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Synthesis of Triazenes of N-Heterocycles Mediated by Resin Immobilized Diazonium Ions

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Diazonium ions were prepared from aromatic amines and immobilized in cation exchange resin support and used for the synthesis of triazenes of piperidine and morpholine in a solid phase synthesis. Immobilization is an excellent technique for the stabilization of diazonium ions and can be preserved in the solid state. Using resin immobilized diazonium ions, triazene synthesis is carried out in the absence of acids thereby increasing the yield of the product and simplifying work up.

Keywords: Solid phase synthesis, Triazenes, Immobilized diazonium ions, Piperidine, Morpholine.

INTRODUCTION

Triazenes are high nitrogen compounds characterized by the presence of the open chain nitrogen triad. Triazenes are classified as monosubstituted (R-N=N-NH_2), disubstituted (R-N=N-NHR_1) and trisubstituted (R-N=N-NR_2). The alkyl as well as aryl triazenes are of considerable interest because of their biological as well as non-biological uses [1-3]. They are often used for *in vivo* generation of diazonium ions in fabric printing industry [4]. They can serve as suitable protecting groups for amines because of their high stability towards bases, organolithium reagents, oxidants, reductants as well as the alkylating agents [5-7]. Triazenes can function as linkers in solid phase organic synthesis of alkyl halides, amides, ureas, thioureas, alcohols, esters, hydrazines, guanidines, sulfoximines *etc*. [8-10]. The Cu(II), Ni(II), Co(II), Zn(II), Fe(II) complexes of triazenes are active antitumor and anticancer agents [11,12]. The cytostatic activity discovered for several substituted triazenes has stimulated intense research efforts towards the development of triazene-based drugs [13].

The classical synthesis of triazene involves the coupling of diazonium salts with primary and secondary aliphatic or aromatic amines in presence of slightly basic aqueous solution at 0-5 °C. Other reported synthetic methods include reaction of alkyl azides with an organometallic reagent such as Grignard reagent or alkyllithium. Further alkylation of the 1,3-dialkyl triazenes in presence of bases like potassium *t*-butoxide or potassium hydride with 18-crown-6 followed by methyl iodide afforded the 1,3,3-trialkyl triazenes [14,15]. The synthesis of a novel triazene was developed by the ring opening of N-substituted tetrazole *via* unusual Vilsmier-Haak reaction. However, long reaction time is required for completion of the reaction [16]. The synthesis of triazenes in both aqueous and non-aqueous solvents was reported by Lazny *et al.* [7], through protection of primary and secondary aliphatic and aromatic amines. The synthesis of methylene-*bis*-(1-oxy-3,3-dialkyl-1-triazene-2-oxide) and their analogues acts as promising exogenous nitric oxide (NO) donor for living organisms these products were synthesized by the reaction of the corres-ponding amines with nitric oxide in presence of sodium methoxide followed by treatment of the resulting salt with dibromomethane in DMF [17].

Most of the reported methods were found to be unsatisfactory as the product triazene is always accompanied by several by products, which consequently lower the yield. Further it has been observed that triazenes are not particularly stable in acidic medium and decomposes to regenerate the diazonium ions resulting in low yield. Therefore, isolation of the pure triazene requires stringent pH and temperature control and also demands tedious and time-consuming separation and purification procedures. Therefore synthesis of triazene in quantitative yield is a challenging topic for investigation. Quantitative synthesis of triazene may be possible provided their synthesis is carried out in solid phase under neutral condition and this can be accomplished by using resin immobilized diazonium ions in a solid phase synthetic procedure. The solid phase synthesis reported herein gives the comparatively pure triazenes in high yield.

EXPERIMENTAL

All reagents were purchased from Merck and Loba chieme (India) and were purified by procedures reported in literature

[18]. Resin immobilized diazonium ions were prepared. The products were characterized by comparing their melting points with authentic samples for solid products and spectroscopic methods UV-visible, FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectrometry. UV-visible spectra were recorded in UV-1800 Shimadzu UV spectrophotometer, IR spectra were recorded in KBr pellets in a Perkin Elmer FT-IR 1600 spectrophotometer and ^{1}H and ^{13}C NMR were recorded in Bruker Bio Spin 300 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal standard. The cation exchange resin chosen was Amberlite IR-120 (Na^+) macroporous type according to Rohm & Haas specification with type analysis SO^{3-}, 20-50 mesh, Na^+ form, styrene-DVB (8 %). Aromatic amines, from which the diazonium ions were prepared, were obtained commercially and purified by procedures as described in literature [18].

Preparation of resin immobilized diazonium ion: 15 g of the cation exchange resin Amberlite IR-120 (Na^+) was washed several times with deionized water, dried and taken in a column. 0.05 mol of the aromatic amine diazotized using $NaNO_2$ conc. HCl at 0-5 °C. On passing the solution of diazonium ions through the column of the resin, the diazonium ions are grafted onto the cation exchange resin by displacement of the Na^+ ions. The loaded resin was washed several times with deionized water till the washing was free of diazonium ions. (alkaline 2-naphthol test). The resin was then recovered and dried over P_2O_5 at 50 °C under reduced pressure (50 mm Hg). Thus a variety of diazonium ions were prepared by taking different aromatic amines and immobilized onto the cation exchange resin.

Estimation and characterization of the resin immobilized diazonium ions

Reductometric titration test: The dried resin was analyzed for diazonium ion content by reductometric titration procedure using 10 mL of 57 % hydroiodic acid and 5 g of immobilized diazonium ion. The liberated iodine was titrated with standard sodium thiosulphate solution using starch as indicator [11,12]. This experiment was done with diazonium ions obtained from different aromatic amines (Table-1) and the average loading was found to be 2.26 meqv. of ArN_2^+ per g of the resin. The dried resin was stored at room temperature and the diazonium ion content was found to remain constant over a period of six months. Immobilization of diazonium ions on cation exchange resin proves to be an excellent method for their stabilization.

TABLE-1
DIAZONIUM ION CONTENT IN THE LOADED RESIN

Entry	Resin immobilized diazonium ions obtained from	Diazonium ion content	Average capacity (m eqv/g)
1	4-Nitro aniline	2.46	
2	4-Methyl aniline	2.32	
3	4-Chloro aniline	2.21	2.26
4	2,4-Dichloro aniline	2.26	
5	4-Methoxy aniline	2.38	
6	2-Nitro aniline	2.07	

FT-IR spectra of cation exchange resin before and after immobilization were recorded in KBr pellets using Perkin Elmer FT-IR 1600 spectrophotometer to examine the presence of diazonium ions in the resin surface after immobilization. Solid state IR spectra obtained of resin immobilized diazonium ions of 4-nitrobenzenediazonium ions and 4-acetyl benzene diazonium ions gave additional band appears in the region of 2390-2340 cm^{-1} possibly due to the presence of -N≡N-stretching vibration, this absorption band is absent in the preloaded Amberlite IR-120 (Na^+) [19].

Synthesis of triazenes by immobilized diazonium ions: To a solution of secondary amine (piperidine or morpholine, 1 mmol) in cyclohexane (25 mL), 5 g of freshly prepared resin beads containing the diazonium ions were added and the reaction mixture was stirred at room temperature. The progress of the reaction was observed by colour change of the resin beads. On completion of the reaction, the coloured beads were recovered by simple filtration, washed 2 to 3 times with deionized water and then dried at room temperature. The product triazenes which remained adsorbed onto the surface of the beads were extracted with ethyl acetate (100 mL) in a soxhlet extraction apparatus. Evaporation of the solvent under reduced pressure gave the desired triazene. Complete extraction of the triazenes from the resin beads could not be achieved due to strong association of the triazene to the surface of the resin nevertheless yield obtained to the extent of 80-90 %. Most triazenes formed were found to be coloured viscous liquids except a few as shown in Table-2. The products were purified by TLC using silica gel H plates and ethyl acetate as the eluent. A single spot in TLC indicated the excusive formation of the triazene.

Spectral data of some representative compounds

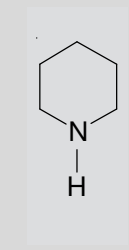
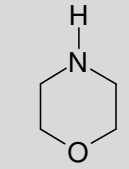
N-(2-Nitrophenylazo)piperidine (1a): Pale yellow oil, IR (KBr, ν_{max}, cm^{-1}): 1625.99, 1311.59 (-N=O), 1462.04 (-N=N-), 1154.26 (-N-N=N-), UV-visible (EtOH) λ_{max} (-N=N-): 380.54 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H): 7.844 (1H, d, *J* = 7.2 Hz, ArH), 7.635 (2H, t, *J* = 8.4 Hz, ArH), 7.295 (1H, d, *J* = 6.9 Hz, ArH), 3.887 (4H, brs, piper-CH_2), 2.174 (6H, brs, piper-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 153.49, 146.47, 134.47, 130.80, 129.60, 129.44, 129.19, 120.57, 52.60, 29.22, 26.44. HRMS (ESI): M^+ Calcd: 234.11; found: 235.5629.

N-(2,4-Dichlorophenylazo)piperidine (1b): Pale yellow oil, IR (KBr, ν_{max}, cm^{-1}): 1469.76 (-N=N-), 1114.86 (-N=N-N-). UV-visible (EtOH) λ_{max} (-N=N-): 357.84 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H): 8.56 (1H, d, *J* = 7.2 Hz (1H, d, ArH, *J* = 7.2 Hz), 7.548 (1H, s, ArH), 7.472 (1H, d, *J* = 6.8 Hz, ArH), 2.241 (4H, brs, piper-CH_2), 1.756 (6H, brs, piper-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 153.87, 150.60, 144.67, 125.17, 115.89, 36.15, 28.67, 24.48. HRMS (ESI): M^+ Calcd: 257.05; Found: 258.2125.

N-(4-Methoxyphenylazo)piperidine (1d): Brown solid, IR (KBr, ν_{max}, cm^{-1}): 1486.19 (-N=N-), 1146.32 (-N-N=N-). UV-visible (EtOH) λ_{max} (-N=N-): 351.06 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H): 7.788 (2H, d, *J* = 8.4 Hz, ArH), 7.605 (2H, d, *J* = 7.8 Hz, ArH), 4.115 (3H, s, OCH_3), 3.563 (4H, brs, piper-CH_2), 2.317 (6H, brs, piper-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 158.60, 147.88, 125.60, 118.56, 58.74, 48.15, 27.67, 23.98. HRMS (ESI): M^+ Calcd: 219.14; Found: 220.6748.

N-(4-Methylphenylazo)piperidine (1e): Dark red solid, IR (KBr, ν_{max}, cm^{-1}): 1450.47 (-N=N-), 1251.80 (C-N), 1184.29

TABLE-2
PHYSICAL CHARACTERISTICS OF TRIAZENES USING RESIN IMMOBILIZED DIAZONIUM IONS WITH 2° AMINES

S. No.	2° Amine	R	Product	Time (min)	Yield[a] (%)	m.p. (°C)	
						Lit	Obs
1		2-NO_2	**1a**	15	80	Oil [Ref. 20]	Oil
2		2,4-diCl	**1b**	15	81	–	Oil
3		3-Br	**1c**	10	83	–	Oil
4		4-OCH_3	**1d**	10	86	29-31 [Ref. 21]	34-35
5		4-CH_3	**1e**	10	85	43-45 [Ref. 21]	42-45
6		4-CH_3CO	**1f**	10	87	–	48-50
7		4-NO_2	**1h**	10	86	96 [Ref. 22]	94-97
8		2-CH_3	**1i**	15	80	Oil [Ref. 20]	Oil
9		4-Cl-2-NO_2	**1j**	15	81	–	Oil
11		H	**2a**	15	85	–	Oil
12		4-OCH_3	**2b**	15	87	–	67-70
13		4-Br	**2c**	15	82	–	62-65
14		4-NO_2	**2d**	10	85	–	78-80
15		4-CH_3CO	**2e**	10	83	–	Oil
16		4-CH_3	**2f**	15	80	Oil [Ref. 20]	Oil
17		2-Cl	**2g**	20	78	–	Oil
18		4-Cl-2-NO_2	**2h**	15	75	–	Oil
19		2-CH_3	**2i**	20	82	–	Oil

[a]Yields refer to the pure isolated products. [b]Melting point reported for solid products

(-N-N=N-), UV-visible (EtOH) λ_{max} (-N=N-): 330.42 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H): 7.028 (2H, d, *J* = 4.8 Hz, ArH), 6.771 (2H, d, *J* = 8.6 Hz, ArH), 2.471 (4H, brs, piper-CH_2), 2.185 (3H, s, CH_3), 1.348 (6H, brs, piper-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 153.43, 137.61, 130.90, 121.02, 49.09, 29.64, 22.64, 20.40. HRMS (ESI): M^+ Calcd: 203.14; Found: 203.0709.

N-(4-Acetylphenylazo)piperidine (1f): Red solid, IR (KBr, ν_{max}, cm^{-1}): 1646.35 (Ar-C=O), 1418.04 (-N=N-), 1147.65 (-N=N-N-). UV-visible (EtOH) λ_{max} (-N=N-): 363.37 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H): 7.932 (2H, d, *J* = 8.4 Hz, ArH), 7.491 (2H, d, *J* = 8.1 Hz, ArH), 3.858 (3H, s, OCH_3), 2.639 (4H, brs, piper-CH_2), 1.575 (6H, brs, piper-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 197.65, 154.62, 133.79, 129.52, 120.21, 60.40, 53.41, 29.63, 24.99, 21.02. HRMS (ESI): M^+ Calcd: 231.14; Found: 232.1445.

N-(4-Chloro-2-nitrophenylazo)piperidine (1j): Red oil, IR (KBr, ν_{max}, cm^{-1}): 1586.66, 1385.78 (-N=O), 1483.67 (-N=N-), 1148.55 (-N=N-N-). UV-visible EtOH λ_{max} 393.65 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H): 7.832 (1H, s, ArH), 7.742 (1H, d, *J* = 8.4 Hz, ArH), 7.545 (1H, t, *J* = 7.6 Hz, ArH), 3.684 (4H, brs, piper-CH_2), 1.862 (6H, brs, piper-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 154.67, 139.34, 132.45, 131.89, 130.34, 122.56, 43.87, 26.68. HRMS (ESI): M^+ Calcd: 268.07; Found: 269.1637.

N-(4-Methoxyphenylazo)morpholine (2b): Pale yellow oil, IR (KBr, ν_{max}, cm^{-1}): 1494.83 (-N=N-), 1155.36 (-N=N-N-). UV-visible EtOH λ_{max} (-N=N-): 375.51 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H): 7.445 (2H, d, *J* = 8.7 Hz, ArH), 6.915 (2H, d, *J* = 8.7 Hz, ArH), 3.865 (4H, brs, morph-CH_2), 3.429 (3H, s, OCH_3), 3.170 (4H, brs, morph-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 158.37, 143.75, 127.98, 127.75, 121.80, 66.27, 55.18, 51.33. HRMS (ESI): M^+ Calcd: 221.12; Found: 222.1315.

N-(4-Nitrophenylazo)morpholine (2d): Red solid, IR (KBr, ν_{max}, cm^{-1}): 1624.67, 1323.71 (Ar-N=O), 1436.57 (-N=N-), 1157.29 (-N=N-N-). UV-visible EtOH λ_{max} (-N=N-): 389.49 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H ppm): 7.986 (2H, d, *J* = 8.7 Hz, ArH), 7.597 (2H, d, *J* = 9.0 Hz, ArH), 3.122 (4H, brs, morph-CH_2), 2.102 (4H, brs, morph-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 152.43, 138.97, 126.25, 121.32, 66.32, 54.0. HRMS (ESI): M^+ Calcd: 236.09; Found: 236.1211.

N-(4-Methylphenylazo)morpholine (2f): Red solid. IR (KBr, ν_{max}, cm^{-1}): 1624.67, 1444.68 (-N=N-), 1155.36 (-N=N-N-). UV-visible EtOH λ_{max} (-N=N-): 372.84 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H): 7.385 (2H, d, *J* = 8.4 Hz, ArH), 7.171 (2H, d, *J* = 8.1 Hz, ArH), 3.825 (4H, brs, morph-CH_2), 3.308 (4H, brs, morph-CH_2), 2.344 (3H, s, CH_3). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 152.43, 138.97, 126.25, 121.32, 66.32, 54.0. HRMS (ESI): M^+ Calcd: 205.12; Found: 205.9423.

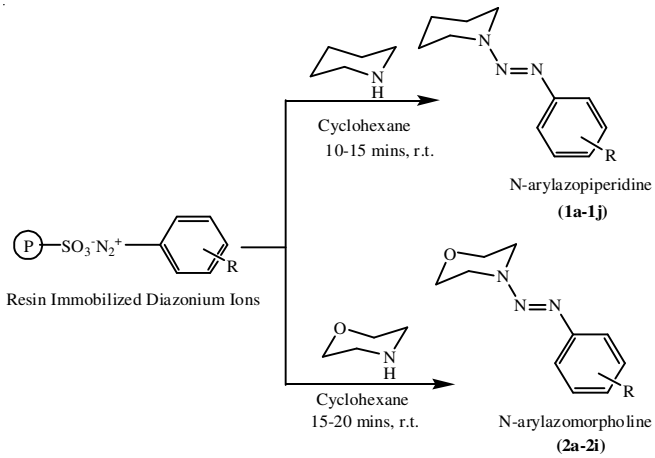
N-(4-Chloro-2-nitrophenylazo)morpholine (2h): Pale yellow oil IR (KBr, ν_{max}, cm^{-1}): 1602, 13, 1387.61 (Ar-N=O), 1495.34 (-N=N-), 1138.97 (-N=N-N-). UV-visible EtOH λ_{max} (-N=N-): 382.44 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H): 8.103 (1H, s, ArH), 7.738 (1H, d, *J* = 7.2 Hz, ArH), 7.526 (1H, d, *J* = 8.4 Hz, ArH), 3.739 (4H, brs, morph-CH_2), 3.118 (4H, brs, morph-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 159.11, 147.65, 135.58, 126.75, 122.71, 118.86, 66.02, 54.85. HRMS (ESI): M^+ Calcd: 300.10; found: 301.1210.

N-(4-Bromophenylazo)morpholine (2i): Pale yellow solid, IR (KBr, ν_{max}, cm^{-1}): 1435.04 (-N=N-), 1153.43 (-N=N-N-). UV-visible EtOH λ_{max} (-N=N-): 346.16 nm. ^{1}H NMR (300 MH_Z, $CDCl_3$, Me_4Si) (δ_H): 7.477 (2H, d, *J* = 6.9 Hz, ArH), 7.340 (2H, d, *J* = 6.9 Hz, ArH), 3.787 (4H, brs, morph-CH_2), 2.178 (4H, brs, morph-CH_2). ^{13}C NMR (75 MH_Z, $CDCl_3$, Me_4Si) δ: 154.26, 148.33, 129.81, 124.90, 64.12, 48.66. HRMS (ESI): M^+ Calcd: 299.06; Found: 299.9771.

RESULTS AND DISCUSSION

Herein is reported a method for preparation of resin immobilized diazonium ions which were subsequently used to synthesize the triazene in neutral organic solvents resulting in

high yield of the target molecule. In this study, the heterocyclic amines namely piperidine and morpholine were chosen as the starting compounds for the synthesis of the corresponding triazenes namely the N-(arylazo)piperidines and N-(arylazo)-morpholines. The resin immobilized diazonium ions were reacted with the heterocyclic amines at room temperature in presence of organic solvents (**Scheme-I**). Several solvents such as toluene, benzene, chloroform, dichloromethane and acetonitrile were screened for their suitability and cyclohexane was found to be the solvent of choice primarily because in cyclohexane the product triazenes are insoluble and remains embedded onto the resin support which has inherent advantages in solid phase synthesis. Resin embeded triazenes not only prevents its contamination with unreacted substrates but also offers the advantage of using excess of the reagents to speed up the reaction. The formation of the triazene can be easily followed by the instant colour change of the resin beads. Recovery of products requires simple filtration of the beads and extraction of the triazenes with ethyl acetate. Reduced pressure removal of solvent yielded triazene in a pure form and near quantitative yield. Resin immobilized diazonium ions with both electron-withdrawing and electron-donating substituents gave comparable yield of the product indicating that electronic factors do not play any significant control on the reaction. To examine the fesibility of the solid phase synthesis reaction, a representative reaction was carried out by preparing the resin immobilized diazonium ion with 4-methoxyaniline and brought into reaction with piperidine. The results obtained were encouraging and the procedure generalized by using diazonium ions prepared from several aromatic amines, immobilizing them unto the cation exchange resin and carrying out the N-coupling reaction with both piperidine and morpholine as the substrates.



Scheme-I: Solid phase synthesis of triazene namely the N-arylazopiperidines and N-arylazomorpholines using resin immobilized diazonium ions

UV-visible spectra of triazenes: All the substituted triazenes show the UV-visible absorption maxima at λ_{max} = 330-390 nm due to the presence of -N=N- chromophore (Fig. 1).

Presence of different functional groups like OCH_3, $COCH_3$, NO_2, Cl, Br *etc*. shifts the absorption maxima towards longer wavelength. Thus, the UV-visible spectroscopy can be

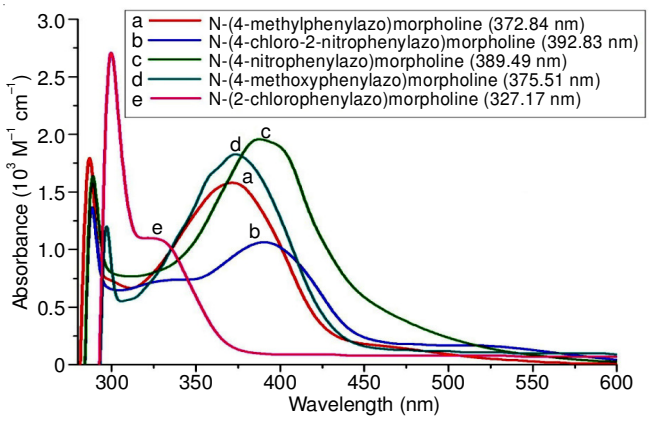


Fig. 1. UV-visible spectra of some selected N-arylazopiperidines in 95 % ethanol

used as an effective technique for the identification of the triazene derivatives. Further, triazenes are unstable in acids and this characteristic can be utilized as an analytical method for the detection of trizenes. In the present study, UV-visible spectra of an alcoholic solution of the triazenes were recorded before and after acidification with conc. H_2SO_4 (Figs. 2 and 3) and the hypsochromic shift observed in the triazene maxima confirmed the formation of the trizenes (Table-3).

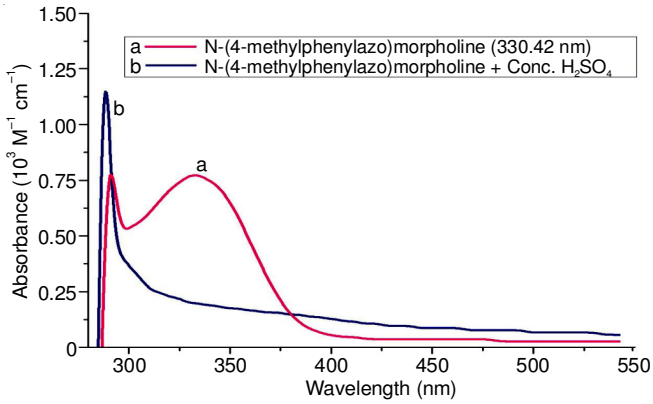


Fig. 2. UV-visible spectra of compound **1e** in EtOH before and after treatment with conc. H_2SO_4

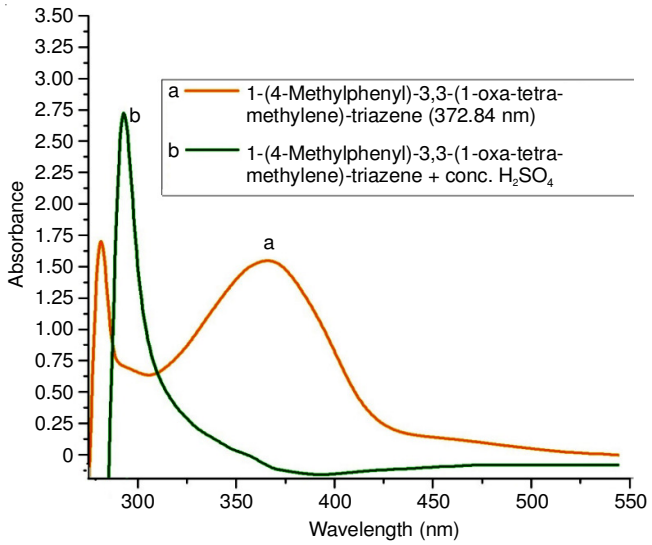


Fig. 3. UV-visible spectra of compound **2f** in EtOH before and after treatment with conc. H_2SO_4

TABLE-3
SHIFT IN THE UV-VISIBLE MAXIMA OF TRIAZENES ON ACIDIFICATION OF EtOH SOLUTION

S. No.	Triazene	λ_{max} (nm)	λ_{max} (nm)
1	N-(4-Methylphenylazo)piperidine	330	285
2	N-(4-Methoxyphenylazo)piperidine	361	305
3	N-(2-Nitrophenylazo)piperidine	380	320
4	N-(4-Methylphenylazo)morpholine	372	330
5	N-(4-Methoxyphenylazo)morpholine	375	345
6	N-(2-Nitrophenylazo)morpholine	395	370

Conclusion

In conclusion, a solid phase technique have been developed for the synthesis of triazenes namely N-arylazopiperidine and N-arylazomorpholine in good yield using resin immobilized diazonium ions. Resin immobilized diazonium ions are stable and can be isolated and stored, further the diazo coupling reaction can be carried out in organic solvent which is not possible in the classical synthesis. The absence of acids results in high yield of the acid labile triazene. Recovery and isolation of the products are simple.

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