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

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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].

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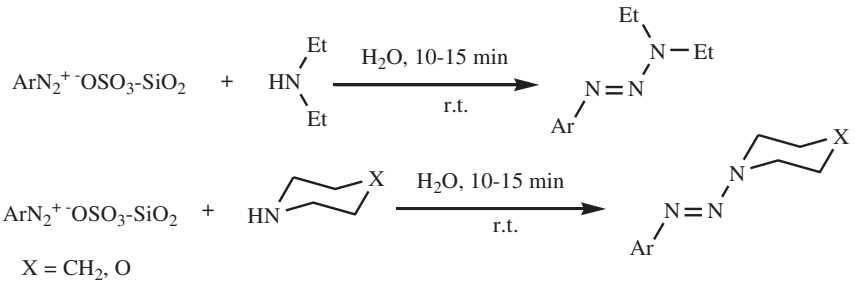


Scheme 1. An efficient, convenient and environmentally friendly method for the synthesis of aryltriazenes by employing aryldiazonium silica sulfates with secondary amines.

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.

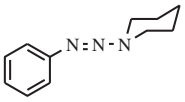
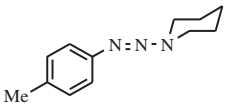
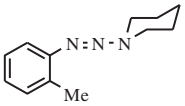
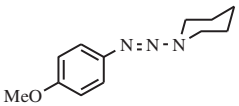
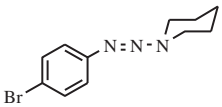
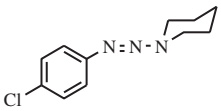
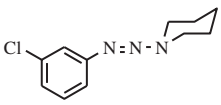
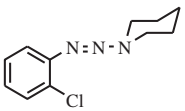
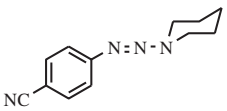
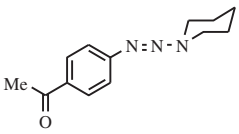
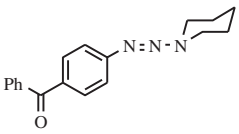
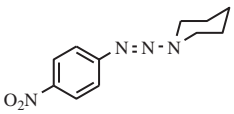
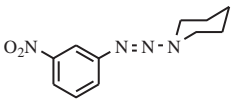
2.3.6. (Table 1, entry 23) Yellow oil

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

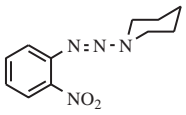
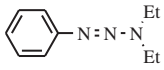
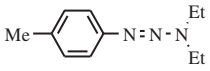
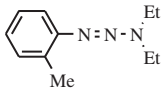
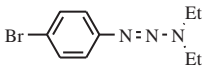
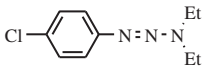
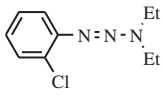
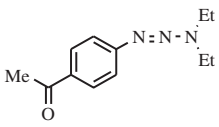
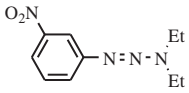
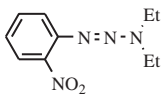
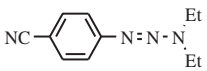
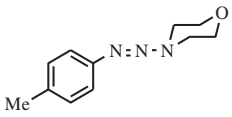
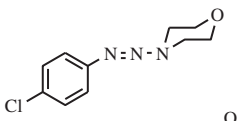
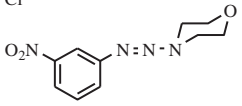
Aryldiazonium salts ($ArN_2^+X^-$) have been prepared and studied as useful intermediates in classical and modern organic synthesis

Table 1
Preparation of (*E*)-aryltriazenes using aryl diazonium silica sulfates with secondary amines in water at room temperature.[a]

Entry	Amine	Diazonium salt	Product	Time (min)	Yield (%)
1	Piperidine	$C_6H_5N_2^+$-OSO_3–SiO_2		10	86
2		4-$MeC_6H_4N_2^+$-OSO_3–SiO_2		10	83
3		2-$MeC_6H_4N_2^+$-OSO_3–SiO_2		15	80
4		4-$MeOC_6H_4N_2^+$-OSO_3–SiO_2		15	79
5		4-$BrC_6H_4N_2^+$-OSO_3–SiO_2		10	82
6		4-$ClC_6H_4N_2^+$-OSO_3–SiO_2		10	82
7		3-$ClC_6H_4N_2^+$-OSO_3–SiO_2		10	84
8		2-$ClC_6H_4N_2^+$-OSO_3–SiO_2		15	81
9		4-$NCC_6H_4N_2^+$-OSO_3–SiO_2		10	84
10		4-$MeCOC_6H_4N_2^+$-OSO_3–SiO_2		15	83
11		4-$PhCOC_6H_4N_2^+$-OSO_3–SiO_2		15	80
12		4-$NO_2C_6H_4N_2^+$-OSO_3–SiO_2		10	85
13		3-$NO_2C_6H_4N_2^+$-OSO_3–SiO_2		10	87

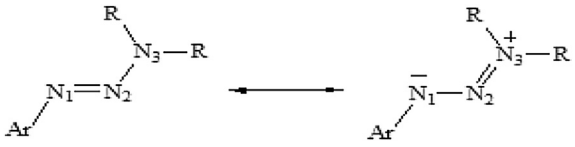
(*continued on next page*)

Table 1 (*continued*)

Entry	Amine	Diazonium salt	Product	Time (min)	Yield (%)
14		2-$NO_2C_6H_4N_2^+$-OSO_3–SiO_2		15	82
15	Diethylamine	$C_6H_5N_2^+$-OSO_3–SiO_2		10	83
16		4-$MeC_6H_4N_2^+$-OSO_3–SiO_2		10	80
17		2-$MeC_6H_4N_2^+$-OSO_3–SiO_2		15	76
18		4-$BrC_6H_4N_2^+$-OSO_3–SiO_2		10	81
19		4-$ClC_6H_4N_2^+$-OSO_3–SiO_2		10	79
20		2-$ClC_6H_4N_2^+$-OSO_3–SiO_2		15	78
21		4-$MeCOC_6H_4N_2^+$-OSO_3–SiO_2		10	81
22		3-$NO_2C_6H_4N_2^+$-OSO_3–SiO_2		10	85
23		2-$NO_2C_6H_4N_2^+$-OSO_3–SiO_2		15	81
24		4-$CNC_6H_4N_2^+$-OSO_3–SiO_2		10	82
25	Morpholine	4-$MeC_6H_4N_2^+$-OSO_3–SiO_2		10	80
26		4-$ClC_6H_4N_2^+$-OSO_3–SiO_2		10	83
27		3-$NO_2C_6H_4N_2^+$–OSO_3–SiO_2		10	82

[a] The yields refer to isolated pure products which were characterized from their spectral data by comparison with those reported in the literature [47–56].

due to their ready availability and high reactivity. These salts have been prepared by a wide variety of methods. One of the oldest and commonly used methods involves the diazotation of aromatic amines with sodium nitrite in the presence of an aqueous Brønsted acid [26,41]. The counterion (X^-), determined by the choice of the acid, has an important role for both stability and reactivity of the diazonium salt [41]. For example, aryl diazonium chlorides are usually highly unstable above 0 °C and even explosive. Moreover, because of this instability, subsequent reactions with diazonium salts must be carried out under the same conditions that these salts



Scheme 2. Obvious effect of the resonance in rotation barrier around the N(2)–N(3) bond.

are formed. Thus, aryldiazonium salts with higher stability and versatility that can be easily made and stored under solid state conditions with explosion-proof properties are desired and necessary. Later developments showed that the stability of diazonium salts can be modulated by change of the counterion. In this area of research, tetrafluoroborates [42,43] became the most used salts. Moreover, disulfonimides [44], carboxylates [45] and tosylates [46] have also been described for their good stability. Diazotization reactions of these anhydrous aryl diazonium salts are carried out in an appropriate organic solvent and to precipitate the corresponding aryl diazonium salt, it is necessary to add Et_2O into the reaction mixture. Moreover, in some of these procedures, it is required to control the reaction temperature. Recently, we have reported a new method for the preparation of anhydrous aryldiazonium salts on the surface of silica sulfuric acid named aryldiazonium silica sulfates (ArN_2^+-$^-OSO_3$–SiO_2) [31–40]. Diazotization reactions of these aryl diazonium salts are easily carried out in a few minutes under solvent-free conditions at room temperature. In the present work, the reaction of aryldiazonium silica sulfates with a number of secondary amines was studied. As shown in Table 1, all reactions were carried out in water at room temperature under mild and heterogeneous conditions. The corresponding (*E*)-aryltriazenes were obtained in good to high yields. The yields refer to isolated pure products which were characterized from their spectral data by comparison with those reported in the literature [47–56]. Aryldiazonium silica sulfates with electron-withdrawing groups or electron-donating groups also reacted effectively. The steric effects of *ortho* substituents had relatively little influence on the yields and reaction times. The corresponding phenol derivatives were formed in trace amounts as by-products. Another advantage of this method was the easy work-up since the crude products were extracted with ethyl acetate and, if necessary, were purified by flash column chromatography. Finally, after completion of the reaction and isolation of the product, the solid support could be recycled according to the previous work [32].

It is known that aryldialkyltriazenes with an extended π-conjugated system exhibit considerable delocalization of charge density. As shown in Scheme 2, an obvious effect of this resonance is an increase in rotation barrier around the N(2)–N(3) bond determined by dynamic NMR spectroscopy [57].

In the present work, by studying the NMR spectral data of the triazene derivatives, it was found that only 1-(2-nitrophenyl)-3,3-diethyltriazene (Table 1, entry 23) showed a restriction in rotation around the N(2)–N(3) bond at room temperature. This phenomenon led to formation of two diastereotopic ethyl groups. Therefore, the methylene and methyl groups gave different respective signals in ^{13}C NMR and ^1H NMR spectroscopy (Figs. 1 and 2). At room temperature and in $CDCl_3$, the methylene carbons appear at 49.91 and 42.53 ppm and the methyl carbons resonate at 14.81 and 11.65 ppm (Fig. 1). Moreover, at ambient temperature, the ^1H NMR spectrum of this compound in $CDCl_3$ indicates that the diastereotopic methylene protons appear as two broad quartet peaks between 3.82 and 3.71 ppm and the diastereotopic methyl protons resonate as two equally intense triplets at 1.34 and 1.22 ppm (Fig. 2). By studying the temperature of the ^1H NMR (400 MHz) of this molecule in $CDCl_3$ (Fig. 3), it is found that the methylene and methyl peaks broaden and coalesce when the temperature is raised. The chemical shift for all protons were unaffected by increase of the temperature. Moreover, to increase the clearness of the spectra, we moved each spectrum as much as 0.1 ppm to right in comparison with the former spectrum (Fig. 3). As shown in Figs. 2 and 3, the appearance of the ^1H NMR spectra for the diastereotopic methyl groups is clearer than that of the corresponding methylene ones. Therefore, the thermodynamic parameters of the present compound were calculated for the methyl groups. These parameters are the coalescence temperature (T_c), the rate constant of the exchange at the coalescence temperature (k_c) and the free energy of activation ($\Delta G_c^{\ddagger}$) for the exchange. As shown in Fig. 3, the coalescence temperature was 326 K and the rate constant was calculated to be 117 s^{-1} for the exchange of the methyl groups at the coalescence temperature by using the Gutowsky–Holm equation ($k_c = (\pi/\sqrt{2})(\Delta\upsilon^2 + 6J^2)^{1/2}$) [57]. In the present equation, $\Delta\upsilon$ is the difference in chemical shift of the two sites and J is the coupling constant. So, for this molecule the difference in chemical shift of the two methyl groups was calculated 50 Hz and the coupling constant between the methyl and methylene protons was obtained 6.8 Hz (Fig. 3). Moreover, the free energy of activation was obtained 16.07 kcal mol^{-1} for the exchange of the methyl groups by following the Eyring equation ($\Delta G_c^{\ddagger} = 4.57T_c\,[9.97 + \log(T_c/\Delta\upsilon)]$) [57]. It is clear that the Gutowsky–Holm equation and the Eyring equation are strictly valid where the populations of two sites are equal [57–59].

We also synthesized [(2-nitrophenyl)diazenyl]-1-azacyclohexane using piperidine instead of diethylamine under the same conditions

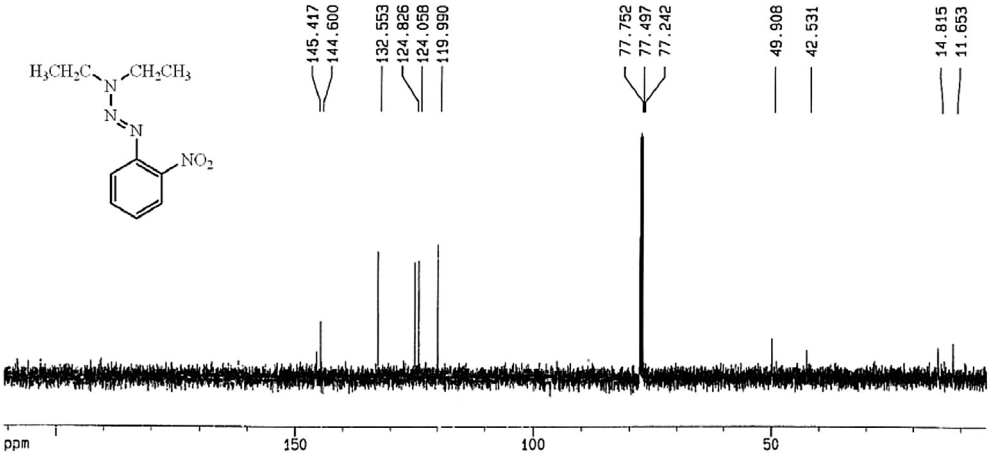


Fig. 1. ^{13}C NMR spectrum (100 MHz) of 1-(2-nitrophenyl)-3,3-diethyltriazene in $CDCl_3$ at room temperature.

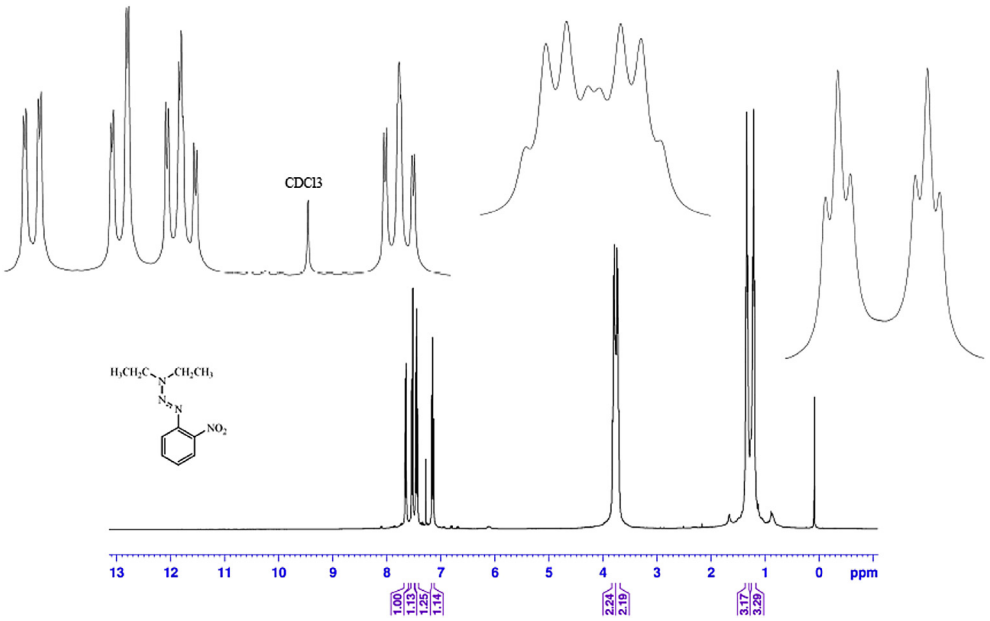


Fig. 2. ^{1}H NMR spectrum (400 MHz) of 1-(2-nitrophenyl)-3,3-diethyltriazene in $CDCl_3$ at room temperature.

(Table 1, entry 14) and studied its NMR spectral data. In contrast to 1-(2-nitrophenyl)-3,3-diethyltriazene, it was not observed the rotation restriction around the N(2)—N(3) bond at room temperature. It may be due to the inversion of the piperidyl ring that decreases the coplanarity of the lone-pair electrons on the piperidine nitrogen with N═N bond [57,60]. This reason decreases π-conjugated system of the present triazene which leads to lower rotational barrier energy around N(2)—N(3) bond. Therefore, the rotation around the present bond is almost unhindered at room temperature and consequently it was not observed diastereotopic methylene in this molecule.

Finally, we compared $\Delta G_c^{\ddagger}$ of 1-(2-nitrophenyl)-3,3-diethyltriazene with a number of triazenes reported in the literature. As shown in Table 2, the rotational barrier energy of the aryltriazenes is more than that of the aliphatic ones. It may be due to decrease of π-conjugated system in the structure of the aliphatic triazenes. Moreover, the substituted functional groups on the aromatic ring of the aryltriazenes affect the rotational barrier. In comparison with electron donating groups, electron withdrawing groups on the aromatic triazenes increase the $\Delta G_c^{\ddagger}$ values owing to extension of π-conjugated system. Furthermore, the steric effect of the aliphatic groups on N(3) has a little influence on rotational barrier energy when the size of R increases from methyl to ethyl and isopropyl (Table 2, entries 3, 7, 10). Also 1-(2-nitrophenyl)-3,3-diethyltriazene has the highest $\Delta G_c^{\ddagger}$ value among these aryltriazene derivatives (Table 2, entry 9). It may be due to

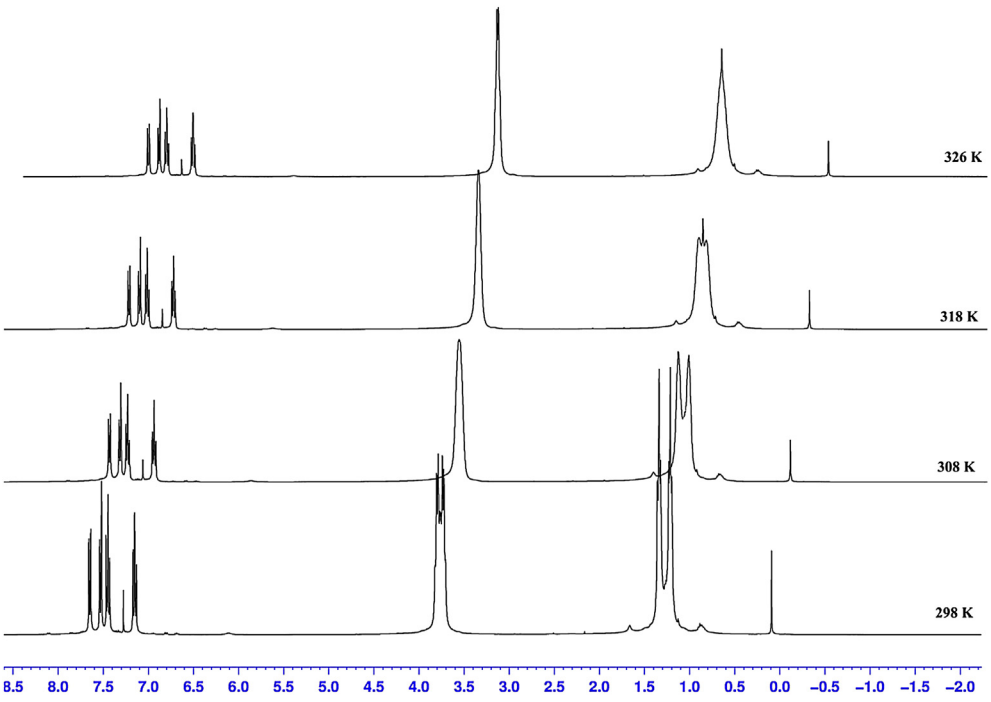
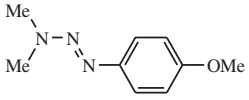
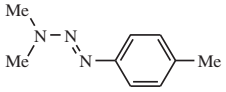
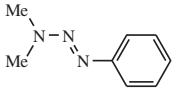
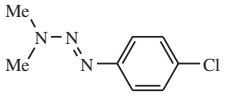
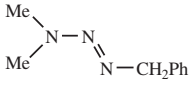
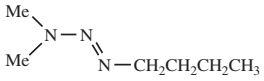
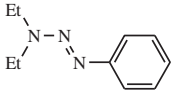
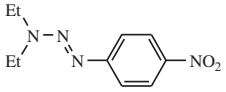
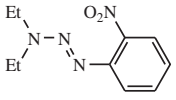
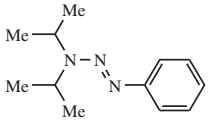
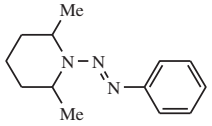


Fig. 3. Temperature-dependent ^{1}H NMR spectra (400 MHz) of 1-(2-nitrophenyl)-3,3-diethyltriazene in $CDCl_3$.

Table 2
Rotational barrier energy of some triazenes in different solvents.

Entry	Triazene	Solvent	$\Delta G_c^{\ddagger}$ (kcal mol^{-1})	Ref.
1		$CDCl_3$	12.7	[59]
2		$CDCl_3$	13	[59]
3		$CDCl_3$	13.8	[60]
4		$CDCl_3$	13.9	[59]
5		CD_2Cl_2	10.7	[57]
6		CD_2Cl_2	10.5	[57]
7		CS_2	13.8	[60]
8		$CDCl_3$	15.7	[57]
9		$CDCl_3$	16.1	Present work
10		CS_2	14.4	[60]
11		CS_2	10.8	[60]

electronic and resonance effect of nitro group at *ortho* situation. It is notable that 2,6-dimethyl-1-piperidinoazobenzene has the lowest $\Delta G_c^{\ddagger}$ value among these aryltriazenes (Table 2, entry 11). This phenomenon may be owing to the inversion of the piperidyl ring that decreases the coplanarity of the lone-pair electrons on the piperidine nitrogen with N=N bond [57, 60]. This reason decreases π-conjugated system of the present triazene which leads to lower $\Delta G_c^{\ddagger}$ value.

4. Conclusion

To sum up, what has been done in the present study can be considered as an efficient, rapid, experimentally simple and environmentally benign method for the preparation of aryltriazenes using aryl diazonium silica sulfates with secondary amines. These reactions proceed in water at room temperature under mild and heterogeneous conditions in good to high yields. Furthermore, 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. Among the notable advantages of this method, we can mention the following: operational simplicity, generality, availability of reactants, short reaction times, and easy work-up.

Acknowledgment

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