JOC The Journal of Organic Chemistry

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Push-Pull Triazenes Derived from 1-(Benzylideneamino)- and 1-(Sulfonimido)-azolylidenes

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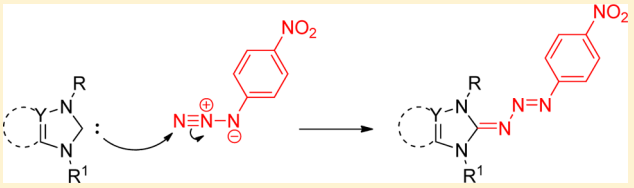
Supporting Information

ABSTRACT: In-situ-generated neutral 1-(benzylideneamino)- and novel anionic 1-(sulfonimido)-azolylidenes react with organic azides to afford diverse classes of push-pull triazenes and triazene salts. The scope of the heterocyclic core and substituents at the N1 and N3 positions of NHC precursors together with the thermal properties of resulting compounds were examined.



The unique properties of compounds containing a triazene linkage such as stability and adaptability to numerous synthetic transformations[1] have encouraged current interest. Triazenes have been utilized as masking groups,[2,3] alkylating agents for DNA,[4,5] protecting groups for amines and diazonium salts,[6,7] photoactive materials,[8] building blocks for the synthesis of various phenylacetylene-based systems,[1] ligands for transition metals,[1,9] and intermediates for the synthesis of diverse heterocycles including 1,2,3,5-tetrazinones, triazoles, benzotriazoles,[10−12] cinnolines, isoindazoles,[13,14] benzotriazinones,[15,16] and azolium salts.[17−19]

Most triazenes are of Type **I** or **II** (Figure 1). In Type **I** triazenes, the subject of this paper, the triazene group

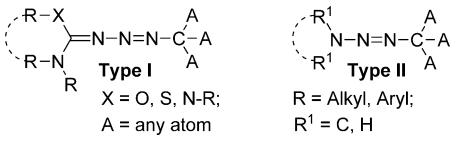


Figure 1. Types of triazenes.

terminates with a C═N double bond carrying electron-donating substituents, which thus allows direct conjugation through the triazene linkage (Figure 1).[20] Type **I** triazenes are also called "push-pull" or "donor-acceptor" triazenes.[20,21]

Earlier reports demonstrated that the presence of electron-donating and electron-withdrawing groups on opposite sides of donor-acceptor triazenes enhances the electronic communication even further.[21−23] Although such Type **I** triazenes are interesting chromophores for electronic applications,[20] literature reports are limited to imidazole and benzimidazole moieties with symmetric *N*-alkyl substituents.[22]

Synthetic methodologies reported for triazenes include: (i) coupling of amines with aryl diazonium salts,[24,25] (ii) addition of organometallic reagents (RMgX, RLi, etc.) to organic azides,[26,27] and (iii) the reaction of *N*-heterocyclic carbenes (NHCs) or their dimers with organic azides.[22,28−31] Methods (i) and (ii) are usually employed for the synthesis of Type **II** triazenes, whereas Type **I** triazenes are produced by method (iii).

While triazenes of Type **II** are numerous and extensively investigated,[1] surprisingly little is known about Type **I** compounds. Herein, we report the synthesis, reactivity, and thermal properties of push-pull triazenes derived from 1-aminobenzimidazolium and 4-amino-1,2,4-triazolium salts, from 1,3-dialkylbenzimidazolium and 1,3-dialkylimidazolium salts and from 1,2,4-triazolium *N*-imides with diverse symmetric or asymmetric N-substitution via in situ formation of neutral and novel anionic NHCs. This method has significant advantages in terms of safety, atom economy, and reaction simplicity together with tolerance toward a broad array of functional groups and structural variations.[22,31−35] We found no literature reports for the synthesis of such derivatives and therefore investigated the substrate scope with respect to substitution in the ring and at N1 and N3 together with the chemical and electronic properties of the resultant Type **I** triazenes.

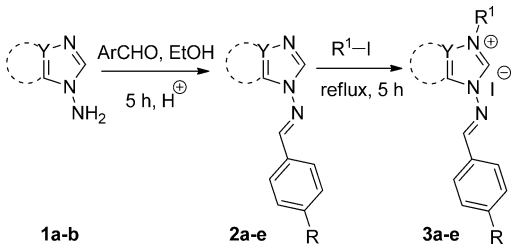
1-Benzylidineamino-3-alkyl-1,2,4-triazolium iodides **3a,b** and 1-benzylidineamino-3-alkylbenzimidazolium iodides **3c−e** were prepared according to methodology previously described by our group.[36] Condensation of 4-amino-1,2,4-triazole **1a** or 1-

Received: December 11, 2012

   dx.doi.org/10.1021/jo302697q | J. Org. Chem. XXXX, XXX, XXX−XXX

amino-benzimidazole **1b** with various aromatic aldehydes,[37] generated imines **2a–e** in 79–98% yields. Quaternization of imines **2a–e** with the corresponding alkyl halides gave the desired 1,2,4-triazolium **3a,b** and benzimidazolium salts **3c–e** in near quantitative yields (Table 1).

Table 1. Synthesis of 1,2,4-Triazolium and Benzimidazolium Salts 3a–e



R	Y	R^1	reagent	product (%)
CH_3O	N		**1a**	**2a** (95)
Et_2N	N		**1a**	**2b** (98)
H	C-(CH=CH)$_2$-		**1b**	**2c** (94)
CH_3O	C-(CH=CH)$_2$-		**1b**	**2d** (92)
NO_2	C-(CH=CH)$_2$-		**1b**	**2e** (79)
CH_3O	N	Me	**2a**	**3a** (99)
Et_2N	N	Me	**2c**	**3b** (99)
H	C-(CH=CH)$_2$-	Bu	**2d**	**3c** (99)
CH_3O	C-(CH=CH)$_2$-	Bu	**2e**	**3d** (99)
NO_2	C-(CH=CH)$_2$-	Bu	**2f**	**3e** (99)

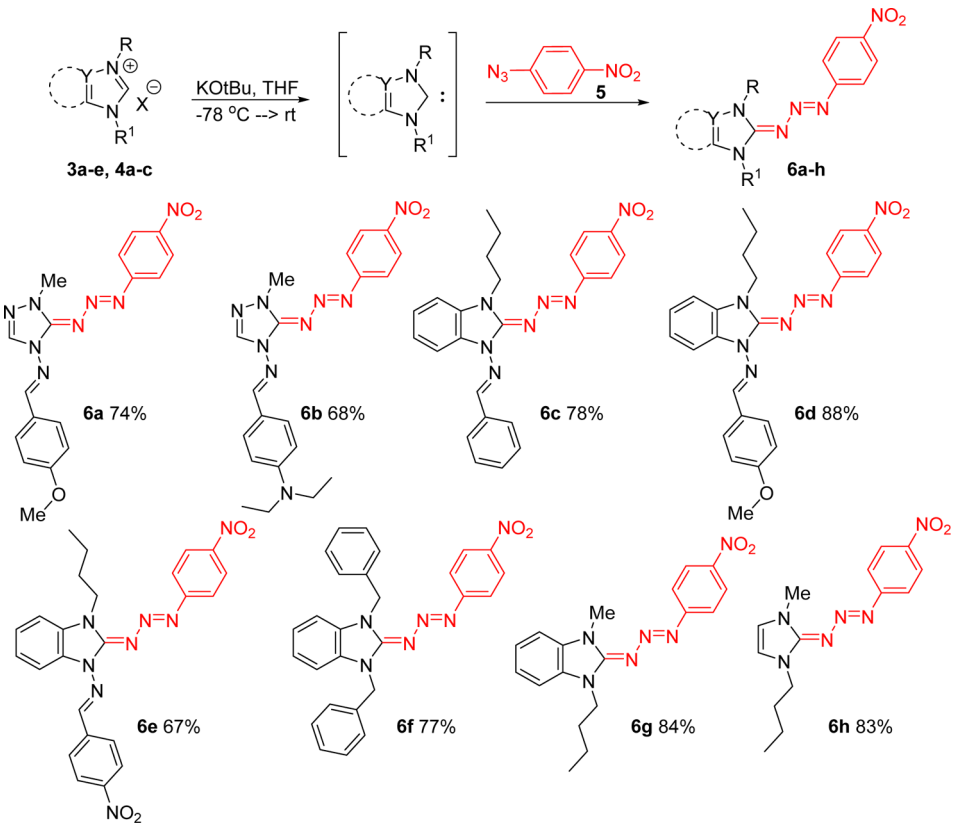
1,3-Dibenzyl-benzimidazolium bromide **4a**, 1-butyl-3-methyl-benzimidazolium iodide **4b**, and 1-butyl-3-methylimidazolium chloride **4c** were selected as model examples of symmetrically and asymmetrically substituted *N*-alkyl azoles. 1,3-Dibenzyl-benzimidazolium bromide **4a** and 1-butyl-3-methyl-benzimidazolium iodide **4b** were generated from commercially available 1*H*-benzimidazole in one- and two-step literature procedures,[38,39] while 1-butyl-3-methylimidazolium chloride **4c** was commercially available.

Deprotonation of azolium halides **3a–e** and **4a–c** using potassium *tert*-butoxide generated NHCs, which by reaction with 1-azido-4-nitrobenzene **5** at −78 °C formed the corresponding donor-acceptor triazenes **6a–h** in 67–88% yields (Table 2), all isolated by crystallization. The structures of representative triazenes, **6d** and **6f**, were confirmed by single crystal X-ray diffraction. X-ray crystal data revealed that in **6d** the carbon-nitrogen double bond of the triazene linkage adopts an *E* geometry and the terminal nitrogen is hydrogen-bonded to a molecule of methanol (see Supporting Information). On the basis of this finding, *E* geometry was assigned to a carbon-nitrogen double bond of similar systems.

The in situ generation of novel anionic NHCs **8a–d** was effected by the deprotonation of 1,2,4-triazolium *N*-imides **7a–d** with potassium *tert*-butoxide. The reaction of **8a–d** with 1-azido-4-nitrobenzene **5** generated the corresponding triazene potassium salts **9a–d** in 79–95% yields.

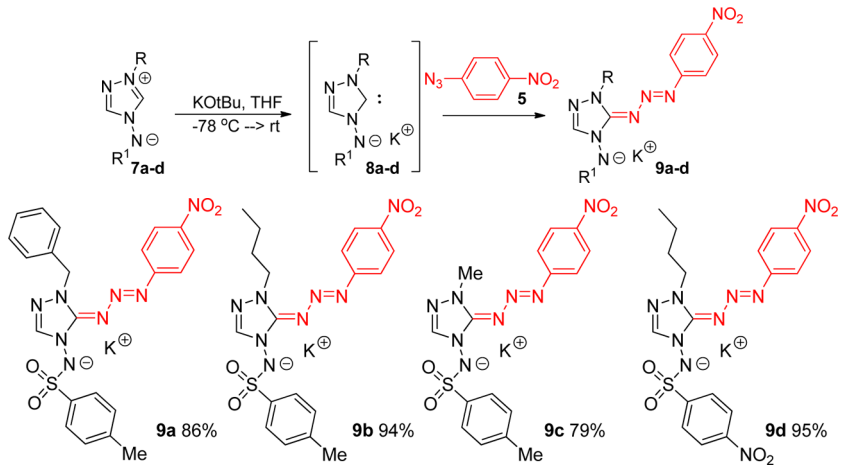
In addition, we examined the reactivity of the novel triazene **6f** and salt **9a** with various electrophiles. Given their push-pull character, triazenes are expected to have increased electron density on the terminal nitrogen of the triazene linkage (Scheme 1). Our findings supported this argument. The reaction of **6f** with methyl iodide gave triazenium iodide **10** where the methyl group is located on the terminal nitrogen.

Table 2. Synthesis of Donor-Acceptor Triazenes

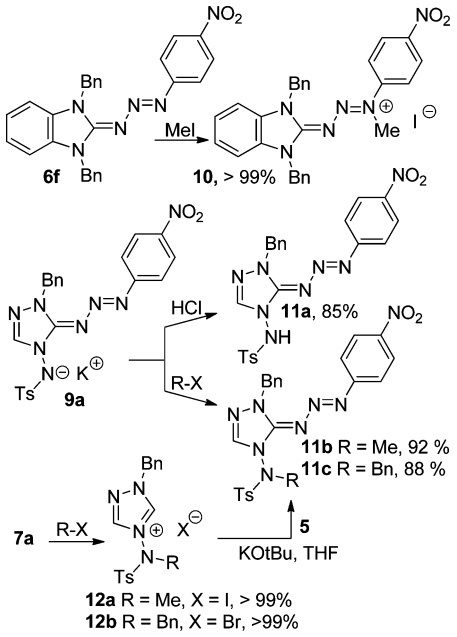


dx.doi.org/10.1021/jo302697q | J. Org. Chem. XXXX, XXX, XXX–XXX

Table 3. Synthesis of Donor-Acceptor Triazene Salts via Novel Anionic NHCs



Scheme 1. Reactivity of Push-Pull Triazenes



The structure of **10** was unambiguously confirmed by X-ray crystallography (see Supporting Information). Reaction of **9a** with 1 NHCl, methyl iodide, and benzyl bromide, however, resulted in the formation of neutral compounds **11a–c**; evidently the sulfonamide moiety is the most nucleophilic center of **9a**. The spectra of **11b** and **11c** were identical to those obtained by the reaction of 1-azido-4-nitrobenzene **5** with 1,2,4-triazolium salts **12a** and **12b** under basic conditions (Scheme 1).

Exploration of the thermal properties of **9a–d** and **11a** by TGA revealed their exceptional thermal stability. Most compounds were found to be stable at temperatures over 200 °C. Compounds **11a** and **9d**, however, showed sharp decomposition at 176 and 251 °C, losing 22% and 54% of their mass over 1 and 2 min, respectively (Figure 2). Such rapid decomposition at high temperatures could make these compounds promising blowing agents for energetic formulations.[40]

In conclusion, in situ generated 1-(benzylideneamino) and 1-(sulfonimide) azolylidenes react with organic azides to afford novel classes of donor-acceptor triazenes in high yield and purity. Furthermore, a novel class of anionic NHCs was generated, and their reactivity was explored in the preparation of push-pull triazenes. The chemical properties of triazenes proved that the push-pull nature of triazenes increased the electron density on the terminal nitrogen. X-ray analysis of key products revealed the double bond geometry of the terminal double bond of the triazene linkage. Thermal analysis of selected targets by TGA demonstrated potential usefulness as blowing agents.

EXPERIMENTAL SECTION

Materials and Methods. All reactions were performed in single-neck round-bottom flasks fitted with rubber septa under positive nitrogen pressure. Solvents were freshly distilled and degassed. Reaction progress was monitored by thin-layer chromatography (TLC) and visualized by UV light. Melting points were determined on a capillary point apparatus equipped with a digital thermometer and are uncorrected. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with TMS for ^{1}H (300 MHz) and ^{13}C (75 MHz) as an internal reference. Compounds **1b**, **2c–e**, **3c–e**, and **7a–d** were prepared according to literature procedures reported earlier by our group.[36,41] 4-Amino-1,2,4-triazole **1a** and 1-butyl-3-methylimidazolium chloride **4c** were purchased from Sigma-Aldrich and used without further purification. 1-Azido-4-nitrobenzene **5** was prepared in one step according to a literature procedure.[42] Elemental analyses were performed on a Carlo Erba EA 1108 instrument.

General Method for the Preparation of Imines 2a,b. 4-Amino-1,2,4-triazole (4.2 g, 50 mmol) and the corresponding aldehyde (1.05 equiv) were dissolved in absolute ethanol (50 mL) and stirred under reflux in the presence of a catalytic amount of conc sulfuric acid. After 5 h, the reaction mixture was cooled to room temperature and concentrated under reduced pressure, and the residue was recrystallized from EtOAc/hexanes to obtain pure **2a–e**.

(*E*)-*N*-(4-Methoxybenzylidene)-4*H*-1,2,4-triazol-4-amine (2a).[43] White crystals (9.6 g, 95%), mp 164–165 °C (lit.[43] mp 164 °C); ^{1}H NMR ($CDCl_3$) δ 8.59 (s, 2H), 8.52 (s, 1H), 7.80 (d, J = 9.3 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 163.4, 156.7, 138.2, 130.7, 124.1, 114.7, 55.6. Anal. Calcd For $C_{10}H_{10}N_4O$: C, 59.40; H, 4.98; N, 27.71. Found: C, 59.57; H, 5.34; N, 27.96.

(*E*)-*N*-(4-(Diethylamino)benzylidene)-4*H*-1,2,4-triazol-4-amine (2b).[44] Green crystals (11.9 g, >98%), mp 176–180 °C; ^{1}H NMR (DMSO-d_6) δ 9.04 (s, 2H), 8.81 (s, 1H), 7.64 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 9.0 Hz, 2H), 3.42 (q, J = 7.0 Hz, 4H), 1.13 (t, J = 6.9 Hz, 6H); ^{13}C NMR (DMSO-d_6) δ 158.1, 150.3, 138.7, 130.4, 118.0, 111.0, 43.8, 12.3.

dx.doi.org/10.1021/jo302697q | J. Org. Chem. XXXX, XXX, XXX–XXX

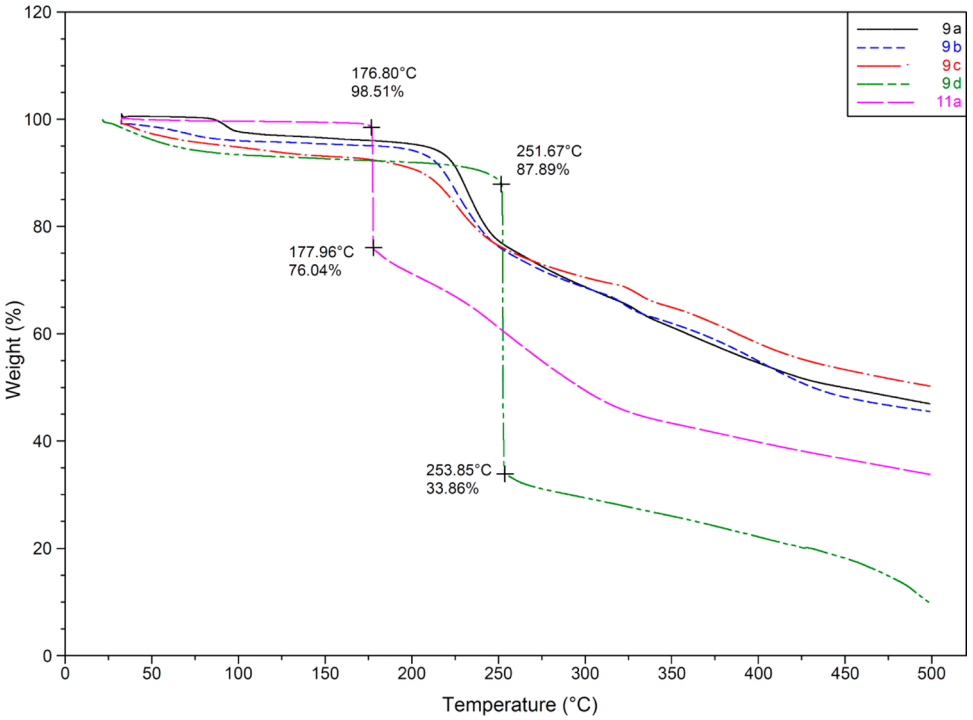


Figure 2. TGA data for **9a−d** and **11a**.

General Method for the Preparation of Benzimidazolium and 1,2,4-Triazolium Salts 3a,b. A mixture of iodomethane (3 equiv) and the corresponding imines **2a,b** (2.0 g) was stirred without solvent under reflux. After 5 h, excess iodomethane was removed under reduced pressure to give pure salts **3a,b** in near quantitative yields.

(*E*)-4-((4-Methoxybenzylidene)amino)-1-methyl-4*H*-1,2,4-triazol-1-ium Iodide (3a).[45] Yellow crystals (3.4 g, >99%), mp 185−186 °C (lit.[45] mp 185 °C); ^{1}H NMR (DMSO-d_6) δ 10.70 (s, 1H), 9.81 (s, 1H), 9.21 (s, 1H), 7.91 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 4.14 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 164.1, 163.6, 139.7, 139.2, 131.4, 122.8, 115.0, 55.7, 39.1. Anal. Calcd For $C_{11}H_{13}IN_4O$: C, 38.39; H, 3.81; N, 16.28. Found: C, 38.68; H, 3.94; N, 16.24.

(*E*)-4-((4-(Diethylamino)benzylidene)amino)-1-methyl-4*H*-1,2,4-triazol-1-ium Iodide (3b). Yellow crystals (3.16 g, >99%), mp 187−188 °C; ^{1}H NMR (DMSO-d_6) δ 10.58 (s, 1H), 9.71 (s, 1H), 8.92 (s, 1H), 7.70 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 9.0 Hz, 2H), 4.10 (s, 3H), 3.47 (q, J = 7.1 Hz, 4H), 1.15 (t, J = 6.9 Hz, 6H); ^{13}C NMR (DMSO-d_6) δ 163.9, 151.5, 139.4, 139.2, 131.6, 116.0, 111.2, 43.9, 39.0, 12.3. Anal. Calcd For $C_{14}H_{20}IN_5$: C, 43.65; H, 5.23; N, 18.18. Found: C, 43.79; H, 5.09; N, 18.18.

General Method for the Preparation of Push-pull Triazene 6a−h. Potassium *tert*-butoxide (0.08 g, 0.8 mmol) was added to a mixture of 1-azido-4-nitrobenzene **5** (0.10 g, 0.63 mmol) and corresponding azolium halide **3a−e**, **4a−c** (0.63 mmol) in dry THF (10 mL) at −78 °C. After 10 min, the reaction mixture was warmed to room temperature and stirred. After 24 h the precipitate was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from MeOH to obtain pure triazene **6a−h**.

(*E*)-1-(4-Methoxyphenyl)-*N*-((*E*)-1-methyl-5-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-1,5-dihydro-4*H*-1,2,4-triazol-4-yl)methanimine (6a). Red crystals (0.18 g, 74%), mp 219−220 °C; ^{1}H NMR (DMSO-d_6) δ 9.08 (s, 1H), 9.01 (s, 1H), 8.14 (d, J = 9.0 Hz, 2H), 7.86 (d, J = 9.0 Hz, 2H), 7.58 (d, J = 9.0 Hz, 2H), 7.15 (d, J = 9.0 Hz, 2H), 3.93 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 162.7, 161.8, 156.7, 151.3, 144.4, 135.6, 130.6, 124.6, 124.4, 121.2, 114.7, 55.5, 38.8; HRMS (+ESI-TOF) m/z for $C_{17}H_{16}N_8O_3Na$ [M + Na]$^+$ calcd 403.1238, found 403.1239.

***N*,*N*-Diethyl-4-((*E*)-(((*E*)-1-methyl-5-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-1,5-dihydro-4*H*-1,2,4-triazol-4-yl)imino)-methyl)aniline (6b).** Purple crystals (0.18 g, 68%), mp 305−307 °C; ^{1}H NMR ($CDCl_3$) δ 8.99 (s, 1H), 7.99 (d, J = 9.3 Hz, 2H), 7.81 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 9.6 Hz, 2H), 6.77 (d, J = 9.0 Hz, 2H), 3.54 (s, 3H), 3.45 (q, J = 6.9 Hz, 4H), 1.14 (t, J = 7.1 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 162.3, 160.1, 159.7, 155.4, 150.4, 138.3, 131.2, 125.0, 122.1, 117.2, 110.8, 43.8, 28.6, 12.3; HRMS (+ESI-TOF) m/z for $C_{20}H_{24}N_9O_2$ [M + H]$^+$ calcd 422.2059, found 422.2059.

(*E*)-*N*-((*E*)-3-Butyl-2-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-1-phenylmethanimine (6c). Red crystals (0.22 g, 78%), mp 157−158 °C; ^{1}H NMR ($CDCl_3$) δ 9.42 (s, 1H), 8.05 (d, J = 9.0 Hz, 2H), 7.89 (d, J = 9.0 Hz, 2H), 7.59−7.42 (m, 6H), 7.38−7.20 (m, 3H), 4.33 (t, J = 7.5 Hz, 2H), 1.96−1.81 (m, 2H), 1.48−1.34 (m, 2H), 0.94 (t, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 162.8, 156.2, 151.7, 145.8, 133.1, 132.3, 130.2, 129.7, 129.0, 128.6, 124.6, 123.9, 123.5, 121.9, 110.3, 109.2, 45.5, 31.0, 20.1, 13.9; HRMS (+ESI-TOF) m/z for $C_{24}H_{24}N_7O_2$ [M + H]$^+$ calcd 442.1986, found 442.1993.

(*E*)-*N*-((*E*)-3-Butyl-2-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-1-(4-methoxyphenyl)-methanimine (6d). Red crystals (0.26 g, 88%), mp 95−97 °C; ^{1}H NMR ($CDCl_3$) δ 9.24 (s, 1H), 8.07 (d, J = 9.0 Hz, 2H), 7.88 (d, J = 9.0 Hz, 2H), 7.58 (d, J = 9.0 Hz, 2H), 7.52−7.44 (m, 1H), 7.36−7.24 (m, 3H), 7.01 (d, J = 9.0 Hz, 2H), 4.37 (t, J = 7.5 Hz, 2H), 3.91 (s, 3H), 2.01−1.85 (m, 2H), 1.52−1.37 (m, 2H), 0.98 (t, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 163.9, 163.1, 156.3, 151.5, 145.6, 130.6, 130.2, 129.7, 125.5, 124.5, 123.8, 123.4, 121.8, 114.5, 110.2, 109.2, 55.6, 50.8, 45.1, 31.0, 20.1, 13.9; HRMS (+ESI-TOF) m/z for $C_{25}H_{25}N_7O_3Na$ [M + Na]$^+$ calcd 494.1911, found 494.1907.

(*E*)-*N*-((*E*)-3-Butyl-2-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-1-(4-nitrophenyl)-methanimine (6e). Red crystals (0.21 g, 67%), mp 226−227 °C; ^{1}H NMR ($CDCl_3$) δ 10.12 (s, 1H), 8.36−8.23 (m, 4H), 8.12 (d, J = 9.0 Hz, 2H), 7.75−7.62 (m, 3H), 7.43−7.34 (m, 2H), 7.33−7.24 (m, 1H), 4.43 (t, J = 7.5 Hz, 2H), 2.08−1.87 (m, 2H), 1.55−1.35 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 155.7, 155.4, 151.9, 149.1, 146.3, 139.9, 130.4, 129.7, 128.8, 124.8, 124.4, 124.0, 123.9, 121.9, 111.0, 109.0, 46.9, 31.3, 20.0, 13.9; HRMS (+ESI-TOF) m/z for $C_{24}H_{22}N_8O_4Na$ [M + Na]$^+$ calcd 509.1656, found 509.1646.

dx.doi.org/10.1021/jo302697q | *J. Org. Chem.* XXXX, XXX, XXX−XXX

(*E*)-1,3-Dibenzyl-2-((4-nitrophenyl)triaz-2-en-1-ylidene)-2,3-dihydro-1*H*-benzo[*d*]imidazole (6f). Red crystals (0.0.23 g, 77%), mp 190−191 °C; ^{1}H NMR ($CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.39−7.29 (m, 10H), 7.20−7.15 (m, 6H), 5.65 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 156.1, 154.9, 145.5, 135.5, 131.4, 129.0, 128.0, 126.7, 124.5, 123.7, 121.7, 109.9, 48.4. Anal. Calcd For $C_{27}H_{22}N_6O_2$: C, 70.12; H, 4.76; N, 18.17. Found: C, 70.26; H, 4.87; N, 18.19.

(*E*)-1-Butyl-3-methyl-2-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-2,3-dihydro-1*H*-benzo[*d*]imidazole (6g). Red crystals (0.19 g, 84%), mp 158−161 °C; ^{1}H NMR ($CDCl_3$) δ 8.24 (d, J = 12.0 Hz, 2H), 7.67 (d, J = 9.0 Hz, 2H), 7.38−7.28 (m, 4H), 4.36 (t, J = 7.5 Hz, 2H), 3.92 (s, 3H), 1.97−1.82 (m, 2H), 1.51−1.37 (m, 2H), 0.98 (t, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 155.9, 153.6, 145.4, 131.6, 131.1, 124.8, 123.5, 123.5, 121.5, 109.5, 109.3, 44.8, 32.0, 30.9, 20.1, 13.9; HRMS (+ESI-TOF) m/z for $C_{18}H_{21}N_6O_2$ $[M + H]^+$ calcd 353.1721, found 353.1731.

(*E*)-1-Butyl-3-methyl-2-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-2,3-dihydro-1*H*-imidazole (6h). Red crystals (0.16 g, 83%), mp 144−145 °C; ^{1}H NMR ($CDCl_3$) δ 8.20 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 9.0 Hz, 2H), 6.67−6.56 (m, 2H), 4.12 (t, J = 7.5 Hz, 2H), 3.78 (s, 3H), 1.84−1.77 (m, 2H), 1.46−1.31 (m, 2H), 0.95 (t, J = 6.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 157.7, 125.6, 124.8, 120.6, 119.3, 117.6, 116.2, 47.8, 36.3, 31.7, 19.8, 13.7; HRMS (+ESI-TOF) m/z for $C_{14}H_{19}N_6O_2$ $[M + H]^+$ calcd 303.1564, found 303.1573.

General Method for the Preparation of Push-Pull Triazene Salts 9a−d. Potassium *tert*-butoxide (0.063 g, 0.63 mmol) was added to a mixture of 1-azido-4-nitrobenzene **5** (0.10 g, 0.63 mmol) and the corresponding 1,2,4-triazolium *N*-imide **7a−d** (0.63 mmol) in dry THF (10 mL) at −78 °C. After 10 min, the reaction mixture was warmed to room temperature and stirred. After 24 h the precipitate was collected by filtration, washed with THF (5 mL), and dried to obtain pure triazene salt **9a−d**.

Potassium ((*E*)-1-Benzyl-5-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-1*H*-1,2,4-triazol-4(5*H*)-yl)(tosyl)amide (9a). Yellow-orange crystals (0.29 g, 86%), mp 216−217 °C; ^{1}H NMR (DMSO-d_6) δ 8.11 (s, 1H), 8.03 (d, J = 8.7 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 7.36−7.29 (m, 3H), 7.23 (d, J = 8.7 Hz, 2H), 7.10−6.97 (m, 4H), 5.35 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 157.7, 153.7, 143.2, 142.5, 141.5, 139.6, 136.5, 128.4, 128.3, 127.4, 126.7, 126.3, 124.4, 120.5, 53.3, 20.7; HRMS (-ESI-TOF) m/z for $C_{22}H_{19}N_8O_4S$ $[M - K]^-$ calcd 491.1255, found 491.1267.

Potassium ((*E*)-1-Butyl-5-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-1*H*-1,2,4-triazol-4(5*H*)-yl)(tosyl)amide (9b). Orange crystals (0.28 g, 94%), mp 215−216 °C; ^{1}H NMR (DMSO-d_6) δ 8.16 (d, J = 9.0 Hz, 2H), 8.00 (s, 1H), 7.50−7.39 (m, 4H), 7.01 (d, J = 8.1 Hz, 2H), 4.08 (t, J = 7.1 Hz, 2H), 2.17 (s, 3H), 1.67−1.60 (m, 2H), 1.28−1.14 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 158.4, 153.0, 143.0, 142.1, 142.0, 139.2, 128.2, 126.5, 124.5, 120.3, 49.6, 30.4, 20.7, 18.8, 13.4; HRMS (-ESI-TOF) m/z for $C_{19}H_{21}N_8O_4S$ $[M - K]^-$ calcd 457.1412, found 457.1430.

Potassium ((*E*)-1-Methyl-5-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-1*H*-1,2,4-triazol-4(5*H*)-yl)(tosyl)amide (9c). Yellow-orange crystals (0.23 g, 79%), mp 202−203 °C; ^{1}H NMR (DMSO-d_6) δ 8.15 (d, J = 9.0 Hz, 2H), 7.94 (s, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 9.0 Hz, 2H), 7.05 (d, J = 7.8 Hz, 2H), 3.76 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 158.3, 153.6, 143.1, 142.4, 141.8, 139.3, 128.3, 126.6, 124.7, 120.5, 39.0, 20.8; HRMS (-ESI-TOF) m/z for $C_{16}H_{15}N_8O_4S$ $[M - K]^-$ calcd 415.0942, found 415.0954.

Potassium ((*E*)-1-Butyl-5-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-1*H*-1,2,4-triazol-4(5*H*)-yl)((4-nitrophenyl)sulfonyl)amide (9d). Orange crystals (0.32 g, 95%), mp 245−246 °C; ^{1}H NMR (DMSO-d_6) δ 8.18 (s, 1H), 8.12 (d, J = 9.3 Hz, 2H), 8.00 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 9.3 Hz, 2H), 4.05 (t, J = 7.1 Hz, 2H), 1.70−1.58 (m, 2H), 1.31−1.12 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 158.0, 153.0, 151.2, 147.5, 143.2, 142.5, 127.8, 124.6, 123.1, 120.2, 49.7, 30.5, 19.0, 13.5; HRMS (-ESI-TOF) m/z for $C_{18}H_{18}N_9O_6S$ $[M - K]^-$ calcd 488.1106, found 488.1125.

(*E*)-3-(1,3-Dibenzyl-1*H*-benzo[*d*]imidazol-2(3*H*)-ylidene)-1-methyl-1-(4-nitrophenyl)triaz-1-en-1-ium Iodide (10). Methyl iodide (0.15g, 1.1 mmol) was added to a solution of **6f** (0.10 g, 0.22 mmol) in CH_3CN (3 mL) and stirred under reflux. After 5 h, the reaction mixture was concentrated under reduced pressure to afford **10** as red crystals (0.13g, >99%), mp 223 °C, dec; ^{1}H NMR (DMSO-d_6) δ 8.14 (d, J = 9.3 Hz, 1H), 8.13 (d, J = 9.3 Hz, 1H), 8.03−7.94 (m, 2H), 7.68−7.59 (m, 2H), 7.48−7.30 (m, 12H), 5.92 (s, 4H), 3.99 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 148.8, 146.7, 145.5, 134.8, 130.5, 128.8, 127.9, 126.8, 126.5, 124.6, 120.0, 112.9, 48.5, 36.5.

***N*-((*E*)-1-Benzyl-5-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-1*H*-1,2,4-triazol-4(5*H*)-yl)-4-methylbenzenesulfonamide (11a).** HCl (1 N) was added dropwise to the solution of **9a** (0.10 g, 0.19 mmol) in MeOH (10 mL) until the formation of a yellow precipitate stopped. The resulting precipitate was collected by filtration, washed with water (10 mL), and dried to obtain pure **11a** as yellow crystals (0.079 g, 85%), mp 173 °C, dec; ^{1}H NMR (DMSO-d_6) δ 8.11 (s, 1H), 8.03 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 7.8 Hz, 2H), 7.37−7.28 (m, 3H), 7.23 (d, J = 7.8 Hz, 2H), 7.07−6.99 (m, 4H), 5.35 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 157.9, 153.9, 143.4, 142.7, 141.7, 139.7, 136.7, 128.6, 128.5, 127.5, 126.8, 126.5, 124.5, 120.7, 53.5, 20.9. Anal. Calcd For $C_{22}H_{20}N_8O_4S$: C, 53.65; H, 4.09; N, 22.75. Found: C, 53.36; H, 3.80; N, 22.64.

General Method for the Preparation of 11b,c. A mixture of **9a** (0.1 g, 0.19 mmol) and alkyl halide (0.19 mmol, 1.9 mmol in the case of methyl iodide) in acetonitrile (3 mL) was stirred under reflux. After 5 h, the precipitate was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was recrystallized from MeOH to obtain pure **11b,c**.

***N*-((*E*)-1-Benzyl-5-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-1*H*-1,2,4-triazol-4(5*H*)-yl)-*N*,4-dimethylbenzenesulfonamide (11b).** Orange crystals (0.088 g, 92%), mp 174−175 °C; ^{1}H NMR (DMSO-d_6) δ 8.82 (s, 1H), 8.11 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 7.5 Hz, 2H), 7.45−7.33 (m, 3H), 7.28 (t, J = 7.7 Hz, 4H), 7.19 (d, J = 8.0 Hz, 2H), 5.40 (s, 2H), 3.47 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 155.7, 152.4, 145.1, 144.9, 140.4, 135.7, 132.4, 129.9, 128.5, 128.1, 127.6, 126.5, 124.4, 121.4, 53.5, 38.0, 21.0; HRMS (+ESI-TOF) m/z for $C_{23}H_{23}N_8O_4S$ $[M + H]^+$ calcd 507.1557, found 507.1553.

***N*-Benzyl-*N*-((*E*)-1-benzyl-5-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-1*H*-1,2,4-triazol-4(5*H*)-yl)-4-methylbenzenesulfonamide (11c).** Red crystals (0.097 g, 88%), mp 172−173 °C; ^{1}H NMR (DMSO-d_6) δ 8.64 (s, 1H), 8.14 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 7.3 Hz, 2H), 7.37−7.26 (m, 12H), 6.91 (d, J = 7.6 Hz, 2H), 5.41 (d, J = 16.8 Hz, 1H), 5.32 (d, J = 16.2 Hz, 1H), 5.04 (d, J = 13.8 Hz, 1H), 5.00 (d, J = 13.8 Hz, 1H), 2.26 (s, 3H).; ^{13}C NMR (DMSO-d_6) δ 155.6, 152.4, 145.3, 145.1, 140.8, 135.6, 132.9, 130.0, 129.0, 128.6, 128.5, 128.3, 127.5, 126.0, 124.4, 121.5, 53.8, 53.3, 21.0; HRMS (+APCI-TOF) m/z for $C_{29}H_{27}N_8O_4S$ $[M + H]^+$ calcd 583.1870, found 583.1861.

General Method for the Preparation of 12a,b. A mixture of **7a** (0.5 g, 1.5 mmol) and alkyl halide (1.5 mmol, 15.0 mmol in the case of methyl iodide) in acetonitrile (15 mL) was stirred under reflux. After 5 h, the reaction mixture was concentrated under reduced pressure to afford pure **12a,b**.

1-Benzyl-4-(*N*,4-dimethylphenylsulfonamido)-1*H*-1,2,4-triazol-4-ium Iodide (12a). White crystals (0.71 g, >99%), mp 168−170 °C; ^{1}H NMR (DMSO-d_6) δ 10.89 (s, 1H), 9.61 (s, 1H), 7.69 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 7.51−7.41 (m, 5H), 5.66 (s, 2H), 3.43 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 147.2, 143.7, 143.3, 132.2, 130.9, 129.2, 129.0, 128.9, 127.0, 55.9, 39.2, 21.4. Anal. Calcd For $C_{17}H_{19}IN_4O_2S$: C, 43.41; H, 4.07; N, 11.91. Found: C, 43.39; H, 3.78; N, 11.93.

1-Benzyl-4-(*N*-benzyl-4-methylphenylsulfonamido)-1*H*-1,2,4-triazol-4-ium Bromide (12b). White crystals (0.76 g, >99%), mp 137−139 °C; ^{1}H NMR (DMSO-d_6) δ 11.21 (s, 1H), 9.69 (s, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.45−7.37 (m, 3H), 7.36−7.27 (m, 5H), 7.25−7.13 (m, 2H), 5.64 (s, 2H), 4.98 (s, 2H), 2.50 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 147.2, 144.9, 143.8, 132.3, 131.6, 131.0, 129.1, 128.9, 128.9, 128.6, 128.4, 55.9, 55.2, 21.4. Anal. Calcd For $C_{23}H_{23}BrN_4O_2S$: C, 55.31; H, 4.64; N, 11.22. Found: C, 55.40; H, 4.44; N, 11.28.

dx.doi.org/10.1021/jo302697q | J. Org. Chem. XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C spectra for **2a,b**, **3a,b**, **6a−h**, **9a−d**, **10**, **11a−c**, and **12a,b**. X-ray CIF files for **6e**, **6f**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the U.S. Navy, Kenan Foundation (University of Florida), and the King Abdulaziz University (Saudi Arabia) for their financial support. The authors also thank Dr. Mirna El Khatib for her help in TGA analysis.

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