A One-Step, Safe Synthesis of 2,4-Dinitrostyrene and Related (Di)nitrodivinylbenzenes via Stille Coupling

Nathalie Eloy, Eric Pasquinet,* Eric Grech, Frank David-Quillot, Olivier Besnard, Didier Poullain

CEA Le Ripault, BP16, 37260 Monts, France Fax +33(2)47345142; E-mail: eric.pasquinet@cea.fr *Received 12 December 2007; revised 19 December 2007*



Abstract: A one-step synthesis of 2,4-dinitrostyrene is described. Based on a Stille coupling, the procedure is more amenable to scale-up than the existing methods that require longer reaction sequences and hazardous nitration processes. This easily polymerizable monomer was isolated using a continuous extraction method. The reaction was extended to the synthesis of two other related vinyl monomers including the previously unknown 1,3-dinitro-4,6-divinylbenzene.

Key words: Stille reaction, cross-coupling, polymers, nitro compounds, styrenes



Scheme 1

2,4-Dinitrostyrene (**2a**) is a well-known monomer which has been primarily used in the field of energetic materials.¹ Unusually, it does not polymerize under classical radical or cationic conditions, but generates poly(2,4-dinitrostyrene) upon the action of basic species. Charge-transfer complexes with some organic amines were shown to be involved in the polymerization process.² The copolymerization of **2a** with 2,4,6-trinitrostyrene was also described.³ This ability of **2a** to produce a number of energetic polymers surely makes it an interesting target for synthetic chemists. Moreover, due to the strongly electron-withdrawing nitro groups in the ortho and para positions, Michael-type additions are expected to occur on **2a**. This reactivity, which could lead to an interesting class of compounds, was exploited using nitrogen nucleophiles.⁴

SYNTHESIS 2008, No. 11, pp 1805–1807 Advanced online publication: 06.03.2008 DOI: 10.1055/s-2008-1032117; Art ID: Z28707SS © Georg Thieme Verlag Stuttgart · New York Nevertheless, the synthetic utility of 2a as a Michael acceptor could increase in the future, since azoles as well as S-nucleophiles were also shown to add on the related 2,4,6-trinitrostyrene.⁵

Two main methods have been described for the synthesis of **2a**. The first is lengthy (four steps from a commercial product) and low yielding (overall yield <33%).⁶ The other involves the dehydration or dehydrohalogenation of a hydroxy- or haloethyldinitrobenzene, followed by elimination to generate the vinyl functionality.^{6,7} The latter was obtained in one or two steps using a nitration reaction. This nitration step suffers from safety drawbacks since 1-(2-nitratoethyl)-2,4-dinitrobenzene, which may exhibit explosive properties, can be formed in certain conditions. Moreover, in our hands, the elimination procedure proved unreliable, mainly because of polymerization (certainly explaining the insoluble product mentioned in reference 7a). These bibliographical and experimental results prompted us to design a new synthesis for 2,4-dinitrosty-

rene (2a) which could meet the industrial requirements in terms of efficiency and safety.

Considering the commercial availability of both 1-chloroand 1-bromo-2,4-dinitrobenzene, the Stille reaction⁸ using tributyl(vinyl)tin as the stannylated partner was an obvious choice. Since 1-bromo-2,4-dinitrobenzene (**1a**) was reported to couple with other tin substrates,⁹ it was selected to optimize the process. However, the cheaper chloro derivative could also be used.

Standard Stille conditions [Pd(PPh₃)₄, tributyl(vinyl)tin (1.3 equiv), toluene, 80 °C, 16 h] with 1a resulted in a clean conversion into the desired 2,4-dinitrostyrene (2a) as indicated by NMR analysis of the crude product. However, removal of tin salts and isolation of the product proved to be the main issues. This usual problem in Stille reaction was crucial here considering the high polymerizability of 2a and the need for an industrially amenable process. As a matter of fact, chromatography on silica gel resulted in almost complete degradation, with only traces of 2a being recovered. Recrystallization in different solvents was also ineffective mainly because of polymerization during heating. Chemically pure 2a was obtained in a 65% yield by using the following sequence: (i) KF treatment followed by liquid/liquid extraction with heptane to remove tin residues, (ii) continuous extraction of the crude product with petroleum ether, and (iii) filtration of the pure 2,4-dinitrostyrene precipitated upon concentration of the petroleum ether extraction phase. This process enabled the synthesis of 15 grams of 2a in a single batch.

The method used for 2a (Scheme 1, Procedure 1) was further extended to the synthesis of two related compounds: 1,3-dinitro-4,6-divinylbenzene (2b) (Scheme 1, Procedure 2) and 1-nitro-2,5-divinylbenzene (2c) (Scheme 1, Procedure 3). The previously unknown 2b polymerized very easily and was therefore isolated as for **2a**. The yield was 44% in one step from the commercially available 4,6dichloro-1,3-dinitrobenzene (1b). The unique combination of two nitro and vinyl groups in 2b makes it an interesting building block. As a matter of fact, the use of 2b as a co-monomer would allow the synthesis of cross-linked polymers with energetic properties. Compound 2c was much less prone to polymerization than 2a,b. Therefore, the continuous extraction method was not needed and pure 2c was easily obtained in good yield (88%) after flash chromatography. This synthesis of 2c avoids the use of pressure, which was the main drawback of the reported procedure.¹⁰

NMR measurements were performed at r.t. on a Bruker Avance 200 spectrometer. IR spectra were recorded with an attenuated total reflectance Perkin-Elmer SpectrumOne spectrometer. Melting points were determined on a Kofler apparatus and are uncorrected. Elemental analyses were performed on a ThermoFisher Scientific Flash EA 1112CHNS/O apparatus. All reactions were performed under N₂. Anhydrous toluene and Pd(PPh₃)₄ were purchased from Aldrich and were used as received. Petroleum ether used refers to the fraction boiling in the range 30–60 °C.

Procedure 1

2,4-Dinitrostyrene (2a)^{7a}

To a solution of 1-bromo-2,4-dinitrobenzene (**1a**; 30 g, 107 mmol) in anhyd toluene (300 mL) were added tributyl(vinyl)tin (42.9 g, 135.3 mmol) and Pd(PPh₃)₄ (1.12 g, 9.7 mmol). The mixture was stirred for 16 h at 80 °C. After cooling, an aq 1 M KF solution (410 mL) was added. The mixture was stirred for 2 h, and then filtered on Celite. The organic layer was separated from the filtrate, dried (MgSO₄), and concentrated to dryness. The residue was dissolved in MeCN (400 mL) and washed with heptane (4 × 100 mL). The MeCN phase was extracted continuously with petroleum ether for 4 days. Upon concentration of the petroleum ether, the product precipitated. After filtration and drying in vacuo, pure **2a** was obtained as a pale yellow powder; yield: 15.0 g (65%); mp 53 °C.

IR: 3112, 3096, 1603, 1591, 1541, 1524, 1419, 1338, 1148, 985, 946, 908, 861, 831 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): δ = 5.74 (d, *J* = 11.0 Hz, 1 H, H_{βcis}), 5.96 (d, *J* = 17.3 Hz, 1 H, H_{βrms}), 7.23 (dd, *J* = 11.0, 17.3 Hz, 1 H, H_a), 7.86 (d, *J* = 8.7 Hz, 1 H, H-4), 8.44 (dd, *J* = 2.3, 8.7 Hz, 1 H, H-5), 8.80 (d, *J* = 2.3 Hz, 1 H, H-3).

 ^{13}C NMR (50 MHz, CDCl₃): δ = 120.2, 123.1, 127.2, 129.7, 130.8, 139.0, 146.8, 147.4.

Procedure 2

1,3-Dinitro-4,6-divinylbenzene (2b)

To a solution of 4,6-dichloro-1,3-dinitrobenzene (**1b**; 10.1 g, 42.6 mmol) in anhyd toluene (40 mL) were added tributyl(vinyl)tin (29.3 g, 92.5 mmol) and Pd(PPh₃)₄ (0.98 g, 0.85 mmol). The mixture was stirred for 15 h at 80 °C. After cooling, an aq 1 M KF solution (80 mL) was added. The mixture was stirred for 2 h, then diluted with EtOAc (150 mL), and filtered on Celite. The organic layer was separated from the filtrate, dried (MgSO₄), and concentrated to dryness. The residue was dissolved in MeCN (100 mL) and washed with petroleum ether (3 × 40 mL). The MeCN phase was extracted continuously with petroleum ether for 4 days. Upon concentration of the petroleum ether, the product precipitated. After filtration and drying in vacuo, pure **2b** was obtained as an orange powder; yield: 4.16 g (44%); mp 64–68 °C.

IR: 3115, 2988, 1889, 1603, 1579, 1516, 1419, 1343, 1156, 979, 944, 908, 894, 832 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): $\delta = 5.73$ (d, J = 11.4 Hz, 2 H, 2 H_{βcis}), 6.21 (d, J = 17.3 Hz, 2 H, 2 H_{βtrans}), 7.09 (dd, J = 11.4, 17.3 Hz, 2 H, 2 H_a), 8.08 (s, 1 H, H-5), 8.62 (s, 1 H, H-2).

¹³C NMR (50 MHz, CDCl₃): δ = 121.5, 123.2, 128.1, 130.6, 136.5, 145.7.

Anal. Calcd for $C_{10}H_8N_2O_4$: C, 54.55; H, 3.66; N, 12.72. Found: C, 55.24; H, 3.72; N, 12.65.

Procedure 3

1-Nitro-2,5-divinylbenzene (2c)¹⁰

To a solution of 2,5-dibromo-1-nitrobenzene (**1c**; 1.12 g, 4 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (9 mg, 0.04 mmol) in anhyd toluene (10 mL) were added tributyl(vinyl)tin (2.63 mL, 9 mmol) and Pd(PPh₃)₄ (139 mg, 0.12 mmol). The mixture was stirred for 8 h at 110 °C. After cooling, an aq 1 M KF solution (27 mL) was add-ed. The mixture was stirred for 2 h, and then filtered on Celite. The organic layer was separated from the filtrate, dried (MgSO₄), and concentrated to dryness. The residue was chromatographed over silica gel (eluent: heptane–EtOAc, 8:2) to give pure **2c** as a yellow oil; yield: 0.62 g (88%).

IR: 3092, 1848, 1737, 1626, 1547, 1522, 1493, 1344, 1309, 1288, 983, 915, 843, 806 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): δ = 5.42 (d, *J* = 10.9 Hz, 1 H, H_{βcis}), 5.47 (d, *J* = 10.9 Hz, 1 H, H_{βcis}), 5.75 (d, *J* = 17.1 Hz, 1 H, H_{βtrans}),

5.85 (d, J = 17.1 Hz, 1 H, H_{β*trans*}), 6.70 (dd, J = 10.9, 17.1 Hz, 1 H, H_a), 7.13 (dd, J = 10.9, 17.1 Hz, 1 H, H_a), 7.58 (m, 2 H, H-3 + H-4), 7.91 (s, 1 H, H-6).

¹³C NMR (50 MHz, CDCl₃): δ = 116.7, 118.7, 121.8, 128.4, 130.3, 131.9, 132.0, 134.3, 138.1, 148.0.

References

- Boileau, J. In *Materials Research Society Symposium Proceedings*, Vol. 418; Brill, T. B.; Russell, T. P.; Tao, W. C.; Wardle, R. B., Eds.; Materials Research Society: Pittsburgh, **1996**, 91.
- (2) (a) Barba, N. A.; Nedelko, M. S.; Shukla, R. K. Koordinats. Soedin. Perekhod. Elementov. Vopr. Khimii i Khim. Tekhnol., Kishinev 1983, 108; Chem. Abstr. 1983, 99, 158944. (b) Shukla, R. K. Ind. Polym. Radiat. Proc. Symp. 1979, 33; Chem. Abstr., 1981, 94, 103903.
- (3) Barba, N. A.; Botnar, M. S.; Pogrebnoi, I. L.; Manole, S. F. Sint. Fiz.-Khimcheskoe Issled. Koord. Polim. Soedin. 1986, 118; Chem. Abstr. 1987, 107, 78281.

- (4) Barba, N. A.; Botnar, M. S.; Manole, S. F.; Pogrebnoi, I. L. Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya 1987, 30, 40; Chem. Abstr. 1988, 109, 73079.
- (5) Sapozhnikov, O. Y.; Mezhnev, V. V.; Dutov, M. D.; Shevelev, S. A. *Russ. Chem. Bull. Int. Ed.* **2005**, *54*, 1048.
- (6) Barba, N. A.; Shukla, R. K. J. Org. Chem. USSR 1977, 13, 609.
- (7) (a) Gandler, J. R.; Yokohama, T. J. Am. Chem. Soc. 1984, 106, 130. (b) Naruta, Y.; Ishihara, N.; Tani, F.; Maruyama, K. Bull. Chem. Soc. Jpn. 1993, 66, 158.
- (8) (a) Farina, V.; Krishnamurthy, V.; Scott, W. J. Org. React. 1998, 50, 1. (b) Kosugi, M.; Fugami, K. In Handbook of Organopalladium Chemistry for Organic Synthesis; Negishi, E., Ed.; Wiley: Hoboken, 2002, 263.
- (9) (a) Buynak, J. D.; Ramana Doppalapudi, V.; Frotan, M.; Kumar, R.; Chambers, A. *Tetrahedron* 2000, *56*, 5709.
 (b) Kashin, A. N.; Bumagina, I. G.; Bumagin, N. A.; Beletskaya, I. P. *J. Org. Chem. USSR* 1981, *17*, 18.
- (10) Detert, H.; Sugiono, E. J. Prakt. Chem. 1999, 341, 358.