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Synthesis of 1,2,4-Triazol-5-ylidenes and Their Interaction with Acetonitrile and Chalcogens

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Abstract: Two new, more convenient methods for the synthesis of 1,2,4-triazol-5-ylidenes are described. Four new 1,2,4-triazol-5-ylidenes have been prepared using these methods: 1-(1-adamantyl)-3,4-diphenyl-1,2,4-triazol-5-ylidene (**2a**), 1-(1-adamantyl)-3-phenyl-4-(*p*-bromophenyl)-1,2,4-triazol-5-ylidene (**2b**), 1-(1-adamantyl)-3-phenyl-4-(α-naphthyl)-1,2,4-triazol-5-ylidene (**2c**), and 1-(1-adamantyl)-3,4-di(*p*-bromophenyl)-1,2,4-triazol-5-ylidene (**2d**). The X-ray crystal structures of **2d** and the precursor salt 1-(1-adamantyl)-3,4-di(*p*-bromophenyl)-1,2,4-triazolium bromide (**1e**) are described. Compound **2a** reacts with CH_3CN via C−H insertion to form 1-(1-adamantyl)-3,4-diphenyl-5-cyanomethyl-5*H*-1,2,4-triazoline (**3**), and **2a** and **2d** react with elemental sulfur and elemental selenium, respectively, to form the corresponding thione (**4**) and selenone (**5**).

Following the postulation of nucleophilic heteroaromatic carbenes by Breslow[1] and pioneering experimental work on imidazol-2-ylidenes by Wanzlick and co-workers,[2] over two decades were to elapse before Arduengo et al.[3] reported the isolation and structural characterization of a stable nucleophilic carbene. The synthetic route employed by Arduengo et al. involved the deprotonation of an imidazolium chloride with sodium or potassium hydride in the presence of either KO-*t*-Bu or the DMSO anion.[4a−c] Subsequently, other bases such as *n*-BuLi,[5] $KN(SiMe_3)_2$,[6] and LDA[7] have been used, and Herrmann et al.[8] demonstrated that a liquid NH_3/THF solvent system is very effective for the NaH deprotonation of imidazolium salts at relative low temperatures. A completely new synthetic route to stable nucleophilic carbenes was developed by Kuhn et al.,[9] namely the reduction of imidazole-2(3)-thiones with potassium in refluxing THF. The range of stable nucleophilic carbenes has also expanded significantly, not only in terms of the elaboration of substituents and the development of multidentate systems but also from the standpoint of new structure types.[10] For example, Alder et al.[7] have shown that it is possible to isolate acyclic nucleophilic carbenes, and Enders et al.[11] reported the preparation of 1,2,4-triazol-5-ylidenes by deprotonation of the corresponding triazolium salts with NaOMe in MeOH, followed by the elimination of MeOH under reduced pressure (0.1 mbar) at 80 °C. In the present contribution, we describe (i) two new, more convenient approaches to the synthesis of 1,2,4-triazol-5-ylidenes, (ii) the X-ray crystal structure of a representative 1,2,4-triazol-5-ylidene along with that of the precursor triazolium salt, (iii) a C−H insertion reactions of a 1,2,4-triazol-5-ylidene and the related triazolium salt, and (iv) the reactions of 1,2,4-triazol-5-ylidenes with sulfur and selenium.

The triazolium perchlorates **1a**−**d** were prepared by a two-stage procedure. First, the triazolium bromide salts were prepared by heating the 3,4-diaryl-1,2,4-triazols with 1-bromoadamantane in acetic acid. In the second stage, anion exchange to form **1a**−**d** was effected by treatment of the bromide salts with aqueous $NaClO_4$. In general, the intermediate triazolium bromides were converted directly into the corresponding perchlorate salts. However, in one case, the crystals of the triazolium bromide (**1e**) were prepared and found to be suitable for X-ray crystallographic study (see later). Two procedures, A and B, were employed for the preparation of the 1,2,4-triazol-5-ylidenes **2a**−**d**. In method A, a suspension of the triazolium perchlorate (**1a**−**d**) was treated with an equimolar quantity of potassium *tert*-butoxide in benzene. The replacement of perchlorate by *tert*-butoxide anions in the first stage of this procedure occurs quantitatively due to very low solubility of $KClO_4$ in aromatic solvents, thus minimizing the potential danger of explosion. In method B, a solution of the triazolium perchlorate in acetonitrile was allowed to react with a 55% dispersion of sodium hydride in mineral oil, the progress of the

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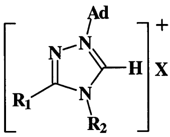
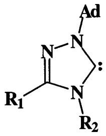
reaction being monitored by the volume of hydrogen evolved. Compounds **2a** and **2c** were prepared in isolated yields of 64 and 51%, respectively, by method A, while the isolated yields of **2a**, **2b**, and **2d** using method B were 40, 95, and 73%, respectively. Generally speaking, the yields realized by both methods A and B[12] are comparable to that reported by Enders et al.[11] for the preparation of a triphenyl-substituted 1,2,4-triazol-5-ylidene (63%). However, methods A and B have the twin advantages of being one-step procedures that also involve milder reaction conditions. Moreover, in contrast to the methods employed for the synthesis of imidazol-2-ylidenes, methods A and B avoid the evaporation of solvent and the extraction of the product with aromatic solvents.



1a-e



2a-d

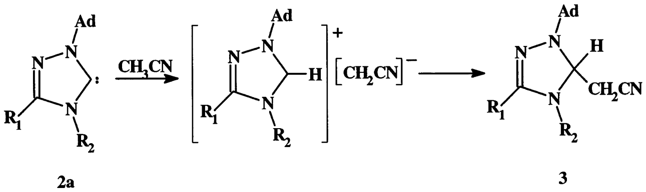
1a $R_1 = R_2 = C_6H_5$; $X = ClO_4^-$
1b $R_1 = C_6H_5$; $R_2 = p\text{-}BrC_6H_4$; $X = ClO_4^-$
1c $R_1 = C_6H_5$; $R_2 = \alpha\text{-}C_{10}H_7$; $X = ClO_4^-$
1d $R_1 = R_2 = p\text{-}BrC_6H_4$; $X = ClO_4^-$
1e $R_1 = R_2 = p\text{-}BrC_6H_4$; $X = Br^-$
Ad = 1-adamantyl

2a $R_1 = R_2 = C_6H_5$
2b $R_1 = C_6H_5$; $R_2 = p\text{-}BrC_6H_4$
2c $R_1 = C_6H_5$; $R_2 = \alpha\text{-}C_{10}H_7$
2d $R_1 = R_2 = p\text{-}BrC_6H_4$
Ad = 1-adamantyl

New compounds **1a**−**e** and **2a**−**d** are white, crystalline solids that were characterized on the basis of elemental analysis, ^{1}H NMR, ^{13}C NMR, and infrared spectroscopy (see the Experimental Section). The ^{1}H NMR spectra of **1a**−**d** are consistent with the presence of the aryl and adamantyl substituents and the C(5)−H proton peak, which is present in **1a**−**d** but is absent in **2a**−**d**. In general, the proton signals for **2a**−**d** are upfield in comparison with those for **1a**−**d**. In accord with the proposed structures for **2a**−**d**, the ^{13}C NMR spectra exhibit carbene carbon (C 5) resonances in the range δ 210.1 to 212.7 and triazole carbon (C 3) resonances in the range δ 149.8−152.6.

Compounds **1e** and **2d** were also characterized by X-ray crystallography.[13] ORTEP drawings and metrical parameters are available as Supporting Information. The triazolium rings of **1e** and **2d** are both planar as reflected by the sums of ring bond angles of 539.1(3)° and 539.9(3)°, respectively. In each case, the two aryl substituents are twisted out of the plane of the N_3C_2 ring. The C(3)−N(2) bond distances in **1e** (1.315(4) Å) and **2d** (1.300(5) Å) correspond essentially to a bond order of two. The C(3)−N(4) bond distances are virtually identical in the two structures, and the C(3)−N(2) bond distances differ only slightly. The remaining three intra-ring bond distances increase when the triazolium cation undergoes deprotonation. In particular, the average C−N bond distance at the carbenic carbon is ~0.04 Å less in the triazolium cation than that in the resulting carbene. Such a change is expected from the standpoint of the development of a positive charge at C(5), the increased s-character as the angle at this center increases from 100.3(3)° to 107.6(3)°, and possibly on account of increased conjugation between nitrogen lone pairs and the vacant C(2p) orbital. The observed N−C−N bond angle of ~100° is typical of that found for other singlet carbenes.[10]

SCHEME 1



The reactivities of representative 1,2,4-triazoline-5-ylidenes with acetonitrile, elemental sulfur and elemental selenium have also been investigated. Interestingly, the present work represents the first report of the reaction of a heteroaromatic carbene 1,2,4-triazoline-5-ylidene with CH_3CN. Previously, Enders et al.[11] reported that attempts to isolate insertion products of their phenyl-substituted 1,2,4-triazol-5-ylidene into a C−H bond were unsuccessful and expressed the view that possibly such reactions would require temperatures that exceeded the stability of the carbene (>150 °C). On the other hand, Wanzlick et al.[15] reported C−H insertion reactions of 1,3-diphenyldihydroimidazol-2-ylidene with. e.g., cyclopentanone and nitromethane. However, the products were not identified definitively, and moreover, it is not clear whether the observed reactivities emanated from the monomer or the corresponding dimer. More recently, Arduengo et al.[16] have reported that 1,3-dimesityldihydroimidazol-2-ylidene will undergo C−H insertion reactions with inter alia CH_3CN. However, the analogous unsaturated (heteroaromatic) carbene 1,3-diadamantylimidazol-2-ylidene failed to react with CH_3CN but instead yielded a CH_3CN solvate. Herrmann et al.[7e] have also noted the failure of imidazol-2-ylidenes to react with CH_3CN. In a preliminary report, we addressed the possibility that stable heteroaromatic carbenes would undergo reaction with acetonitrile.[17] In the present work, we have found that a benzene solution of 1,2,4-triazol-5-ylidene **2a** reacts with CH_3CN in a sealed tube at 100 °C to afford 1-(1-adamantyl)-3,4-diphenyl-5-cyanomethyl-5*H*-1,2,4-triazoline, **3** (Scheme 1). According to the ^{1}H NMR data, the yield of compound **3** in the reaction

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(12) We note, however, that it is not possible to prepare **2c** by method B.

(13) Crystal Data. **1e**: $C_{24}H_{24}Br_3N_3$, $M = 594.19$, monoclinic, space group $C2/c$, $a = 28.819(5)$ Å, $b = 10.496(5)$ Å, $c = 19.591(5)$ Å, $\beta = 119.054(5)°$, $V = 5180(3)$ Å^3, $D_{\text{calcd}} = 1.905$ g cm^{-3}, $Z = 4$, λ (Mo Kα) = 0.71073 Å, μ (Mo Kα) = 5.859 mm^{-1}. **2d**: $C_{24}H_{23}Br_2N_3$, $M = 513.27$, triclinic, space group P-1, $a = 7.489(5)$ Å, $b = 12.008(5)$ Å, $c = 12.485(5)$ Å, $\alpha = 80.890(5)°$, $\beta = 75.043(5)°$, $\gamma = 79.011(5)°$, $D_{\text{calcd}} = 1.612$ g cm^{-3}, $Z = 2$, λ (Mo Kα) = 0.71073 Å, μ (Mo−Kα) = 3.848 mm^{-1}. Totals of 6955 and 5309 independent reflections were collected for **1e** and **2d**, respectively at 153(2) K on a Nonius Kappa diffractometer. Both structures were solved by direct methods and refined by full-matrix, least-squares on F^2 using the Siemens SHELX PLUS 5.0 (PC) software package[14] to $R_1 = 0.0509$, w$R_2 = 0.1089$ for **1e** and $R_1 = 0.0499$, w$R_2 = 0.1107$ for **2d**.

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mixture is approximately 50%; however, the isolated yield is 30%. Compound **3** can also be prepared directly from the triazolium salt **1a** by heating the crude reaction mixture resulting from the preparation of **2a** at 60 °C for 1 h. The overall yield of **3** in this case was 18%. White solid **3** was characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, and IR spectroscopy (see the Experimental Section). Noteworthy are the C−H and CH_2CN resonances at δ 5.22 and 2.70 with a $^3J_{HH}$ of 5.1 Hz in the ^{1}H NMR spectrum and signals corresponding to NCN (δ 78.5), C≡N (δ 117.9), and CH_2 carbon atoms (δ 30.1) in the ^{13}C NMR spectrum. As postulated by Moss et al.,[18] carbenes can undergo X−H insertion reactions by electrophilic or nucleophilic pathways (or possibly via a route intermediate between these extremes). Since 1,2,4-triazol-5-ylidene **2a** is strongly nucleophilic, it is expected to undergo reaction with CH_3CN via the nucleophilic or concerted pathway shown in Scheme 1.

As a further indication of the strongly nucleophilic character of the 1,2,4-triazol-5-ylidene carbenes, **2a** was treated with elemental sulfur in benzene and **2d** was allowed to react with elemental selenium in toluene solution. The resulting thione (**4**) and selenone (**5**) were formed in high yields (84−94%) within minutes at room temperature. Similar reactions have been reported by Enders et al.[11b] for a triphenyl-substituted 1,2,4-triazol-5-ylidene and are well-known for imidazol-2-ylidenes.[10]

Experimental Section

General Methods. All experiments with the triazol-5-ylidenes were carried out under an argon atmosphere. All solvents were dried by standard methods prior to use. ^{1}H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane (TMS, $\delta = 0.00$) as internal standard. IR spectra were measured as Nujol mulls and thin-layer chromatography was performed on silica gel with chloroform or a 10:1 mixture of chloroform and methanol as eluent, followed by development with iodine. Elemental analyses were carried out at the Litvinenko Institute of Physical Organic and Coal Chemistry.

CAUTION. Although we have not experienced any problems with the perchlorate salts described herein, the usual precautions should be taken when handling these compounds.

1-(1-Adamantyl)-3,4-diaryl-1,2,4-triazolium Perchlorates (1a−d). General Procedure. A mixture of the 3,4-diaryl-1,2,4-triazole (10 mmol) and 1-bromoadamantane (2.15 g, 10 mmol) in acetic acid (3 mL) was refluxed for 8−10 h, following which an additional portion of 1-bromoadamantane (0.47 g, 2 mmol) was added and heating was continued for 4−5 h. Subsequent filtration of the precipitate, followed by extraction of salt with hot water (90−95 °C), afforded the pure bromide salts. Each bromide salt was converted into the corresponding perchlorate salt by the treatment with excess sodium perchlorate (1.84 g, 15 mmol) in aqueous solution.

1-(1-Adamantyl)-3,4-diphenyl-1,2,4-triazolium perchlorate (1a): yield 96%, mp 223−224 °C (acetic acid); ^{1}H NMR (DMSO-d_6, 200 MHz) 1.78 (m, 6H), 2.31 (m, 9H, 1-Ad), 7.46 (m, 5H), 7.64 (m, 5H, Ar), 10.58 (s, 1H, CHN). Anal. Calcd for $C_{24}H_{26}ClN_3O_4$: C, 63.2; H, 5.7; Cl, 7.8; N, 9.2. Found: C, 63.1; H, 5.7; Cl, 7.9; N, 9.2.

1-(1-Adamantyl)-3-phenyl-4-(*p*-bromophenyl)-1,2,4-triazolium perchlorate (1b): yield 71%; mp 266−268 °C (acetic acid); ^{1}H NMR (DMSO-d_6, 200 MHz) 1.78 (m, 6H), 2.31 (m, 9H, 1-Ad), 7.49 (m, 5H), 7.59 (d, 2H), 7.87 (d, 2H, J = 8.0 Hz, Ar), 10.59 (s, 1H, CHN). Anal. Calcd for $C_{24}H_{25}BrClN_3O_4$: C, 53.9; H, 4.7; Br, 14.9; Cl, 6.6; N, 7.9. Found: C, 53.7; H, 4.8; Br, 14.8; Cl, 6.7; N, 8.1.

1-(1-Adamantyl)-3-phenyl-4-(α-naphthyl)-1,2,4-triazolium perchlorate (1c): yield 79%; mp 256−257 °C (acetic acid); ^{1}H NMR (DMSO-d_6, 200 MHz) 1.90 (m, 6H), 2.19 (m, 3H), 2.22 (m, 6H, 1-Ad), 7.40 (m, 5H), 7.87 (m, 4H), 8.05 (d, 1H), 8.08 (d, 1H), 8.17 (d, 1H, J = 8.2 Hz, Ar), 10.39 (s, 1H, CHN). Anal. Calcd for $C_{28}H_{28}ClN_3O_4$: C, 66.5; H, 5.6; Cl 7.0; N, 8.3. Found: C, 66.6; H, 5.7; Cl, 7.1; N, 8.1.

1-(1-Adamantyl)-3,4-di(*p*-bromophenyl)-1,2,4-triazolium perchlorate (1d): yield 79%; mp 270−273 °C (dimethylformamide); ^{1}H NMR (DMSO-d_6, 200 MHz) 1.78 (m, 6H), 2.29 (m, 9H, 1-Ad), 7.39 (m, 2H), 7.60 (d, 2H), 7.75 (d, 2H), 7.86 (d, 2H, J = 8.0 Hz, Ar), 10.60 (s, 1H, CHN). Anal. Calcd for $C_{24}H_{24}Br_2ClN_3O_4$: C, 47.0; H, 3.9; Br, 26.0; Cl, 5.8; N, 6.9. Found: C, 47.1; H, 3.9; Br, 26.1; Cl, 5.9; N, 6.7.

1-(1-Adamantyl)-3,4-di(*p*-bromophenyl)-1,2,4-triazolium bromide (1e): yield 81%; mp 242−243 °C (water). The ^{1}H NMR spectrum of **1e** is identical to that of **1d**. Anal. Calcd for $C_{24}H_{24}Br_3N_3$: C, 48.5; H, 4.1; Br, 40.3; N, 7.1. Found: C, 48.6; H, 4.2; Br, 40.2; N, 7.1.

1-(1-Adamantyl)-3,4-diaryl-1,2,4-triazol-5-ylidenes. Method A. Potassium *tert*-butoxide (0.56 g, 5 mmol) was added all at once to a suspension of the triazolium perchlorate (5 mmol) in benzene (15 mL) under an argon atmosphere. After the reaction mixture had been stirred for 0.5 h, the precipitate of $KClO_4$ was removed by filtration and the solvent was evaporated from the filtrate under reduced pressure. The resinous residue was triturated with 2−3 mL of hexane to afford the triazol-5-ylidenes that were recrystallized from toluene.

1-(1-Adamantyl-3,4-diaryl-1,2,4-triazol-5-ylidenes. Method B. A 55% dispersion of sodium hydride (0.05 g, 1.1 mmol in mineral oil) was added all at once to a solution of the triazolium perchlorate (1 mmol) in 2−5 mL of CH_3CN. The progress of the reaction was monitored by the volume of hydrogen evolved. At the end of the reaction, the resulting 1,2,4-triazol-5-ylidene was filtered off, washed with CH_3CN and hexane, and recrystallized from toluene or toluene/hexane mixtures.

1-(1-Adamantyl)-3,4-diphenyl-1,2,4-triazol-5-ylidene (2a): yields of 64% and 40% by methods A and B, respectively; mp 167−169 °C (hexane); ^{1}H NMR (C_6D_6, 200 MHz) 1.66 (m, 6H), 2.11 (m, 3H), 2.64 (m, 6H, 1-Ad), 6.95−7.38 (m, 10H, Ar); ^{13}C NMR (C_6D_6, 50.3 MHz) 30.0, 36.6, 43.9, 59.5 (1-Ad), 126.6, 127.3, 127.8, 128.3, 128.9, 129.3, 140.4 (Ar), 150.9 (C 3), 210.7 (C 5); IR (Nujol mull) 3020 w (C−H Ar), 1590 m, 1540 m (C═C Ar). Anal. Calcd for $C_{24}H_{25}N_3$: C, 81.1; H, 7.1; N, 11.8. Found: C, 81.2; H, 7.4; N, 12.0.

1-(1-Adamantyl)-3-phenyl-4-(*p*-bromophenyl)-1,2,4-triazol-5-ylidene (2b): yield of 95% by method B; mp 174−175 °C dec (10:1 hexane/toluene); ^{1}H NMR (C_6D_6, 200 MHz) 1.65 (m, 6H), 2.11 (m, 3H), 2.66 (m, 6H, 1-Ad), 6.93 (m, 5H), 7.33 (m, 4H, Ar); ^{13}C NMR (C_6D_6, 50.3 MHz) 30.5, 36.9, 44.4, 60.0 (1-Ad), 127.8, 128.3, 128.4, 128.8, 129.5, 129.9, 132.4, 139.6 (Ar), 150.3 (C 3), 210.6 (C 5); IR (Nujol mull) 3020 w (C−H Ar), 1580 m, 1510 m (C═C Ar). Anal. Calcd for $C_{24}H_{24}BrN_3$: C, 66.4; H, 5.6; Br, 18.4; N, 9.7. Found: C, 66.8; H, 5.5; Br, 18.5; N, 9.8.

1-(1-Adamantyl)-3-phenyl-4-(α-naphthyl)-1,2,4,-triazol-5-ylidene (2c): yield of 51% by method A; mp 82−83 °C (10:1 hexane/toluene); ^{1}H NMR (C_6D_6, 200 MHz) 1.69 (m, 6H), 2.14 (m, 3H), 2.72 (m, 6H, 1-Ad), 6.77 (m, 2H), 6.99 (m, 1H), 7.15 (m, 5H), 7.47 (m, 3H), 7.90 (m, 1H, Ar); ^{13}C NMR (C_6D_6, 50.3 MHz) 30.0, 36.5, 43.8, 60.3 (1-Ad), 123.6, 125.5 126.3, 126.8, 127.1, 127.4, 128.0, 129.3, 129.7, 130.6, 134.6, 136.0 (Ar), 152.6 (C 3), 212.7 (C 5); IR (Nujol mull) 3060 w (C−H Ar), 1600 m, 1540 m, 1530 m (C═C Ar). Anal. Calcd for $C_{28}H_{27}N_3$: C, 82.9; H, 6.7; N, 10.4. Found: C, 82.8; H, 6.9; N, 10.5.

1-(1-Adamantyl)-3,4-di(*p*-bromophenyl)-1,2,4-triazol-5-ylidene (2d): yield of 73% by method B; mp 155 °C dec (10:1 hexane/toluene); ^{1}H NMR (C_6D_6, 200 MHz) 1.65 (m, 6H), 2.11 (m, 3H), 2.66 (m, 6H, 1-Ad), 6.85 (m, 1H), 6.90 (m, 1H), 6.99 (m, 1H), 7.00 (m, 4H), 7.04 (m, 1H, Ar); ^{13}C NMR (C_6D_6, 50.3 MHz) 30.1, 36.6, 44.0, 59.8 (1-Ad), 121.5, 124.3, 126.5, 129.3, 130.7, 131.7, 131.8, 138.9 (Ar), 149.8 (C 3); 210.1 (C 5); IR (Nujol mull)

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3020 w (C−H Ar), 1590 m (C═C Ar). Anal. Calcd for $C_{24}H_{23}Br_2N_3$: C, 56.2; H, 4.5; Br, 31.1; N, 8.2. Found: C 56.4; H 4.7; Br 31.3; N 8.2.

1-(1-Adamantyl)-3,4-diphenyl-5-cyanomethyl-5*H*-1,2,4-triazoline (3). Acetonitrile (2 mL) was added to a solution of 1,2,4-triazol-5-ylidene **2a** (0,7 g, 1,97 mmol) in 1 mL of benzene. The reaction mixture was sealed in a glass ampule and heated at 100 °C for 10 h. The solvent was removed under reduced pressure, and the resulting resinous material was dissolved in 5 mL of benzene then filtered through a thin layer of silica gel (40/100 mμ). The resinous residue obtained by removing the solvent in vacuo was triturated with 5 mL of hexane to afford a 30% yield of **3** (0.23 g).

Compound **3** can also be prepared by treating **1a** (0.5 g, 1.1 mmol) with a 55% dispersion of sodium hydride (0.5 g, 1.2 mmol) in 2 mL of CH_3CN at 20 °C, followed by heating the reaction mixture to 60 °C for 1 h. After being allowed to stand overnight, the reaction mixture was filtered through a thin layer of neutral silica gel and worked up as described above: yield 18% (0.08 g); mp 133−134 °C (acetonitrile); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.63 (m, 6H), 1.81 (m, 3H), 2.09 (m, 6H, 1-Ad), 2.70 (dd, $J = 5.1$ Hz, CH_2CN), 5.22 (t, 1H, $J = 5.1$ Hz, CHN), 7.10 (m, 4H), 7.25 (m, 4H), 7.62 (m, 2H, Ar); ^{13}C NMR (CD_3CN, 200 MHz) 30.1 (CH_2C), 30.4, 37.2, 40.4, 57.8 (1-Ad), 117.9 (C≡N); 125.7, 126.5, 128.7, 129.4, 129.9, 130.2, 130.3, 144.9 (Ar), 151.0 (C 3); IR (Nujol mull) 3025 w (C−H Ar), 2235 m (C≡N), 1585 m, 1560 m, 1485 (C═C Ar). Anal. Calcd for $C_{26}H_{28}N_4$: C, 78.8; H, 7.1; N, 14.1. Found: C, 78.9; H, 7.0; N, 14.4.

1-(1-Adamantyl)-3,4-diphenyl-1,2,4-triazol-5-thione (4). A solution of carbene **2a** (0.39 g, 1.1 mmol) in benzene (1 mL) was added dropwise to a stirred solution of elemental sulfur (0.049 g, 1.56 mmol) in benzene (5 mL). The resulting reaction mixture was evaporated to dryness in vacuo to afford thione **4** in 94% yield: mp 205−207 °C (2-propanol); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.78 (m, 6H), 2.27 (m, 3H), 2.75 (m, 6H, 1-Ad), 7.35 (m, 5H), 7.50 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$, 200 MHz) 29.8, 36.0, 39.3, 63.6 (1-Ad), 127.1, 127.6, 128.1, 128.4, 128.7, 129.1, 129.4, 130.0 (Ar), 141.1 (C 3), 166.5 (C 5); IR (Nujol mull) 3055 w, 3030 w (C−H Ar), 1685 m (N−C═S), 1595 m, 1500 sh (C═C Ar). Anal. Calcd for $C_{24}H_{25}N_3S$: C, 74.4; H, 6.5; N, 10.8; S, 8.3. Found: C, 74.7; H, 6.7; N, 10.8; S, 8.1.

1-(1-Adamantyl)-3,4-di(*p*-bromophenyl)-1,2,4-triazol-5-selenone (5). Amorphous selenium (0.04 g, 0.05 mmol) was added to a stirred solution of carbene **2d** (0.055 g, 0.1 mmol) in toluene (2 mL) at room temperature. After being stirred overnight, the reaction mixture was filtered, and the filtrate was evaporated to produce 0.05 g of a microcrystalline powder that was recrystallized from a mixture of toluene−hexane (1:1) to afford **5**: 84% yield; mp 238−240 °C (2-propanol); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.79 (m, 6H) 2.28 (m, 3H), 2.79 (m, 6H, 1-Ad), 7.15−7.21 (m, 4H), 7.46 (m, 2H), 7.64 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$, 200 MHz) 30.0, 36.0, 39.8, 65.3 (1-Ad), 124.3, 125.3, 128.6, 129.7, 130.6, 132.1, 133.0, 134.4 (Ar), 148.8 (C 3), 160.0 (C 5); IR (Nujol mull) 3040 w (C−H Ar), 1705 m (N−C═Se), 1600 w, 1485 sh (C═C Ar). Anal. Calcd for $C_{24}H_{23}Br_2N_3Se$: C, 48.7; H, 3.9; Br, 27.0; N, 7.1; Se, 13.3. Found: C, 48.6; H, 3.9; Br, 26.8; N, 7.1; Se, 13.5.

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Supporting Information Available: ORTEP drawings and tables of crystallographic data for **1e** and **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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