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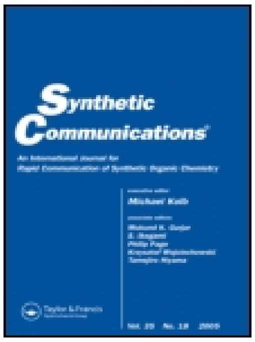

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Synthesis of (*E*) α,2,4-Trinitrostilbenes from (*E*) 2,4-Dinitrostilbenes

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ABSTRACT

A convenient synthesis of (*E*) α,2,4-trinitrostilbenes **2a–d** from (*E*) 2,4-dinitrostilbenes **la–e** by direct nitration is reported. Isomerization of the *trans* geometry of the reactant stilbenes to *cis* in the products was found. The structures of stilbenes **2a**, **2c** and **2d** were confirmed by XRD.

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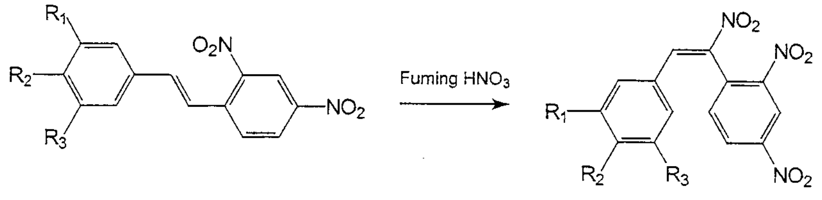
Aromatic nitro compounds are important synthetic targets due to their uses as explosives, dye intermediates and battery cathodes.[1] α-Nitrostilbenes[2] belong to a class of important nitro compounds as potential precursors for biologically active β-phenylethylamines and Michael acceptors.[3] A survey of literature[4] shows that only a few styrenes undergo direct nitration to give β-nitrostyrenes, while there are no reports on side chain nitration of stilbenes. α-Nitrostilbenes are synthesized by condensing α-nitrotoluenes with aromatic aldehydes. Recent reports on the synthesis of α-2,4-trinitrotoluene[5] and α-nitro-alkylbenzenes[6] also prompted us to report our synthesis of (*E*) α,2,4-trinitrostilbenes here.

We report here the first synthesis of (*E*) α,2,4-trinitrostilbenes **2a–d** by direct nitration of easily available[7] (*E*) 2,4-dinitrostilbenes **la–e** in 55–60% yield, using fuming nitric acid[8] (Sch. 1). The nitration was found to be temperature independent in case of stilbenes **la**, **lb**, and **1e**. Whereas in the case of **1c** it gives exclusively **2b** at 25°C and **2c** at 90°C. In the case of **1d** only side chain nitrated product **2b** at 25°C and side chain as well as nuclear nitrated product **2c** at 90°C was obtained (Table 1).

It was found that the *trans* geometry of the reactant stilbenes **la–e** (confirmed by ^{1}H NMR (**la–e**) and XRD in case of **1e** alone) isomerized to *cis* in the products with respect to the aryl rings in the reactant. The *cis* geometry of the products was confirmed by XRD in the case of stilbenes **2a**, **2c** and **2d** (Fig. 1). This isomerization may be due to the favorable π–π interaction between the two aryl rings during nitration.



1a R1= R_2=R_3=H

1b R_1=NO_2; R_2=R_3=H

1c R_1=R_3 = H; R_2=CH_3

1d R_1=NO_2; R_2=CH_3; R_3=H

1e R_1= R_3 = H; R_2=OCH_3

2a R_1=NO_2; R_2= R_3=H

2b R_1=NO_2; R_2=CH_3; R_3=H

2c R_1=R_3=NO_2; R_2=CH_3

2d R_1=NO_2; R_2=OCH_3; R_3=H

Scheme 1.

Table 1.

	Product			
Reactant	25°C	90°C	M.p. (°C)	Yield (%)
1a	**2a**	**2a**	200	55
1b	**2a**	**2a**	200	55
1c	**2b**	**2c**	**2b**, 183	58
1d	**2b**	**2c**	**2c**, 210	60
1e	**2d**	**2d**	215	60

Further work is in progress to study the electrochemical properties of stilbenes **2a–d**.

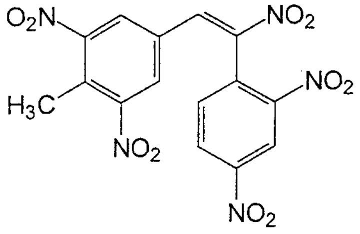
EXPERIMENTAL

Synthesis of 4′-Methyl-2,3′,4-trinitrostilbene (1d)

A mixture of 2,4-dinitrotoluene[7] (5 mM, 0.9 g) and 4-methyl-3-nitrobenzaldehyde[9,10] (5 mM, 0.8 g) and pyrrolidine (0.106 g, 1.5 mM) was stirred for 5 h in dry DMF for 5 h at 25–30°C. Then it was poured over crushed ice. The crude product was filtered, washed with water and then with methanol and dried over anhydrous calcium chloride. Yield 80%; m.p. 200°C. IR (KBr): 3085, 1598, 1526, 1343 $\mathrm{cm^{-1}}$. ^{1}H NMR ($CDC1_3$) 200 MHz: δ 8.8 (d, 1H, $J = 2.3$ Hz), 8.4 (d, 1H, $J = 8.0$ Hz), 8.1 (d, 1H, $J = 2.5$ Hz), 7.9 (d, 1H, $J = 8.1$ Hz), 7.7–7.5 (m, 3H, vinylic and aromatic H), 7.3 (d, 1H, $J = 8$ Hz), 2.6 (s, 3H). MS: m/z 329 (24% M^+), 312 (23%), 164 (90%), 55 (100%).

Representative Procedure for the Synthesis of (*E*) 4′-Methyl-α,2,3′,4,5′-pentanitrostilbene (2c)

To 5 mM (2.095 g) of (*E*) 4′-methyl-2,3′,4-trinitrostilbene 5 mL of fuming HNO_3 was added slowly with stirring. Then the reaction mixture was kept at 90°C for 5 min. After cooling to 25–30°C, the reaction mixture was poured over crushed ice, the crude product was filtered, washed with water and dessicated over anhydrous $CaC1_2$ and recrystallized from acetone. Yield 60%. IR (KBr): 3130, 1649, 1602, 1517, 1326 $\mathrm{cm^{-1}}$. ^{1}H NMR (DMSO-d_6) 400 MHz: δ 2.4 (s, 3H), 7.96 (d, 1H, $J = 8.5$ Hz),



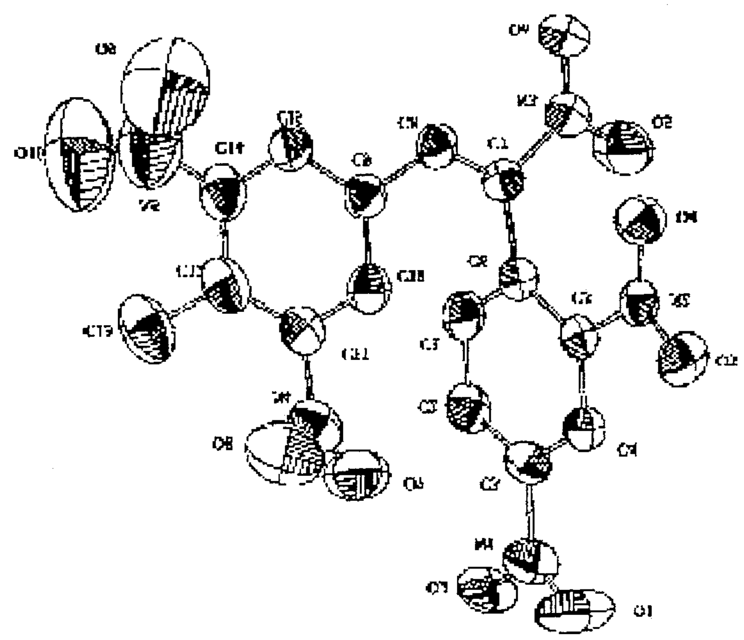


Figure 1. XRD structure of stilbene **2c**.

8.0 (s, 1H), 8.7 (m, 2H, Ar-H and vinylic-H), 9.1 (d, 1H, $J = 3.05$ Hz). Anal. calcd. for $C_{15}H_9N_5O_{10}$; C 42.9, H 2.16, N 16.7; Found C 43.04, H 1.9, N 17.1. M.p. 210°C.

(*E*) α,2,3′,4-Tetranitrostilbene (2a)

Yield 55%. IR (KBr): 1660, 1606, 1533, 1332 cm^{-1}. ^1H NMR ($CDCl_3$) 300 MHz: δ 9.22 (d, 1H, $J = 2.1$ Hz), 8.55 (d, 1H, $J = 8$ Hz), 8.48 (s, 1H), 8.32 (d, 1H, $J = 8$ Hz), 8.1 (s, 1H). Anal calcd. for $C_{14}H_8N_4O_8$; C 46.67, H 2.23, N 15.55; Found C 46.67, H 2.23, N 15.93. M.p. 200°C.

(*E*) 4′-Methyl-α,2,3′,4-tetranitrostilbene (2b)

Yield 58%. IR (KBr): 3125, 1650, 1600, 1526, 1340 cm^{-1}. ^1H NMR ($CDCl_3$) 400 MHz: δ 9.22 (d, 1H, $J = 1.96$ Hz), 8.56 (d, 1H, $J = 8.32$ Hz), 8.42 (s, 1H), 7.70 (s, 1H), 7.58 (d, 1H, $J = 8.28$ Hz), 7.29 (d, 1H, $J = 8.32$ Hz), 7.14 (d, 1H, $J = 8.3$ Hz), 2.7 (s, 3H). Anal. calcd. for $C_{15}H_{10}N_4O_8$; C 48.13, H 2.69, N 15.0; Found C 48.0, H 2.09, N 15.5. M.p. 183°C.

(*E*) 4′-Methoxy-α,2,3′,4-tetranitrostilbene (2d)

Yield 60%. IR (KBr): 3124, 1650, 1614, 1542, 1325 cm^{-1}. ^1H NMR ($CDCl_3$) 400 MHz: δ 9.21 (d, 1H, $J = 1.96$ Hz), 8.58 (d, 1H, $J = 8.52$ Hz), 8.38 (s, 1H), 7.62 (d, 1H, $J = 8.32$ Hz), 7.58 (d, 1H, $J = 8.44$ Hz), 7.22 (d, 1H, $J = 8.8$ Hz), 7.03 (d, 1H, $J = 8.8$ Hz), 3.97 (s, 3H). Anal. calcd. for $C_{15}H_{10}N_4O_9$; C 46.16, H 2.58, N 14.35; Found C 46.38, H 2.46, N 14.59. M.p. 215°C.

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