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Synthesis of triazenes by using aryl diazonium silica sulfates under mild conditions

Amin Zarei [a,b,**], Leila Khazdooz [c,*], Hamidreza Aghaei [d], Ghobad Azizi [e], Alireza Najafi Chermahini [e], Abdol R. Hajipour [e,f]

[a] Department of Science, Fasa Branch, Islamic Azad University, Post Box No 364, Fasa 7461789818, Fars, Iran
[b] Department of Science, Fasa University, Fasa 7461781189, Fars, Iran
[c] Department of Science, Khorasgan Branch, Islamic Azad University, Isfahan 81595-158, Iran
[d] Department of Chemistry, Shahreza Branch, Islamic Azad University, Shahreza 311-86145, Isfahan, Iran
[e] Pharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan 84156, Iran
[f] Department of Pharmacology, University of Wisconsin, Medical School, 1300 University Avenue, Madison, 53706 1532 WI, USA

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ABSTRACT

An efficient, fast and straightforward procedure for the synthesis of aryltriazenes is described in the present paper by using aryl diazonium silica sulfates and secondary amines. Using the present method, different kinds of aryl diazonium silica sulfates, containing electron withdrawing groups as well as electron donating groups, were rapidly converted to the corresponding of aryltriazenes in good yield and short reaction time. These reactions were carried out in water at room temperature under mild and heterogeneous conditions. Moreover, temperature dependent NMR spectra were studied for 1-(2-nitrophenyl)-3,3-diethyltriazene to determine the rotational barrier energy around N(2)–N(3) bond of this molecule. Simple and clean work-up, short reaction times and good yields were the advantages of this method.

1. Introduction

Triazenes are a unique class of polyazo compounds with a long history in both biological and chemical sciences. These compounds are used for many purposes such as anticancer agents [1], against brain tumors [2] and malignant melanoma [3] with minimal side effects, as protecting groups in natural product synthesis [4–6], as useful linkers in solid-phase organic synthesis [7–12], as dyes and photoactive substrates [13–16] and in the formation of novel heterocycles [17–20]. Moreover, they are known as important intermediates for the modern organic synthesis [21–24]. Recently, triazenes have been used as precursors to facilitate coupling of functionalized arenes on the silicon surfaces for the applications in semiconductors and nanoelectronics [25]. Two most widely useful methods for the synthesis of triazenes are the coupling of aryl diazonium salts to primary or secondary amines [26–28] and the addition of organometallic reagents (RMgX, RLi, etc.) to alkyl azides [29,30]. However, some of these reagents are very reactive, commonly flammable, which it is necessary to use special equipment for safety. Therefore, these restrictions necessitate the development of new methods for the preparation of these significant compounds. In continuation of our studies on the stabilization of diazonium salts on silica sulfuric acid and their application in organic synthesis [31–40], we report herein an efficient, convenient and environmentally friendly method for the synthesis of aryltriazenes by employing aryldiazonium silica sulfates with secondary amines (Scheme 1). These reactions were carried out in water at room temperature under mild and heterogeneous conditions. Silica sulfate as a bulky counterion with high surface not only increases the stability of the present salts but also increases the reaction rate so that these salts can be used under solvent-free conditions at room temperature [31,32,34,35].

* Corresponding author. Tel.: +98 9171302525; fax: +98 3112289113.
** Corresponding author. Department of Science, Fasa Branch, Islamic Azad University, Post Box No 364, Fasa 7461789818, Fars, Iran.
E-mail addresses: aj_zarei@yahoo.com (A. Zarei), Leila_khazdooz@yahoo.com, lkhazdooz@yahoo.com (L. Khazdooz).

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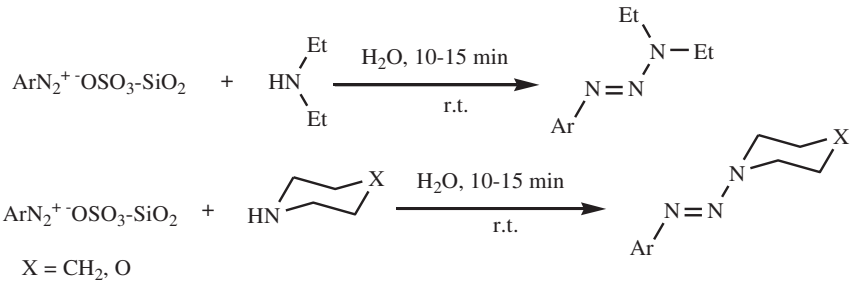

Scheme 1. An efficient, convenient and environmentally friendly method for the synthesis of aryltriazenes by employing aryldiazonium silica sulfates with secondary amines.

2. Experimental

2.1. General

All reagents were purchased from Merck and Aldrich and used without further purification. Aryl diazonium silica sulfates were synthesized according to the previous work [31]. All yields refer to the isolated products after purification. The products were characterized by comparison with authentic samples and by spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR spectra and melting point). All melting points were taken on a Gallenkamp melting apparatus and were uncorrected. UV spectra were recorded on a JASCO V-570 UV/vis/NIR spectrophotometer. IR spectra were recorded on a JASCO FT/IR-680 PLUS spectrometer. ^{1}H NMR spectra were recorded on Bruker 400 and 500 MHz.

2.2. General procedure for the synthesis of triazenes

To a solution of a secondary amine (2 mmol) in water (10 mL), freshly diazonium silica sulfate (1 mmol) was added and the reaction mixture was stirred at room temperature for the time specified in Table 1. The reaction progress was monitored by TLC (hexane/EtOAc, 75:25). After completion of the reaction (absence of azo coupling with 2-naphthol), the mixture was diluted with EtOAc (15 mL) and filtered after vigorous stirring. The residue was extracted with EtOAc (2 × 10 mL) and the combined organic layer was washed with H_2O (2 × 15 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to afford the corresponding product and if necessary, the crude product was purified by flash column chromatography.

2.3. The spectral data of new compounds

2.3.1. (Table 1, entry 3) Pale yellow oil

UV (λ_{max} in CH_2Cl_2): 293 nm. FTIR (KBr) cm^{-1}: 3019, 2938, 2855, 1597, 1483, 1434, 1356, 1292, 1258, 1197, 1175, 1096, 1000, 853, 757, 718. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34 (1 H, d, J = 7.8 Hz), 7.18 (1 H, d, J = 7.5 Hz), 7.14 (1 H, d, J = 7.6 Hz), 7.07 (1 H, t, J = 7.3 Hz), 3.77 (4 H, brs), 2.42 (3 H, s), 1.71 (6 H, brs). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.16, 133.16, 130.96, 126.69, 125.98, 116.96, 48.22, 25.62, 24.94, 18.02. Anal. Calcd for $C_{12}H_{17}N_3$: C, 70.90; H, 8.43; N, 20.67. Found: C, 70.78; H, 8.56; N, 20.75.

2.3.2. (Table 1, entry 8) Pale yellow oil

UV (λ_{max} in CH_2Cl_2): 293 nm. FTIR (KBr) cm^{-1}: 3064, 2939, 2856, 1584, 1468, 1420, 1355, 1296, 1255, 1221, 1186, 1106, 1053, 1001, 852, 753, 701, 644. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.46 (1 H, d, J = 8.0 Hz), 7.39 (1 H, d, J = 7.9 Hz), 7.20 (1 H, t, J = 7.5 Hz), 7.07 (1 H, t, J = 7.6 Hz), 3.85 (4 H, brs), 1.71 (6 H, brs). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 147.68, 130.45, 129.82, 127.53, 126.51, 118.97, 44.79, 24.77. Anal. Calcd for $C_{11}H_{14}ClN_3$: C, 59.06; H, 6.31; N, 18.78. Found: C, 58.92; H, 6.45; N, 18.69.

2.3.3. (Table 1, entry 11) Yellow solid

UV (λ_{max} in CH_2Cl_2): 346 nm. Mp 74–75 °C; FTIR (KBr) cm^{-1}: 3034, 2945, 2858, 1639, 1594, 1457, 1394, 1355, 1300, 1273, 1188, 1142, 1105, 1019, 992, 918, 864, 794, 746, 701. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.82 (2 H, d, J = 8.2 Hz), 7.78 (2 H, d, J = 7.4 Hz), 7.56 (1 H, t, J = 7.3 Hz), 7.51–7.45 (4 H, m), 3.85 (4 H, brs), 1.72 (6 H, brs). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 196.53, 154.79, 138.75, 134.49, 132.37, 131.91, 130.28, 128.60, 120.56, 43.24, 24.50. Anal. Calcd for $C_{18}H_{19}N_3O$: C, 73.69; H, 6.53; N, 14.32. Found: C, 73.58; H, 6.46; N, 14.24.

2.3.4. (Table 1, entry 14) Yellow oil

UV (λ_{max} in CH_2Cl_2): 301 nm. FTIR (KBr) cm^{-1}: 3073, 2941, 2858, 1600, 1576, 1525, 1462, 1420, 1355, 1295, 1266, 1188, 1110, 1084, 1015, 856, 775, 749, 684. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 (1 H, d, J = 8.1 Hz), 7.53, (1 H, d, J = 8.2 Hz), 7.44 (1 H, t, J = 8.3 Hz), 7.17 (1 H, t, J = 8.1 Hz), 3.83 (4 H, brs), 1.71 (6 H, brs). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 145.62, 144.32, 132.63, 125.22, 124.14, 119.92, 42.41, 24.60. Anal. Calcd for $C_{11}H_{14}N_4O_2$: C, 56.40; H, 6.02; N, 23.92. Found: C, 56.32; H, 6.11; N, 24.01.

2.3.5. (Table 1, entry 20) Pale yellow oil

UV (λ_{max} in CH_2Cl_2): 292 nm. FTIR (KBr) cm^{-1}: 3065, 2975, 2935, 2873, 1585, 1571, 1467, 1406, 1341, 1265, 1249, 1201, 1106, 1053, 1033, 998, 939, 753, 722, 698, 632. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42–7.38 (2 H, m), 7.19 (1 H, t, J = 7.3 Hz), 7.04 (1 H, t, J = 7.3 Hz), 3.80 (4 H, q, J = 7.1 Hz), 1.31 (6 H, brs). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 148.05, 130.37, 129.70, 127.46, 126.04, 119.00, 42.63, 11.85. Anal. Calcd for $C_{10}H_{14}ClN_3$: C, 56.74; H, 6.67; N, 19.85. Found: C, 56.67; H, 6.78; N, 19.80.

2.3.6. (Table 1, entry 23) Yellow oil

UV (λ_{max} in CH_2Cl_2): 298 nm. FTIR (KBr) cm^{-1}: 3073, 2977, 2937, 2875, 1600, 1576, 1525, 1468, 1402, 1352, 1269, 1237, 1201, 1114, 1080, 997, 949, 854, 767, 748, 680. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (1 H, dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz), 7.53 (1 H, dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.44 (1 H, td, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 7.15 (1 H, td, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 3.80 (2 H, q, J = 7.2 Hz), 3.73 (2 H, q, J = 7.2 Hz), 1.34 (3 H, J = 7.2 Hz), 1.19 (3 H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.42, 144.60, 132.55, 124.83, 124.06, 119.99, 49.91, 42.53, 14.81, 11.65. Anal. Calcd for $C_{10}H_{14}N_4O_2$: C, 54.04; H, 6.35; N, 25.21. Found: C, 54.11; H, 6.47; N, 25.15.

3. Results and discussion

Aryldiazonium salts ($ArN_2^+X^-$) have been prepared and studied as useful intermediates in classical and modern organic synthesis