈H₂₆PO requires; C, 77.67; H, 5.43; Found: C, 77.74; H, 5.42%.

2-Phosphoranoindan-1,3-dione. 2-Diazoindin-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; \( \nu_{\text{max}} \) 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, 152, 129, 107, 77; (CI) m/z=407 (M+H\(^+ \)), 279, 263 (base), 187, 165, 150, 133, 94, 80; \( \text{C}_2\text{H}_4\text{P} \) 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 (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; \( \text{C}_2\text{H}_4\text{N}_2 \) 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; \( \nu_{\text{max}} \) 1590, 1315, 1190, 1120, 760, 730, 700 cm\(^{-1} \); Mass spec. (EI) m/z=278 (M\(^+ \)), 277 (base), 201, 183, 152, 77; \( \text{C}_2\text{H}_4\text{N}_2 \) 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 LmL 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 reagents 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 (\( \text{N}_2\text{INON}_2 \) (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 (methylen 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, triphenylphosphazane (5). However triphenylphosphazenes in general are unstable in the presence of a small amount of moisture.

It is known that phosphazines can react with water to produce pyrazidones,\(^{22} \) and this result is observed in the electrochemical reaction.

\[
\text{R}_2\text{C}=\text{N}=\text{N}+\text{P}(\text{C}_6\text{H}_5)_3 + \text{H}_2\text{O} \rightarrow \text{R}_2\text{C}=\text{N}-\text{NH}_2 + \text{O}+\text{P}(\text{C}_6\text{H}_5)_3
\]

The reaction of \( \text{N}_2\text{INON}_2 \) (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 bisphosphazene compound (5) could be easily converted into bisphydrazone 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 bisphosphazene (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)-
The solvent was acetonitrile.
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.

\[
k_2 = k_{obs}/[PPh_3]
\]

where \( k_{obs} \) is the pseudo first order rate constant, which is determined by the time-resolved UV/vis spectra variation. \([PPh_3]\) refers the concentration of triphenylphosphine.

The plot of \( k_{obs} \) is 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 group to stabilize the betaine intermediate. (8)

\[
\text{C} \equiv \text{N} = \equiv \text{N} + \text{PPh}_3 \rightarrow \text{C} \equiv \text{N} = \equiv \text{N} \rightarrow \text{PPh}_3
\]

The ability to form betaine intermediate increases with increasing the \( \pi \)-electron localization of the diazo group. That is, \([\text{OINON}_2] \) might more stabilize the \( \pi \)-electron localization by the neighbored oxygen compared with other diazo compounds. On the other hand \([\text{INON}_2] \) might less stabilize the \( \pi \)-electron localization.

The \( \pi \)-electron participation pattern can be interpreted in terms of the interaction of the frontier orbitals77 of the reactants, considering both HOMO(PPh_3)-LUMO(ArCN_2) and HOMO(ArCN_2)-LUMO(PPh_3).

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_2)-LUMO(\( \pi_{\text{orb}}^\text{+) and LUMO(P_2)-HOMO(\pi_{\text{orb}} \) are involved in the primary and secondary interactions, respectively. In these orbitals, only the HOMO(\( \pi_{\text{orb}} \) is strongly dependent on diazo structure as shown in Figure 3.

In Figure 3, the approach of phosphazene toward the diazo group conforms to the principle of least nuclear motion (PLNM). The process of forming phosphazene would be controlled kinetically and the anti-isomer of phosphazene 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(\( P_2 \)-LUMO(\( \pi_{\text{orb}}^\text{+) and LUMO(\( P_2 \)-HOMO(\( \pi_{\text{orb}} \) as shown in Figure 4.

In this case the \( P_2 \) orbital interacts with \( \pi_{\text{orb}} \) 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, the first kind of interaction exists in which the HOMO(\( \pi_{\text{orb}} \)-LUMO(P_2) interactions. However, it seems that the interactions in diazoketones are favorable to HOMO(\( \pi_{\text{orb}} \)-LUMO(P_2) and HOMO(P_2)-LUMO(\( \pi_{\text{orb}}^\text{+) instead of HOMO(P_2)-LUMO(\( \pi_{\text{orb}}^\text{+}) in which both interactions are structure-dependent.

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

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References


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