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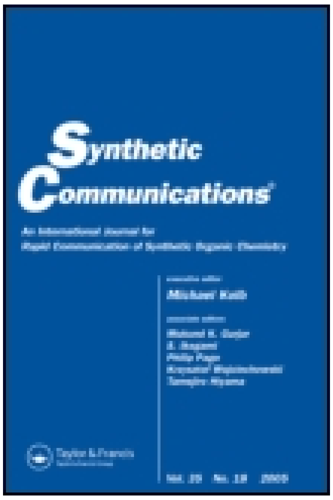

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SYNTHESIS OF POLYMERIC DIARYLIODONIUM SALTS AND ITS USE IN PREPARATION OF DIARYL SULFIDES AND DIARYL ETHERS

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SYNTHESIS OF POLYMERIC DIARYLIODONIUM SALTS AND ITS USE IN PREPARATION OF DIARYL SULFIDES AND DIARYL ETHERS

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ABSTRACT

Polymeric diaryliodonium salts were synthesized and applied to the preparation of diaryl ethers and diaryl sulfides under mild conditions. The byproduct, polyiodostyrene, could be recycled and reused.

Recently much attention has been paid to hypervalent iodine (III) compounds in organic synthesis.[1] The most widely investigated species were diaryliodonium salts, which are used today in imaging systems.[2] As arylating agents, they react with various organic substrates under mild conditions. Typical examples of the conditions with anionic nucleophiles under polar conditions include arylations of thiocarbamates,[3] dialkyl phosphates,[4] aryl selenides,[5] *o*,*o*-dialkyl *s*-aryl phosphoro thiolates,[6] etc. However, in these reactions diaryliodonium salts are converted into iodobenzene, which is difficult to remove from products and hard to reuse.

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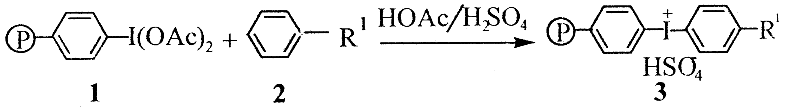
Polymeric diaryliodonium salts were widely used as photo and thermal initiated cationic polymerization.[7] No examples cited their synthetic utility in organic synthesis. In this paper, we report polymeric diaryliodonium salts were used as aryl transfer reagents to react with sodium phenyloxide or sodium thiophenyloxide.

Poly[styrene (iodoso diacetate)] was prepared from commercially available polystyrene (MW 250,000) by literature method.[8] To a mixture of poly[styrene (iodoso diacetate)] and arenes, concentrated sulfuric acid was added dropwise at room temperature. After 1–3 days, the solution was poured into cold water to afford polymeric diaryliodonium salts (Scheme 1). IR spectra showed that the characteristic peak of acetate disappeared and that of bisulfate anion appeared. The exact capacity of functional group was determined by elemental analysis of sulfur, which indicated that the functional groups were 1.35–1.53 mmol/g (Table 1).

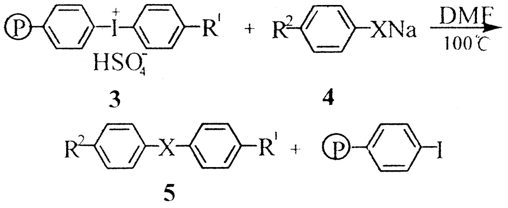


Scheme 1.

As electrophilic reagent, diaryliodonium salts are more reactive than aryl halides. Diaryl ethers and diaryl sulfides could be obtained by the reaction of aryl halides and phenols and thiophenols under critical conditions, such as high temperature and pressure equipment.[9] By using polymeric diaryliodonium salts, we synthesized the diaryl ether and diaryl sulfide under comparative mild conditions. A mixture of sodium benzenethiolate or sodium phenolate and polymeric diaryliodonium salts (3) in DMF was kept at 100°C for 10 or 24 h (Scheme 2). The arylated products (5) were obtained in good yield (Table 2).

Table 1. Synthesis of Polymeric Diaryliodonium Salts

Resin	R^1	Time (h)	Functional group (mmol)
3a	H	72	1.35
3b	CH_3	24	1.48
3c	OCH_3	24	1.53



Scheme 2.

Table 2. Preparation of Diaryl Ethers and Diaryl Sulfides

Products	Resin	R^2	Time (h)	X	Purity (%)	Yields (%)[a]
5a	3a	H	24	O	90	48
5b	3b	H	24	O	90	58
5c	3c	H	24	O	95	52
5d	3a	CH_3	24	O	85	52
5e	3b	CH_3	24	O	80	65
5f	3c	CH_3	24	O	87	56
5g	3a	NO_2	24	O	85	46
5h	3b	NO_2	24	O	92	62
5i	3c	NO_2	24	O	80	55
5j	3a	H	10	S	84	67
5k	3b	H	10	S	90	76
5l	3c	H	10	S	95	74
5m	3a	CH_3	10	S	88	65
5n	3b	CH_3	10	S	88	88
5o	3c	CH_3	10	S	85	81
5p	3a	Cl	10	S	90	76
5a	3a	H	24	O	85	46[b]

[a] Isolated yield.
[b] By using polymeric diaryliodonium salt recycled for 3 times.

EXPERIMENTAL SECTION

^{1}H-NMR spectra were recorded at 60 MHz on a Varian EM-300 spectrometer from a solution in CCl_4 of the products. Infrared spectra were recorded on a Perkin Elmer 683 spectrophotometer in KBr or film with absorption in cm^{-1}. Poly[styrene (iodoso diacetate)] was prepared according to the literature method.[8]

Preparation of polymeric diaryliodonium salts: To a cold mixture of 1.0 g poly[styrene (iodoso diacetate)], 10 mL arenes and 60 mL acetic acid, 10 mL conc. sulfuric acid was added dropwise. The solution was kept at room temperature for 24–72 h. The mixture was diluted with 100 mL of ice water and the precipitate was washed with methanol (10 mL × 3), water (20 mL × 5) and dried to give 0.6–0.8 g polymeric diaryliodonium salts. IR (KBr) ν (cm^{-1}) 3450, 1180, 1040. Resin (3a): S 4.35%, functional group 1.35 mmol/g; Resin (3b): S 4.74%, functional group 1.48 mmol/g; Resin (3c): S 4.89%, functional group 1.53 mmol/g.

Typical procedure of the preparation of diaryl sulfides: 1.5 mmol of phenyl polymeric styryliodonium salts (3a) and 1 mmol sodium p-methyl benzenethiolate were added to 10 mL of DMF. The temperature was kept at 100°C for 10 h. Then the solution was poured into 100 mL cold water to precipitate the polymer. The aqueous layer was extracted with ether (2 × 10 mL) and chloroform (15 mL). The combined organic layer was washed with water (20 mL × 2) and dried over $MgSO_4$. After evaporated the solvent gave *p*-methylphenyl phenyl sulfide (5m).

5a: purity 90%; yield 48%; oil (lit.[10a] m.p. 25–27°C); ^{1}H-NMR (CCl_4) δ: 6.65–7.40 (m, 10H); IR (film) ν (cm^{-1}): 3040, 1580, 1480, 1230, 1160, 1020.

5b: purity 90%; yield 58%; oil (lit.[10a] oil); ^{1}H-NMR (CCl_4) δ: 6.70–7.60 (m, 9H), 2.37 (s, 3H); IR (film) ν (cm^{-1}): 2920, 1690, 1590, 1490, 1235, 1120, 1000, 870, 760, 690.

5c: purity 95%; yield 52%; oil (lit.[10b] oil); ^{1}H-NMR (CCl_4) δ: 6.50–7.70 (m, 9H), 3.70 (s, 3H); IR (film) ν (cm^{-1}): 2920, 2820, 1690, 1595, 1480, 1460, 1230, 1030, 810, 790, 730.

5d: purity 85%; yield 52%; oil (lit.[10a] oil); ^{1}H-NMR (CCl_4) δ: 6.70–7.60 (m, 9H), 2.27 (s, 3H); IR (film) ν (cm^{-1}): 2920, 1590, 1490, 1235, 1120, 1000, 870, 760, 690.

5e: purity 80%; yield 65%; white solid (recrystallized from hexane); m.p. 49–50°C (lit.[10c] m.p. 50°C); ^{1}H-NMR (CCl_4) δ: 6.57–7.06 (m, 8H), 2.26 (s, 6H); IR (KBr) ν (cm^{-1}): 2920, 1480, 1230, 1150, 1020, 820.

5f: purity 87%; yield 56%; white solid (recrystallized from hexane); m.p. 45–46°C (lit.[10c] m.p. 45–46°C); ^{1}H-NMR (CCl_4) δ: 6.45–7.40 (m, 8H), 3.72 (s, 3H), 2.40 (s, 3H); IR (KBr) ν (cm^{-1}): 2920, 2820, 1580, 1490, 1250, 1170, 1070, 1030, 820, 800.

5g: purity 85%; yield 46%; pale yellow solid (recrystallized from hexane); m.p. 59–60°C (lit.[10c] m.p. 61°C); ^{1}H-NMR (CCl_4) δ: 7.80–8.27 (m, 2H), 6.60–7.55 (m, 7H); IR (KBr) ν (cm^{-1}): 2920, 2820, 1590, 1490, 1435, 1340, 1245, 1110, 1000, 870, 810, 750.

5h: purity 92%; yield 62%; pale yellow solid (recrystallized from hexane); m.p. 68–69°C (lit.[10c] m.p. 69°C); ^{1}H-NMR (CCl_4) δ: 8.00–8.15

(m, 2H), 6.70–7.30 (m, 6H), 2.30 (s, 3H); IR (KBr) ν (cm^{-1}): 2920, 1590, 1520, 1490, 1345, 1240, 1115, 870, 850.

5i: purity 80%; yield 55%; pale yellow solid (recrystallized from hexane); m.p. 110–111°C (lit.[10d] m.p. 110–111°C); ^{1}H-NMR (CCl_4) δ: 7.93–8.05 (m, 2H), 6.50–7.05 (m, 6H), 3.65 (s, 3H); IR (KBr) ν (cm^{-1}): 2920, 2820, 1580, 1505, 1490, 1440, 1350, 1250, 1110, 820.

5j: purity 84%; yield 67%; oil (lit.[10e] oil); ^{1}H-NMR (CCl_4) δ: 7.02–7.74 (m, 10H); IR (film) ν (cm^{-1}): 3060, 1580, 1470, 1440, 1080, 1030.

5k: purity 90%; yield 76%; oil (lit.[10e] oil); ^{1}H-NMR (CCl_4) δ: 6.80–7.80 (m, 9H), 2.37 (s, 3H); IR (film) ν (cm^{-1}): 3040, 2930, 1590, 1485, 1080, 1010, 800, 750, 700.

5l: purity 95%; yield 74%; oil (lit.[10e] oil); ^{1}H-NMR (CCl_4) δ: 6.56–7.56 (m, 9H), 3.70 (s, 3H); IR (film) ν (cm^{-1}): 3020, 2920, 2820, 1585, 1490, 1070, 1030, 1000, 810, 755, 690.

5m: purity 88%; yield 65%; oil (lit.[10e] oil); ^{1}H-NMR (CCl_4) δ: 6.80–7.80 (m, 9H), 2.37 (s, 3H); IR (film) ν (cm^{-1}): 3040, 2930, 1590, 1485, 1080, 1010, 800, 750, 700.

5n: purity 88%; yield 88%; pale yellow solid (recrystallized from hexane); m.p. 56–57°C (lit.[10f] m.p. 56–57°C); ^{1}H-NMR (CCl_4) δ: 6.73–7.65 (m, 8H), 2.24 (s, 3H); IR (KBr) ν (cm^{-1}): 3040, 2920, 1595, 1485, 1080, 1005, 790.

5o: purity 85%; yield 81%; pale yellow solid (recrystallized from hexane); m.p. 45–46°C (lit.[10g] m.p. 45–46°C); ^{1}H-NMR (CCl_4) δ: 6.55–7.53 (m, 78H), 3.68 (s, 3H), 2.25 (s, 3H); IR (KBr) ν (cm^{-1}): 2920, 2820, 1595, 1490, 1065, 800.

5p: purity 90%; yield 76%; oil (lit.[10h] oil); ^{1}H-NMR (CCl_4) δ: 7.20–7.55 (m, 9H); IR (film) ν (cm^{-1}): 1685, 1590, 1480, 1090, 1010, 820, 740, 690.

5a (by using recycled resin): purity 85%; yield 46%; oil (lit.[10a]m.p. 25–27°C); ^{1}H-NMR (CCl_4) δ: 6.65–7.40 (m, 10H); IR (film) ν (cm^{-1}): 3040, 1580, 1480, 1230, 1160, 1020.

Regeneration and reuse of polymeric diaryliodonium salts:: After the reaction, polyiodostyrene was recovered simply by filtration, and was oxidized to poly[styrene (iodoso diacetate)] with peracetic acid according the known method.[8] After treatment with arenes and conc. sulfuric acid, polymeric diaryliodonium salts were regenerated. Resin 3a: S 4.32%, functional group 1.34 mmol/g; Resin 3b: S 4.40%, functional group 1.38 mmol/g; Resin 3c: S 4.70%, functional group 1.47 mmol/g.

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REFERENCES

1. (a) Varvoglis, A. Synthesis **1984**, 709. (b) Moriarty, R.M.; Vaid, R.K. Synthesis **1990**, 431.
2. Ito, H.; Ueda, M. J. Photopolym. Sci. Techn. **1989**, 21.
3. Chen, Z.C.; Jin, Y.Y.; Stang, P.J. J. Org. Chem. **1987**, *52*, 4117.
4. Liu, D.D.; Chen, Z.C. Synthesis **1993**, 373.
5. Liu, Z.D.; Zeng, H.; Chen, Z.C. Synth. Commun. **1994**, *24*, 475.
6. Liu, D.D.; Chen, D.W.; Chen, Z.C. Synth. Commun. **1992**, *22*, 2903.
7. (a) Crivello, J.V.; Lee, J.L. Polymer Bull. **1986**, *16*, 243. (b) Crivello, J.V.; Lam, J.H.W. J. Polym. Science: Sym. **1976**, *56*, 383.
8. Wang, G.P.; Chen, Z.C. Synth. Commun. **1999**, *29*, 2859.
9. Bunnett, J.F.; Zahler, R.E. Chem. Rev. **1951**, *49*, 273.
10. (a) Narisada, M.; Nakagawa, T. Yakagaku Zasshi **1959**, *79*, 177. (b) Schono, T.; Iikumi, Oda, R.T. Nippon kagaku Zasshi **1960**, *81*, 1625. (c) Bacon, R.G.R.; Stewart, O.J. J. Chem. Soc. **1965**, 4953. (d) Iijima, H.; Endo, Y.; Shudo, K.; Okamoto, T. Tetrahedron **1984**, *40*, 4981. (e) Petrillo, G.; Novi, M.; Garbarino, G.; Pell'Erba, C. Tetrahedron Lett. **1985**, *26*, 6365. (f) Takagi, B. Chem. Lett. **1987**, 2221. (g) Still, I.W.; Toste, F.D. J. Org. Chem. **1996**, *61*, 7677. (h) Cristan, H.J.; Chabaud, B.; Chene, A.; Christol, H. Synthesis **1981**, 892.

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