molbank

MDPI

Short Note

1-[2,6-Dimethyl-4-(pent-4-yn-1-yloxy)phenyl]-4-phenyl-1,2,4-triazolidine-3,5-dione

Gary W. Breton

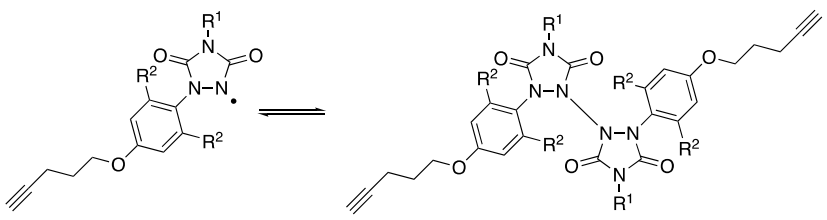
Department of Chemistry and Biochemistry, Berry College, Mount Berry, GA 30149, USA; gbreton@berry.edu; Tel.: +1-706-290-2661

Abstract: Urazolyl radicals are a class of persistent nitrogen-centered radicals. In a previous work, we successfully formed self-assembled monolayers of substituted urazolyl radicals on gold surfaces. To extend the scope of these investigations, we sought to form a self-assembled monolayer using a urazolyl radical species that we knew existed predominantly in the dimerized *N*-*N* form instead of existing predominantly as free *N*-centered radical species, as had previously been investigated. We successfully synthesized the precursor urazole compound needed to generate the desired urazolyl radical, and completely characterized its structure. Most importantly, it was determined that the alkyne functional group that is needed to adhere to the gold surface remained intact. Unfortunately, however, we only obtained ambiguous results from attempts at forming self-assembled monolayers of this species on gold.

Keywords: urazole; radical; urazolyl radical; SAM

1. Introduction

N-aryl substituted urazolyl radicals are a class of persistent nitrogen-centered radicals [1–4]. We recently reported that self-assembled monolayers (SAMS) of appropriately substituted urazolyl radicals (**1a**, Scheme 1) could be formed on gold surfaces [1]. The radicals were anchored to the surface via a terminal alkyne group. The resulting SAMs exhibited interesting EPR and electrochemical (cyclic voltammetry [CV]) properties as a result of the unpaired electron centered on the urazole nitrogen atom [1]. The results observed on the surface-anchored species mimicked the same properties of radical **1a** when it was unbound in the solution, thus suggesting that the urazolyl radical character remained active even when the molecule was tethered to the surface. Solutions of radical **1a** are deep purple in color, despite the fact that they exist in equilibrium with the corresponding colorless *N*-*N* dimer (**2a**, Scheme 1); this suggests that appreciable concentrations of the free radical remain available [2,3]. Phenyl-substituted urazole radicals that bear the *bis*-ortho substitution on the aromatic ring (e.g., **1b**, Scheme 1), on the other hand, are known to favor the *N*-*N* dimer form (**2b**, Scheme 1), even in the solution [3,4]; therefore, we synthesized compound **3** (see Scheme 2), the precursor to urazolyl radical **1b**, to determine whether **1b** would exhibit radical behavior after it adheres to the gold surface.



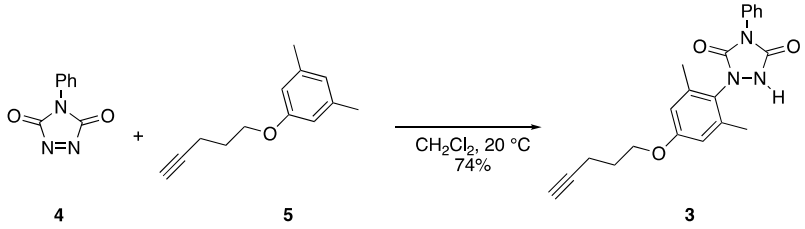
Scheme 1. Urazolyl radicals **1a** and **1b** in equilibrium, in a solution with N-N dimers **2a** and **2b.**

check for updates

Citation: Breton, G.W. 1-[2,6-Dimethyl-4-(pent-4-yn-1-yloxy)phenyl]-4-phenyl-1,2,4-triazolidine-3,5-dione. *Molbank* **2023**, *2023*, M1578. https://doi.org/10.3390/M1578

Academic Editor: Hideto Miyabe

Received: 13 January 2023
Revised: 31 January 2023
Accepted: 1 February 2023
Published: 4 February 2023



Scheme 2. Reaction of ether (**5**) with PhTAD (**4**) to yield urazole (**3**).

2. Results

Urazolyl radicals are generated via the oxidation of the corresponding NH urazole species [2–4]. The synthesis of urazole compound **3**, the precursor to **1b**, was accomplished, the process of which is shown in Scheme 2. The thermal reaction of *N*-phenyl-1,2,4-triazoline-3,5-dione (**4**, PhTAD), with the known phenyl ether **5** [5], in CH_2Cl_2, at room temperature, produced a 74% yield of urazole **3**, in the form of a crystalline white solid. The structural assignment was accomplished via ^{1}H and ^{13}C NMR spectroscopy (including 2D HETCOR), IR analysis, and high-resolution mass spectrometry (HRMS). As triazoline-dione compounds such as PhTAD are known to react with alkynyl compounds in certain circumstances [6], it was important to ensure that the alkyne function remained unaltered during the reaction. The ^{1}H NMR spectrum clearly showed the alkynyl CH as a triplet, with a small coupling constant of only 2.5 Hz, and with a signal integration of only one proton. The ^{13}C NMR displayed the two alkynyl carbons at 83.4 and 69.2 ppm, which were good matches for the same two carbons in compound **5** (at 83.6 and 68.8 ppm) [5]. IR analysis clearly showed the presence of the NH of the urazole ring at 3248 cm^{-1}, along with carbonyl groups (1765 and 1680 cm^{-1}), and C–O stretching (1140 cm^{-1}). Finally, the methyl groups on the aromatic ring were chemically equivalent, as determined by both ^{1}H (a single signal at 2.22 ppm) and ^{13}C NMR spectroscopy (a single signal at 18.2 ppm that was confirmed to be the methyl groups via HETCOR analysis). This observation confirmed that the PhTAD was added at position *para* to the strongly electron donating –OR group on the benzene ring. If PhTAD had been added to the position *ortho* relative to the –OR group site, the two methyls would have been chemically inequivalent. Finally, high-resolution mass spectrometry confirmed the molecular formula for urazole **3**; thus, all spectral data were consistent with the assigned structure.

3. Discussion

The reaction between *N*1-substituted urazoles and the heterogenous oxidant Ni_2O_3 is known to provide high yields of corresponding urazolyl radicals [2–4]. Although solutions of urazolyl radical **1a** were deep blue in color, thus indicating the presence of appreciable amounts of *N*-centered radicals in the solution [1], the oxidation of urazole **3** did not yield a deeply colored solution. The lack of color suggests that urazolyl radical **1b** exists predominantly in the form of the *N*-*N* dimer **2b** when in the solution.

Attempts at tethering solutions of freshly generated **1b**/**2b** onto gold surfaces (as had been successfully accomplished with **1a**) yielded ambiguous experimental results. We could not definitively ascertain as to how (or if) the compound had successfully adhered onto the gold surface as we had been able to do with SAMs that were generated with **1a**; therefore, unfortunately, we had to abandon further studies with this compound. Future work will continue with other urazolyl radical species that are known to exist in a solution, and which retain their radical character.

4. Materials and Methods

4.1. General Methods

The ^{1}H and ^{13}C NMR spectra were obtained using a 400 MHz NMR spectrometer. The chemical shifts were reported in units of parts per million downfield from TMS. High-resolution mass spectra (HRMS) were acquired via electron spray ionization on

an LTQ-FTMS hybrid mass spectrometer. Ether **5** was synthesized, in accordance with the procedure given in the literature [5]. All of the other compounds were commercially available and used as received.

*4.2. Synthesis of 1-[2,6-dimethyl-4-(pent-4-yn-1-yloxy)phenyl]-4-phenyl-1,2,4-triazolidine-3,5-dione (**3**)*

To a solution of 0.5 g (2.66 mmol) of ether **5** [5] in 20 mL of CH_2Cl_2, 0.44 g (0.95 equivalents) of PhTAD was added as a solid, and it was stirred at room temperature. The resultant deep red solution was stirred for 48 h, after which, the red color gave way to a pale orange colored solution. The reaction mixture was concentrated, and the resultant residue was chromatographed (SiO_2; 1:1 hexanes: ethyl acetate) so that 0.71 g (74% yield) of **3** as a crystalline white solid was produced (m.p., 136–138 °C: IR (ATR) cm^{-1} 3248, 2925, 2887, 1766, 1689, 1429, 1140, 1061). ^1H NMR (400 MHz, DMSO-d_6) δ 11.30 (br s, 1H), 7.55–7.49 (m, 4H), 7.47–7.38 (m, 1H), 6.80 (s, 2H), 4.06 (t, J = 6.2 Hz, 2H), 2.84 (t, J = 2.5 Hz, 1H), 2.33 (dt, J = 2.5, 6.8 Hz, 2H), 2.22 (s, 6H), 1.89 (p, J = 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$); δ 159.8, 153.4, 150.4, 139.9, 131.4, 129.3, 128.4, 125.8, 124.8, 114.6, 83.4, 69.2, 66.3, 28.1, 18.2, 15.2. HRMS (electron spray ionization) m/z $[M + H]^+$ Calculated for $C_{21}H_{22}N_3O_3$ 364.16557; Found 364.16541.

Funding: This research was funded by Berry College.

Supplementary Materials: The following supporting information can be downloaded online. For compound **3**: ^1H NMR spectrum, ^{13}C NMR spectrum, HETCOR spectrum, IR spectrum, HRMS spectra.

Data Availability Statement: Copies of spectral data for novel compound **3** are available in the Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compounds are available from the authors.

References

1. Campos-Lendinez, A.; Crivillers, N.; Bromley, S.T.; Rovira, C.; Breton, G.W.; Mas-Torrent, M. Efficient Routes for the Preparation of Urazole Radical Self-Assembled Monolayers on Gold Surfaces. *J. Phys. Chem.* **2022**, *126*, 133358–133365. [CrossRef]
2. Pirkle, W.H.; Gravel, P.L. Persistent Cyclic Diacylhydrazyl Radicals from Urazoles and Pyrazolidine-3,5-diones. *J. Org. Chem.* **1978**, *43*, 808–815. [CrossRef]
3. Breton, G.W.; Martin, K.L. Probing the Dynamic Covalent Chemistry Behavior of Nitrogen-Centered Di- and Triurazole Radicals. *J. Org. Chem.* **2020**, *85*, 10865–10871. [CrossRef] [PubMed]
4. Breton, G.W.; Bowron, J.A. 1-(4-{[3,5-bis({[3,5-Dimethyl-4-(4-methyl-3,5-dioxo-1,2,4-triazolindin-1-yl)-phenoxy]methyl})phenyl] methoxy}-2,6-dimethylphenyl)-4-methyl-1,2,4-triazolidine-3,5-dione. *Molbank* **2023**, *2323*, M1535.
5. Meng, Z.; Xiang, J.F.; Chen, C.F. Directional Molecular Transportation Based on a Catalytic Stopper-Leaving Rotaxane System. *J. Am. Chem. Soc.* **2016**, *138*, 5652–5658. [CrossRef] [PubMed]
6. Cheng, C.C.; Greene, F.D.; Blount, J.F. Reaction of Triazolinediones with Acetylenes. Electrophilic Addition. *J. Org. Chem.* **1984**, *49*, 2917–2922. [CrossRef]