Fast, Efficient, and Convenient Method for the Preparation of Arylazo Aryl Sulfones Using Stable Aryldiazonium Silica Sulfates under Mild Conditions

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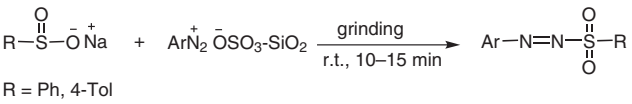
Abstract: An efficient, fast, and straightforward procedure for the synthesis of arylazo aryl sulfones is described by using aryl diazonium silica sulfates and sodium arenesulfinates. The reaction was carried out at room temperature under mild conditions. The use of inexpensive materials, simple and clean workup, short reaction times, and good yields are the advantages of this method.

Key words: aryl diazonium silica sulfates, sodium arenesulfinates, arylazo aryl sulfones

Aromatic diazonium salts have been prepared and studied for years. These salts are important building blocks in classical and modern organic synthesis,[1]and interest in these versatile and reactive species remains high. Arylazo aryl sulfones (arenediazosulfones) have been studied from their thermal[2] and photochemical[3] behavior as well as their stability toward acids[4] and bases[5] and various reagents.[6] Arylazo aryl sulfones are prepared by the reaction of arenediazonium salts with sulfinic acid salts.[6a,7] Although some of these methods are convenient protocols with good yields, some of them suffer from disadvantages such as long reaction times, low yields, and requirement of toxic solvents. In continuation of our studies on the stabilization of diazonium salts on silica sulfuric acid and their applications in organic synthesis,[8] we report herein an efficient, fast, and convenient procedure for the synthesis of arylazo aryl sulfones employing aryl diazonium silica sulfates in the presence of sodium arenesulfinates at room temperature under solvent-free conditions (Scheme 1).

Although diazonium salts have wide applications in the synthesis of various compounds, these salts have a serious drawback in their intrinsic instability and explosive potential. Therefore, these compounds are usually synthesized at around 10 °C, and to avoid their decomposition, they are handled below 0 °C. Moreover, due to this instability, subsequent reactions with diazonium salts must be carried out in the same conditions which were produced. These problems restrict chemists applying potentially important transformations of these salts.[1a] Therefore, new diazonium salts with high stability and versatility that can be easily made and stored under solid-state conditions without risk of explosion are highly desirable. Aryldiazonium tetrafluoroborates,[1a,9] aryldiazonium hexafluorophosphates,[1a–d] arenediazonium *o*-benezenedisulfonimides[10] and arenediazonium arylsufonates[11] are a representative diazonium salts possessing these properties.



Scheme 1

Recently, we have shown that silica sulfuric acid[12] serves as a mild solid acid for the fast preparation of aryldiazonium salts supported on the surface of this solid reagent (aryldiazonium silica sulfates).[8] We found that these new aryldiazonium salts, $ArN_2^+{}^-OSO_3$-SiO_2, were sufficiently stable and could be kept at room temperature under anhydrous conditions.[8] For example, 4-nitrophenyl diazonium silica sulfate, which had been stored in a desiccator at room temperature for three days, reacted with sodium benzenesulfinate under solvent-free conditions and provided almost the same yield of 4-nitrophenylazo phenyl sulfone as when prepared from fresh 4-nitrophenyl diazonium silica sulfate (Table 1, entry 12). To illustrate the scope of the present method, a range of aromatic amines was rapidly converted to the corresponding arylazo aryl sulfones in good to high yields under mild conditions (Table 1). In contrast to related methodology, aromatic amines with electron-withdrawing groups or electron-donating groups also reacted.

The steric effects of *ortho* substituents had relatively little influence on the reaction time (Table 1, entries 5, 7, 14, 16). The corresponding phenol derivatives were formed in trace yields as byproducts. The crude products were extracted with ethyl acetate and, if necessary, were purified by short column chromatography. In contrast to conventional methods, the reaction rate is rapid because, by supporting the aryldiazonium salt on silica sulfuric acid, the surface area of the reaction increases.[8,13] Finally, after completion of the reaction and isolation of the product, the

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solid support could be recycled.[8] In addition, the present procedure for the preparation of arylazo aryl sulfones is safe and nonexplosive because by supporting aryldiazonium salts on the surface of silica sulfuric acid as a bulky support, the stability of these salts increases.[8,14]

Table 1 Preparation of (*E*)-Arylazo Aryl Sulfones Using Aryl Diazonium Silica Sulfates at Room Temperature[a]

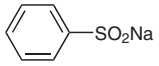
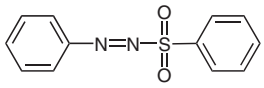
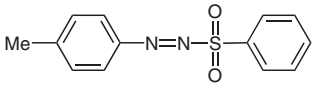
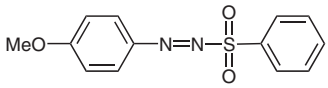
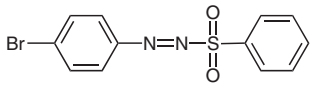
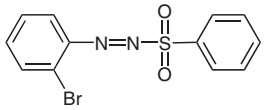
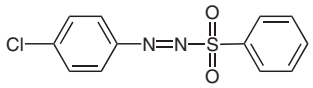
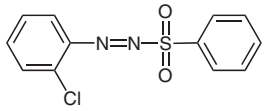
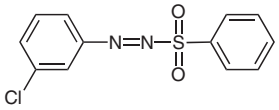
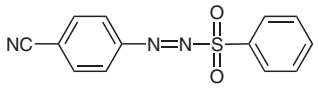
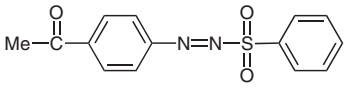
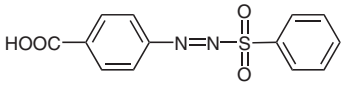
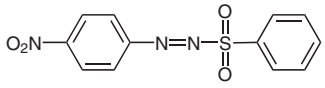
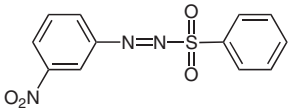
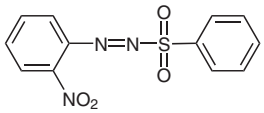
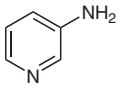
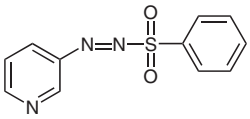
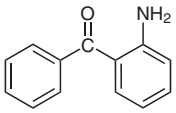
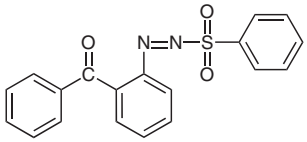
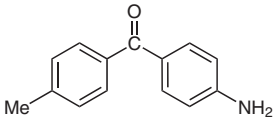
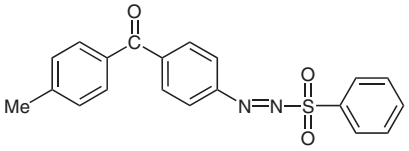
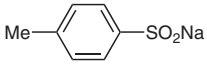
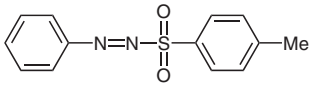
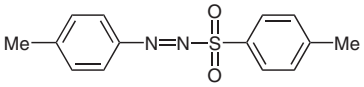
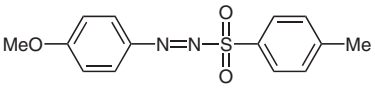
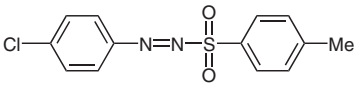
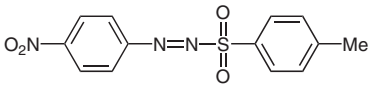
Entry	Sodium arenesulfinates	Aromatic amines	Products	Time (min)	Yield (%)
1		$PhNH_2$		10	77
2		$4\text{-}MeC_6H_4NH_2$		10	75
3		$4\text{-}MeOC_6H_4NH_2$		10	72
4		$4\text{-}BrC_6H_4NH_2$		10	81
5		$2\text{-}BrC_6H_4NH_2$		15	79
6		$4\text{-}ClC_6H_4NH_2$		10	83
7		$2\text{-}ClC_6H_4NH_2$		15	89
8		$3\text{-}ClC_6H_4NH_2$		10	80
9		$4\text{-}NCC_6H_4NH_2$		10	82
10		$4\text{-}MeCOC_6H_4NH_2$		10	85
11		$4\text{-}H_2NC_6H_4COOH$		15	76
12		$4\text{-}O_2NC_6H_4NH_2$		10	82
13		$3\text{-}O_2NC_6H_4NH_2$		10	76
14		$2\text{-}O_2NC_6H_4NH_2$		15	78

Table 1 Preparation of (*E*)-Arylazo Aryl Sulfones Using Aryl Diazonium Silica Sulfates at Room Temperature[a] (continued)

Entry	Sodium arenesulfinates	Aromatic amines	Products	Time (min)	Yield (%)
15				10	70
16				15	81
17				10	80
18		$PhNH_2$		10	76
19		$4\text{-}MeC_6H_4NH_2$		10	74
20		$4\text{-}MeOC_6H_4NH_2$		10	72
21		$4\text{-}ClC_6H_4NH_2$		10	81
22		$4\text{-}O_2NC_6H_4NH_2$		10	80

[a] The yields refer to isolated pure products which were characterized from their spectroscopic data and by comparison with authentic samples.[6,7]

In summary, we have developed an efficient, rapid, experimentally simple, and environmentally benign method for the preparation of arylazo aryl sulfones using aryldiazonium silica sulfates. These reactions proceed at room temperature under mild conditions in good to high yields. Further investigations on new applications of these salts are ongoing in our laboratories.

Typical Procedure for the Preparation of 4-Nitrophenyazo Phenyl Sulfone

Sodium benzenesulfinate (1.8 mmol, 0.3 g) was added to freshly prepared 4-nitrophenyl diazonium silica sulfate[8] (1 mmol), and the reaction mixture was ground with a pestle in a mortar for 10 min at r.t. The mixture was diluted with EtOAc (12 mL) and, after vigorous stirring, was filtered. The residue was extracted with EtOAc (3 × 12 mL), and the combined organic layer was washed with 5% NaOH solution and then dried over anhyd Na_2SO_4. The solvent was evaporated to afford 4-nitrophenyazo phenyl sulfone in 82% yield (0.0.238 g).

The Spectral Data of New Compounds

Table 1, Entry 9

Brown solid; mp 104–106 °C. IR (KBr): 3096, 2226, 1581, 1496, 1447, 1404, 1353, 1305, 1183, 1164, 1084, 882, 853, 785, 753, 730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00 (2 H, d, *J* = 8.0 Hz), 7.91 (2 H, d, *J* = 8.4 Hz), 7.82 (2 H, d, *J* = 8.4 Hz), 7.77 (1 H, t, *J* = 7.2 Hz), 7.64 (2 H, t, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.85, 135.22, 133.55, 132.31, 130.54, 129.42, 124.74, 117.65, 117.45. ESI-HRMS: *m/z* calcd for $C_{13}H_9N_3O_2S$ $[M + H]^+$: 272.0415; found: 272.1811. Anal. Calcd for $C_{13}H_9N_3O_2S$: C, 57.55; H, 3.34; N, 15.49; S, 11.82. Found: C, 57.36; H, 3.51; N, 15.61; S, 11.67.

Table 1, Entry 10

Light brown solid; mp 113–115 °C. IR (KBr): 3093, 1689, 1598, 1579, 1464, 1445, 1404, 1352, 1310, 1256, 1171, 1147, 1082, 1004, 959, 883, 844, 755, 729 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 (2 H, d, *J* = 8.4 Hz), 8.01 (2 H, d, *J* = 7.2 Hz), 7.89 (2 H, d, *J* = 8.4 Hz), 7.75 (1 H, t, *J* = 7.6 Hz), 7.64 (2 H, t, *J* = 7.6 Hz), 2.66 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.85, 151.28, 141.19, 135.00, 132.65, 130.50, 129.47, 129.33, 124.52, 26.93. ESI-HRMS: *m/z* calcd for $C_{14}H_{12}N_2O_3S$ $[M + H]^+$: 289.0569; found, 289.1922. Anal. Calcd for $C_{14}H_{12}N_2O_3S$: C, 58.32; H, 4.20; N, 9.72; S, 11.12. Found: C, 58.12; H, 4.34; N, 9.63; S, 11.25.

Table 1, Entry 11

Orange solid; mp 132–134 °C. IR (KBr): 3101-2550, 1691, 1603, 1580, 1470, 1430, 1351, 1321, 1294, 1166, 1085, 1012, 955, 871, 808, 777, 720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$/DMSO-d_6): δ = 7.99 (2 H, d, *J* = 8.8 Hz), 7.79 (2 H, d, *J* = 7.8 Hz), 7.66 (2 H, d, *J* = 8.8 Hz), 7.60 (1 H, t, *J* = 7.6 Hz), 7.47 (2 H, t, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ = 166.82, 151.03, 136.37, 134.93, 132.45, 130.86, 130.27, 129.23, 123.95. Anal. Calcd for

$C_{13}H_{10}N_2O_4S$: C, 53.79; H, 3.47; N, 9.65; S, 11.05. Found: C, 53.68; H, 3.56; N, 9.54; S, 10.94.

Table 1, Entry 13

Yellow solid; mp 119–121 °C. IR (KBr): 3100, 1608, 1582, 1527, 1349, 1312, 1171, 1075, 997, 906, 843, 814, 752, 740, 727 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.63 (1 H, s), 8.46 (1 H, d, *J* = 8.4 Hz), 8.18 (1 H, d, *J* = 7.6 Hz), 8.01 (2 H, d, *J* = 7.6 Hz), 7.81–7.73 (2 H, m), 7.66 (2 H, t, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.39 148.96, 135.27, 132.31, 130.71, 130.56, 129.46, 128.45, 119.35. ESI-HRMS: *m/z* calcd for $C_{12}H_9N_3O_4S$ $[M + H]^+$: 292.0314; found, 292.2346. Anal. Calcd for $C_{12}H_9N_3O_4S$: C, 49.48; H, 3.11; N, 14.43; S, 11.01. Found: C, 49.29; H, 3.32; N, 14.37; S, 11.18.

Table 1, Entry 15

Yellow solid; mp 103–105 °C. IR (KBr): 3095, 3071, 1575, 1488, 1466, 1451, 1420, 1348, 1195, 1167, 1083, 1016, 970, 879, 818, 775, 755, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.05 (1 H, s), 8.82 (1 H, d, *J* = 4.0 Hz), 8.07 (1 H, d, *J* = 8.0 Hz), 8.00 (2 H, d, *J* = 7.6 Hz), 7.77 (1 H, t, *J* = 7.6 Hz), 7.64 (2 H, t, *J* = 7.6 Hz), 7.48 (1 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.33, 149.00, 144.66, 135.10, 132.46, 130.47, 129.37, 127.56, 124.39. ESI-HRMS: *m/z* calcd for $C_{11}H_9N_3O_2S$ $[M + H]^+$: 248.0415; found: 248.02451. Anal. Calcd for $C_{11}H_9N_3O_2S$: C, 53.43; H, 3.67; N, 16.99; S, 12.97. Found: C, 53.49; H, 3.79; N, 16.84; S, 12.88.

Table 1, Entry 16

Yellow solid; mp 105–107 °C. IR (KBr): 3062, 1666, 1593, 1579, 1491, 1449, 1348, 1317, 1287, 1246, 1182, 1160, 1082, 998, 931, 885, 806, 767, 720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (1 H, d, *J* = 8.4 Hz), 7.71 (1 H, t, *J* = 7.6 Hz), 7.64 (1 H, t, *J* = 7.2 Hz), 7.57 (1 H, t, *J* = 7.2 Hz), 7.53–7.48 (4 H, m), 7.44–7.36 (4 H, m), 7.27 (2 H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.75, 146.17, 141.37, 136.94, 134.82, 134.40, 133.57, 131.52, 130.83, 130.19, 129.91, 128.79, 128.70, 128.46, 117.13. ESI-HRMS: *m/z* calcd for $C_{19}H_{14}N_2O_3S$ $[M + H]^+$: 351.0725; found: 351.01651. Anal. Calcd for $C_{19}H_{14}N_2O_3S$: C, 65.13; H, 4.03; N, 7.99; S, 9.15. Found: C, 65.02; H, 4.21; N, 7.86; S, 9.01.

Table 1, Entry 17

Orange solid; mp 115–117 °C. IR (KBr): 3065, 1648, 1604, 1582, 1466, 1448, 1406, 1352, 1311, 1285, 1167, 1084, 932, 883, 861, 833, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (2 H, d, *J* = 8.4 Hz), 7.92 (2 H, d, *J* = 8.4 Hz), 7.88 (2 H, d, *J* = 8.8 Hz), 7.76 (1 H, t, *J* = 7.6 Hz), 7.70 (2 H, d, *J* = 8.0 Hz), 7.64 (2 H, t, *J* = 7.6 Hz), 7.30 (2 H, d, *J* = 8.0 Hz), 2.46 (3 H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.00, 150.66, 144.27, 143.07, 134.96, 133.94, 132.79, 131.10, 130.81, 130.49, 130.30, 129.28, 124.34, 21.73. ESI-HRMS: *m/z* calcd for $C_{20}H_{16}N_2O_3S$ $[M + H]^+$: 365.0882; found: 365.1694. Anal. Calcd for $C_{20}H_{16}N_2O_3S$: C, 65.92; H, 4.43; N, 7.69; S, 8.80. Found: C, 65.78; H, 4.39; N, 7.83; S, 8.93.

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References

(1) (a) Roglands, A.; Pla-Quintana, A.; Moreno-Mañas, M. *Chem. Rev.* **2006**, *106*, 4622. (b) Zollinger, H. *Diazo Chemistry I*; VCH: Weinheim, **1994**. (c) Galli, C. *Chem. Rev.* **1988**, *88*, 765. (d) Zollinger, H. *The Chemistry of Amino, Nitroso, Nitro and Related Groups*; Patai, S., Ed.; Wiley and Sons: New York, **1996**. (e) Tour, J. M. *J. Org. Chem.* **2007**, *72*, 7477. (f) Yu, S. S. C.; Downnard, A. J. *Langmuir* **2007**, *23*, 4662. (g) Olah, G. A.; Laali, K. K.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; Wiley: New York, **1998**.

(2) (a) Rosenthal, A. J.; Overberger, C. G. *J. Am. Chem. Soc.* **1960**, *82*, 108. (b) Kice, J. L.; Gabrielsem, R. S. *J. Org. Chem.* **1970**, *35*, 1004. (c) Yoshida, M.; Futura, N.; Kobayashi, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2356.

(3) Kobayashi, M.; Fujii, S.; Minatno, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2039.

(4) Kobayashi, M.; Minato, H.; Kobori, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 219.

(5) (a) Bunnett, J. F.; Happer, D. A. R.; Takayama, H. *J. Chem. Soc., Chem. Commun.* **1966**, 367. (b) Bunnett, J. F.; Happer, D. A. R. *J. Org. Chem.* **1967**, *32*, 2701.

(6) (a) Ahren, M. F.; Leopold, A.; Beadle, J. R.; Gokel, G. W. *J. Am. Chem. Soc.* **1982**, *104*, 548. (b) Evers, M. J.; Christiaens, L. E.; Guillaume, M. R.; Renson, M. J. *J. Org. Chem.* **1985**, *50*, 1779. (c) Evers, M. J.; Christiaens, L. E.; Guillaume, M. R.; Renson, M. J. *J. Org. Chem.* **1986**, *51*, 5196. (d) Kamigata, N.; Satoh, A.; Yoshida, M.; Kameyama, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 605. (e) Yoshida, M.; Yano, A.; Kobayashi, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2679.

(7) Kojima, M.; Minato, H.; Kobayashi, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2032.

(8) (a) Zarei, A.; Hajipour, A. R.; Khazdooz, L.; Mirjalili, B. F.; Najafichermahini, A. *Dyes Pigments* **2009**, *81*, 240. (b) Zarei, A.; Hajipour, A. R.; Khazdooz, L. *Synthesis* **2009**, 941. (c) Zarei, A.; Hajipour, A. R.; Khazdooz, L.; Aghaei, H. *Tetrahedron Lett.* **2009**, *50*, 4443.

(9) (a) Doyle, M. P.; Bryker, W. J. *J. Org. Chem.* **1979**, *44*, 1572. (b) Cygler, M.; Przybylska, M.; Elofson, R. M. *Can. J. Chem.* **1982**, *60*, 2852. (c) Hubbard, A.; Okazaki, T.; Laali, K. K. *J. Org. Chem.* **2008**, *73*, 316.

(10) (a) Barbero, M.; Crisma, M.; Degani, I.; Fochi, R.; Perracino, P. *Synthesis* **1998**, 1171. (b) Barbero, M.; Degani, I.; Dughero, S.; Fochi, R. *J. Org. Chem.* **1999**, *64*, 3448.

(11) (a) Krasnokutskaya, E. A.; Semenischeva, N. I.; Filimonov, V. D.; Knochel, P. *Synthesis* **2007**, 81. (b) Filimonov, V. D.; Trusova, M.; Postnikov, P.; Krasnokutskaya, E. A.; Lee, Y. M.; Hwang, H. Y.; Kim, H.; Chi, K. W. *Org. Lett.* **2008**, *10*, 3961.

(12) (a) Zolfigol, M. A. *Tetrahedron* **2001**, *57*, 9509. (b) Zolfigol, M. A.; Shirini, F.; Ghorbani Choghamarani, A.; Mohammadpoor-Baltork, I. *Green Chem.* **2002**, *4*, 562. (c) Hajipour, A. R.; Mirjalili, B. B. F.; Zarei, A.; Khazdooz, L.; Ruoho, A. E. *Tetrahedron Lett.* **2004**, *45*, 6607. (d) Zolfigol, M. A.; Mirjalili, B. B. F.; Bamoniri, A.; Karimi, M. A.; Zarei, A.; Khazdooz, L.; Noei, J. *Bull. Korean Chem. Soc.* **2004**, *25*, 1414. (e) Hajipour, A. R.; Zarei, A.; Khazdooz, L.; Mirjalili, B. B. F.; Sheikhan, N.; Zahmatkesh, S.; Ruoho, A. E. *Synthesis* **2005**, 3644. (f) Hajipour, A. R.; Zarei, A.; Ruoho, A. E. *Synth. Commun.* **2006**, *36*, 1039. (g) Hajipour, A. R.; Zarei, A.; Khazdooz, L.; Ruoho, A. E. *Synth. Commun.* **2005**, *35*, 2237.

(13) Clark, J. H. *Catalysis of Organic Reactions by Supported Inorganic Reagents*; VCH: Weinheim, **1994**.

(14) (a) Akelah, A.; Moet, A. *Functionalized Polymers and Their Applications*; Chapman and Hall: London, **1990**. (b) Hodge, P.; Sherrington, D. C. *Polymer-Supported Reactions in Organic Synthesis*; John Wiley and Sons: Chichester, **1980**, .