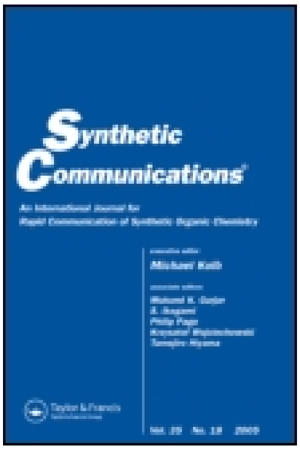

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PREPARATION OF 1,2-DIACYLBENZENES FROM *o*-HYDROXYARYL KETONE ACYLHYDRAZONES USING CROSS-LINKED POLY[STYRENE-(IODOSO DIACETATE)]

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ABSTRACT

The 2% cross-linked poly[styrene(iodoso diacetate)] was used to synthesis of 1,2-diacylbenzenes, which gave high yields, and could be recycled.

Phenyliodine diacetate has attracted wide interest in view of its utility for oxidation and radical reactions.[1] As an easily available and stable reagent, it has many advantages, such as mild reaction conditions, easy handling and high selectivity.[2] But, it also has major shortcomings: the byproduct iodobenzene is difficult to remove from product and the reagent is difficult to reuse. The cross-linked poly[styrene(iodoso diacetate)] can solve these problems. After the reaction, the byproduct cross-linked polyiodostyrene can be removed from the reaction solution just by filtration, and reused.

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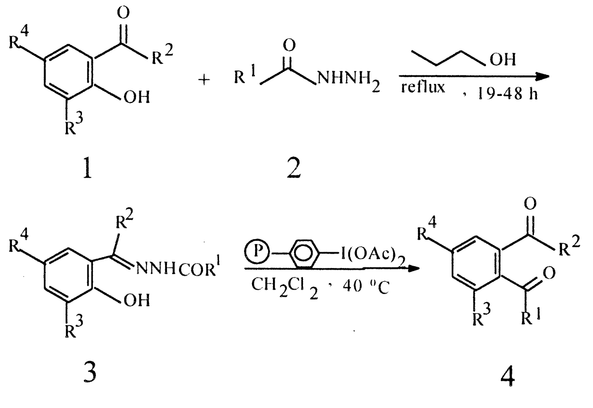
1,2-Diacylbenzenes are fluorescence reagents for both qualitative and quantitative high-sensitivity analyses for amines and amino acids.[3] They are also useful precursors to anthraquinone derivatives,[4] isoquinolines,[5] isoindoles,[6] imidazo[2,1,α]isoindoles,[7] *etc.*

There are several methods for the synthesis of 1,2-diacylbenzenes such as oxidation of benzhydrols with selenium dioxide[7] or *o*-hydroxyaryl ketone acylhydrazones with lead tetracetate.[8] It also can be prepared by oxidation of *o*-ethylacetophenone,[9] benzofurans[10] or by acylating benzene with *o*-acetyl-benzoychloride.[11] It has been reported that phenyliodine diacetate could be used to synthesize 1,2-diacylbenzenes in excellent yield.[12] Therefore, we expected that cross-linked poly[styrene(iodoso diacetate)] has reactivity similar to phenyliodine diacetate.

The 2% cross-linked poly[styrene(iodoso diacetate)] was prepared according to our previous work.[13] First, the 2% cross-linked polystyrene was iodinated with $I_2/I_2O_5/H_2SO_4$ to give poly(4-iodostyrene). Elemental analysis shows that the resin's functional group is 2.64 mmol/g. The polyiodostyrene was then converted to poly[styrene(iodoso diacetate)] by the treatment with peracetic acid. Iodometry shows that 98.5% of the iodinated benzene ring had been converted to phenyliodine diacetate. *o*-Acylphenols **1** and acetic hydrazides **2** were refluxed together in 1-propanol for 19–48 h to afford *o*-hydroxyaryl ketone acylhydrazone **3**. Then hydrazones **3** was oxidized by 2% cross-linked poly[styrene(iodoso diacetate)] in CH_2Cl_2 at 40°C to yield the corresponding 1,2-diacylbenzenes **4** in 58–85% yield (Scheme 1). The results are shown in Table I.

The possible mechanism of the reaction is as follows (Scheme 2). The reaction begins with ligand exchange of the *o*-hydroxyaryl ketone



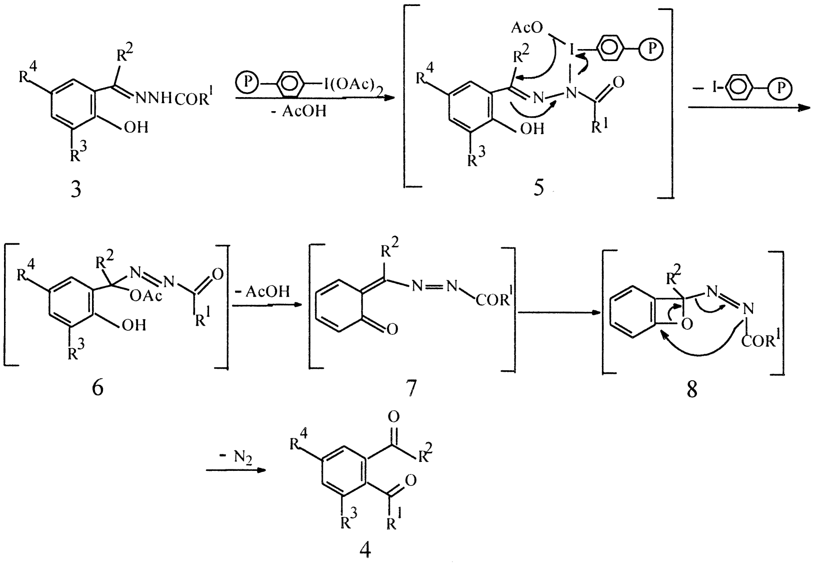
Scheme 1.

Table I. Preparation of 1,2-Diacylbenzenes Using Cross-Linked Poly[styrene(iodoso diacetate)]

Product **4**				Yield[a] (%)	Time (h)
R^1	R^2	R^3	R^4		
Ph	Me	H	H	85	6
p-$CH_3C_6H_4$	Me	H	H	80	5
m-$NO_2C_6H_4$	Me	H	H	63	20
Me	Me	H	H	69	48
Ph	Me	H	Me	81	9
m-$NO_2C_6H_4$	Me	H	Me	60	42
p-$CH_3C_6H_4$	Me	H	Me	75	12
Me	Me	H	Me	64	18
Ph	Me	Cl	Cl	73	45
p-$CH_3C_6H_4$	Me	Cl	Cl	67	40
Me	Me	Cl	Cl	65	38
Me	H	H	H	68	5
Ph	H	H	H	58	5.5
Ph	Me	H	H	85[b]	6

[a] Isolated yield.

[b] By using 2% cross-linked poly[styrene(iodoso diacetate) recycled for 5 times.



Scheme 2.

acylhydrazone with an acetate group on phenyliodine diacetate to produce intermediate **5**. After reductive elimination of iodobenzene, the acetate group undergoes addition to the hydrazone carbon, yielding intermediate **6**. Loss of acetic acid gives **7** which cyclizes to **8**, and losses N_2 to give the product.

EXPERIMENTAL

2% Cross-linked polystyrene was purchased from Aldrich. ^{1}H-NMR spectra were recorded at 60 MHZ or a Varian EM-300 spectrometer from a solution in $CDCl_3$ or CCl_4 of the product. Infrared spectra were recorded on a Perkin Elmer 683 spectrophotometer in KBr with absorption in cm^{-1}. The 2% cross-linked poly[styrene(iodoso diacetate)] was prepared according to the known literature.[13]

1. **The preparation of *o*-hydroxyacetophenone acylhydrazones (3a). Typical procedure**: *o*-Acylphenol **1** (0.68 g, 5 mmol) was added to a stirred solution of benzoic hydrazide **2** (0.68 g, 5 mmol) in 1-propanol (25 mL) and the solution was heated to reflux for 6 h. The solution was filtered to afford the *o*-hydroyaryl ketone acylhydrazone **3a** which was used without further purification.
2. **The preparation of 1,2-Diacylbenzenes (4a). Typical procedure**: 2% Cross-linked poly[styrene(iodoso diacetate)] 1.5 mmol (0.75 g) was added to a stirred solution of the *o*-hydroxy aryl ketone acylhydrazones **3a** (0.08 g, 0.5 mmol) in CH_2Cl_2 10 mL at 40°C. After the *o*-hydroxy aryl ketone acylhydrazone was consumed (monitored by TLC), the mixture was filtered to remove the resin, and washed with 5 mL CH_2Cl_2, 6 mL H_2O. The aqueous layer was extracted with CH_2Cl_2 (3×5 mL). The combined extracts were washed with sat. *aq*. $NaHCO_3$ (3×5 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give crude 1,2-diacylbenzene **4a**. The pure product **4a** was isolated by column chromatography (Rf = 0.6) on silica gel (200–400 mesh) using EtOAc/hexanes (v/v = 2/3) as eluent.

4a: White solid; mp 72–73°C (lit[12] 72–73°C); ^{1}H-NMR (CCl_4) δ: 6.9–7.8 (m, 8H,), 2.3 (s, 6H); IR (KBr) ν (cm^{-1}) 1684, 1612; MS: m/z 238 (M^+ 100) 223(23) 147(75) 119(31).

4b: White solid; mp 95–97°C (lit[12] 95–97°C); ^{1}H-NMR (CCl_4) δ: 7.0–7.9 (m, 9H,), 3.8 (s, 6H); IR (KBr) ν (cm^{-1}) 1680, 1604; MS: m/z 224 (M^+ 5) 209(100) 147(23) 119(31) 105(29).

4c: White solid; mp 125–127°C; ^{1}H-NMR (CCl$_4$) δ: 7.2–8.4 (m, 8H), 4.5 (s, 3H); IR (KBr) ν (cm^{-1}) 1690, 1605; MS: m/z 269 (M^{+} 7) 254(100) 208(14) 180(16) 150(10) 147(29). Anal. Calcad for $C_{15}H_{11}NO_4$: C 66.91 H 4.12 N 5.20 Found: C 66.60 H 4.07 N 5.38.

4d: White solid; mp 38–39°C (lit[8] 39–40°C); ^{1}H-NMR (CCl$_4$) δ: 7.5 (s, 4H), 2.36 (s, 6H); IR (KBr) ν (cm^{-1}) 1670, 1612; MS: m/z 162 (M^{+} 4) 147(100) 91(37).

4e: White solid; mp 69–71°C (lit[12] oil); ^{1}H-NMR (CCl$_4$) δ: 7.06–7.78 (m, 8H,), 2.35 (s, 3H), 2.25 (s, 3H); IR (KBr) ν (cm^{-1}) 1680, 1610; MS: m/z 238 (M^{+} 4) 223(100) 161(22) 105(20).

4f: White solid; mp 113–115°C; ^{1}H-NMR (CCl$_4$) δ: 7.15–8.5 (m, 7H), 2.45 (s, 6H); IR (KBr) ν (cm^{-1}) 1690, 1620; MS: m/z 283 (M^{+} 6) 268(100) 161(30) 119(36). Anal. Calcad for $C_{16}H_{13}NO_4$: C 67.84 H 4.63 N 4.94 Found: C 67.68 H 4.67 N 4.88.

4g: White solid; mp 84–86°C; ^{1}H-NMR (CCl$_4$) δ: 7.0–7.7 (m, 7H), 2.3 (s, 3H), 2.4 (s, 3H); IR (KBr) ν (cm^{-1}) 1687, 1620; MS: m/z 252 (M^{+} 2) 237(100) 119(28) 105(6). Anal. Calcad for $C_{17}H_{16}O_2$: C 80.93 H 6.39 Found: C 81.50 H 6.39.

4h: oil; ^{1}H-NMR (CCl$_4$) δ: 7.06–7.5 (m, 4H,), 2.3 (s, 9H); IR (film) ν (cm^{-1}) 1690, 1610; MS: m/z 176 (M^{+} 2) 161(100) 105(25). Anal. Calcad for $C_{11}H_{12}O_2$: C 74.89 H 6.96 Found: C 74.53 H 6.89.

4i: White solid; mp 138–140°C; ^{1}H-NMR (CCl$_4$) δ: 7.13–7.65 (m, 7H,), 2.35 (s, 3H); IR (KBr) ν (cm^{-1}) 1710, 1605; MS: m/z 292 (M^{+} 22) 277(68) 215(54) 105(100). Anal. Calcad for $C_{15}H_{10}O_2Cl_2$: C 61.46 H 3.44 Found: C 61.59 H 3.45.

4j: White solid; mp 141–142°C; ^{1}H-NMR (CCl$_4$) δ: 7.0–7.8 (m, 6H), 2.3 (s, 3H), 2.4 (s, 3H); IR (KBr) ν (cm^{-1}) 1720, 1600; MS: m/z 306 (M^{+} 6) 291(23) 215(11) 189(15) 119(100). Anal. Calcad for $C_{16}H_{12}O_2Cl_2$: C 62.56 H 3.94 Found: C 62.15 H 3.88.

4k: White solid; mp 70–72°C; ^{1}H-NMR (CCl$_4$) δ: 7.5–7.7 (m, 2H), 2.4 (s, 3H), 2.46 (s, 3H); IR (KBr) ν (cm^{-1}) 1720, 1590; MS: m/z 230 (M^{+} 1) 215(100). Anal. Calcad for $C_{10}H_2O_2Cl_2$: C 51.98 H 3.49 Found: C 51.69 H 3.41.

4l: White solid; mp 40–41°C (lit[14] 41–42°C, lit[12] 39–41°C); ^{1}H-NMR (CCl$_4$) δ: 10.05 (s, 1H), 6.74–7.7 (m, 4H,), 2.5 (s, 3H); IR (KBr) ν (cm^{-1}) 1670, 1612; MS: m/z 148 (M^{+} 3) 147(15) 121(100) 105(27).

4m: White solid, mp 65–67°C (lit[7] 64–67°C); ^{1}H-NMR (CCl$_4$) δ: 9.93 (s, 1H), 7.27–7.87 (m, 9H,); IR (KBr) ν (cm^{-1}) 1680, 1610; MS: m/z 210 (M^{+} 100) 181(86) 133(7) 105(59).

Regeneration and Reuse of poly[styrene (iodoso diacetate)] from recovered Poly(iodostyrene): Hydrogen peroxide (30%, 40 mL) was added dropwise to acetic anhydride (145 mL) at 40°C and was stirred for another

4 h. To this solution, 6.0 g of 2% cross-linked polyiodostyrene, which was recovered by simply filtration after the reaction, was added and the solution was kept at 40°C for one day to give poly[styrene(iodoso diacetate)]. IR ν cm^{-1} 1654, 1500, 1410, 1360, 1280, 1000, 817, 760, 700. The functional group is 1.97 mmol/g. It was applied to the reaction and has the same activity as the first prepared poly[styrene(iodoso diacetate)].

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