Tetrahedron Letters 55 (2014) 2085–2089

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthetic exploitation of halogenated alkenes containing an electron-withdrawing group: synthesis of α-chlorohydrazones and ketene aminals by regiospecific reactions of in situ generated imide chlorides

Amac Fatih Tuyun *

Department of Chemical Engineering, Faculty of Engineering and Architecture, Beykent University, Sisli-Ayazaga, 34396 Istanbul, Turkey

ARTICLE INFO

Article history:
Received 20 November 2013
Revised 22 January 2014
Accepted 12 February 2014
Available online 20 February 2014

Keywords:
Vicinal amines
Ketene aminals
Hydrazones
Electron-deficient alkenes
α-Chlorohydrazones
α-Aminohydrazones

ABSTRACT

A concise approach for the construction of ketene aminals and α-chlorohydrazones has been developed. It involves reactions of the regiodefined *gem*-dihalo nitrovinyl compound of in situ generated imide chlorides in different media with primary arylamines being dependent on the aryl groups. A range of ketene aminals and α-chlorohydrazones are obtained in good to high yields. In addition, α-aminohydrazones are prepared by using α-chlorohydrazones as the precursors.

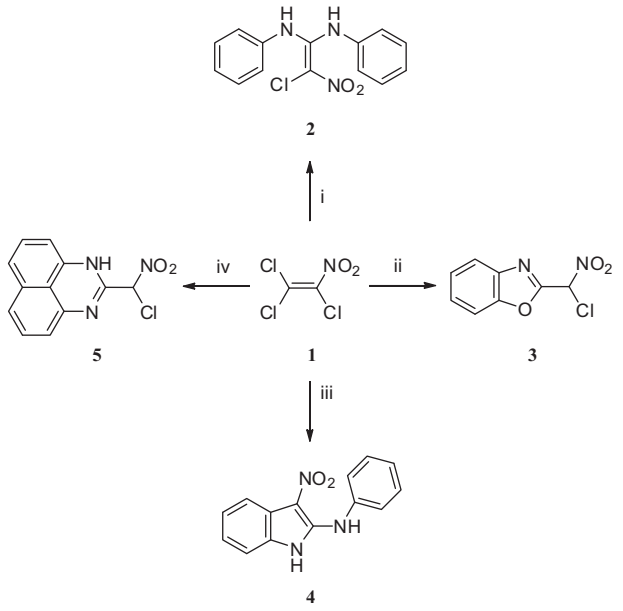
Vicinal amines (ketene aminals) represent a very important class of compounds in organic chemistry as they not only serve as ligands and catalysts in asymmetric reactions, but have also been shown to exhibit a broad spectrum of biological properties,[1] representatives of which have already been patented as control agents for animal pests.[2] Among many methods, amination reactions of simple *gem*-dihalo-1-alkenes, in particular those activated by electron-withdrawing groups (EWG), offer one of the most straightforward and practical approaches to bis (phenylamino)chloronitroethylene (**2**), benzoxazole (**3**), indole (**4**), and 1*H*-perimidine (**5**) derivatives (Scheme 1).[3]

The formation of α-chloro and α-aminohydrazones is widely used in chemistry,[4] examples include precursors of nitrilimine dipoles for use in cycloaddition reactions, in biology[5] as a molecular conjugation strategy for achieving ligation, attachment, and bioconjugation to biomolecules. For reactions involving biomolecules, they represent a versatile approach to conjugation chemistry.[6] Moreover, since certain hydrazone derivatives can be exchanged, such linkages have gained attention in dynamic combinatorial chemistry as well.[7] They can also be considered as highly functionalized electrophiles. Therefore, the development of an efficient method for the preparation of ketene aminals, along with α-chloro, and α-aminohydrazones is still highly desirable.

gem-Dihalo nitrovinyl moieties are valuable synthetic tools in organic chemistry and serve as interesting synthetic intermediates in a variety of chemical reactions,[8] mostly for the formation of carbon-heteroatom bonds, the most typical example probably being thiophene synthesis, where a *gem*-dihalo nitrovinyl moiety is converted into a 5-membered heterocyclic dithiolane structure, which upon treatment with a strong base in DMSO/H_2O, gives the corresponding thiophenes.[9,10] Moreover, the functionality of these molecules (acceptor-substituted alkenes) acts as attractive and versatile bidentate electrophiles for nucleophiles. The presence of an EWG bonded to an alkenyl carbon renders these compounds more reactive toward carbon, nitrogen, sulfur, and oxygen nucleophiles.[11] In 1976, Ol'dekop and Kaberdin reported the first acceptor-substituted alkene containing a nitro group.[12] Their innovative discovery has resulted in numerous further studies of this synthetic process. Since the first exhaustive account on this chemistry by Kaberdin et al., extensive reviews[13] and articles[3,14] have been published on developments in this field, which present novel derivatives of these new generation molecules. Finally, in 1998, another new example of these molecules was introduced by Potkin and Nechai.[15] After these pioneering works, an impressive number of subsequent papers have reported

* Tel.: +90 2128675248.
E-mail addresses: aftuyun@beykent.edu.tr, aftuyun@gmail.com

http://dx.doi.org/10.1016/j.tetlet.2014.02.038
0040-4039/



Scheme 1. Amination reactions of *gem*-dihalo-1-nitroalkene **1**. Reagents and conditions: (i) 2 equiv of $PhNH_2$, Et_2O, −20 °C; (ii) 2-$H_2NC_6H_4$-OH, NaOMe, MeOH; (iii) (1) 2 equiv of $PhNH_2$, Et_2O, 5 °C, (2) EtOH, 78 °C; (iv) 1,8-diaminonaphthalene, Et_2O, 10 °C.

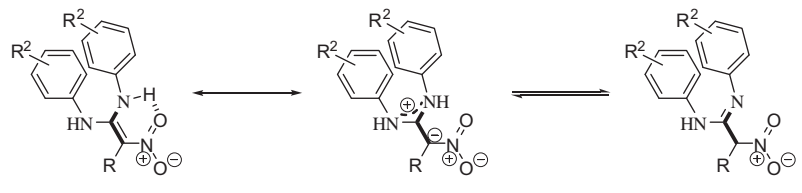
regioselective reactions between *gem*-dihalo nitroalkenes and a variety of nucleophiles.[16] The *gem*-dihalo nitrovinyl moiety also represents a very attractive key unit for syntheses of heterocyclic compounds by selection of difunctional nucleophiles and other reagents.[17] As part of our continuing efforts to explore the synthetic potency of *gem*-dihalo nitroalkene **6** and develop novel reaction pathways, a straightforward method for the divergent synthesis of ketene aminals or α-chloro, and α-aminohydrazones by the reactions of primary arylamines with *gem*-dihalo nitroalkene **6** is reported herein.

The approach to the synthesis of ketene aminals was found to be straightforward. Reactions of *gem*-dihalo nitroalkene **6** with at least four equivalents of an aniline derivative containing an electron-releasing group (ERG) proceeded selectively with simple amination, most probably via the corresponding amidines (see Scheme 3). Such mild conditions for these reactions are logical, considering the activating effect of the additional acceptor, the nitro group, on the alkene bond. The closest analogues are known to react with primary arylamines in boiling benzene.[18] The studied reaction occurs apparently by a nucleophilic vinylic substitution mechanism (S_NVin), via the formation of an intermediate dipolar ion, allowing stabilization caused by a hydrogen bond between an oxygen atom of the nitro group and the proton at the aniline nitrogen atom. Ketene aminals **2A** are a special class of alkenes distinguished by an electron-rich and strong double bond activated by the nitro group. The dipolar character in **2B** is caused by the significant contribution from the tautomeric structure **2C** to the ground-state structure (Scheme 2), and particularly turns out to be an appropriate substrate.

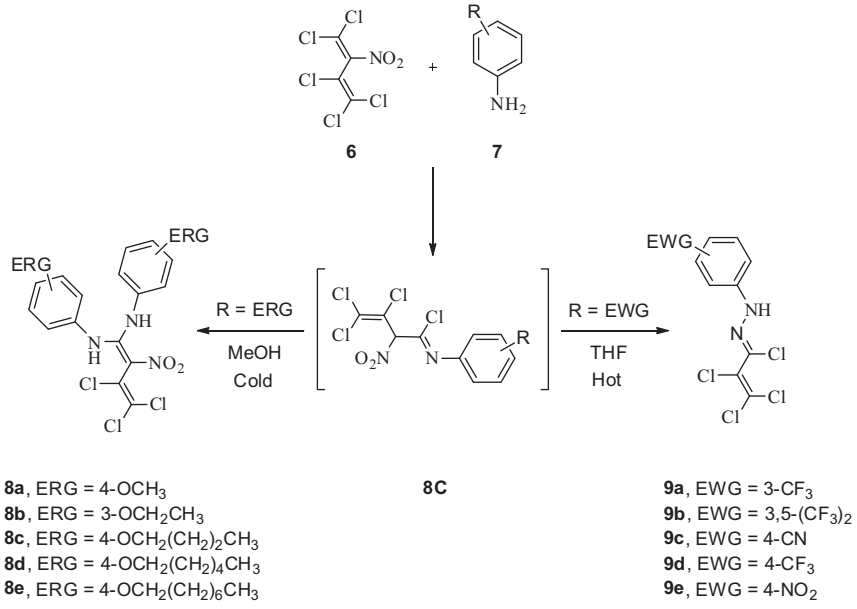
Numerous attempts to obtain monoaminated products that could provide straightforward entry to hydrazones by slight modifications of the reaction conditions and/or the stoichiometry of the reactants resulted in unreacted starting materials and ketene aminals in low yields. The regiospecific monoaminated product is actually one of the most difficult to obtain, mainly because of the extraordinarily high electrophilicity of the assumed imide chloride intermediate. Another halogen atom located on the first carbon must enable attack of further amines. Unfortunately, a monoaminated product was not formed at all. Next, the reaction scope of the primary arylamines containing ERG groups such as methoxy, ethoxy, butoxy, hexyloxy, and octyloxy was explored with respect to the *gem*-dichloro nitroalkene **6** under mild conditions to give ketene aminals **8a–e**. This path, based on classical S_NVin, usually requires, as commented on above, the presence of an EWG group on the alkene bond. Modifications usually allow the reaction to be driven toward the formation of ketene aminals **8a–e**, resulting from double substitutions, where two halogen atoms are formally substituted. Eventually, it was found that this alkene diamination process proceeded smoothly with four equivalents of a primary arylamine containing an ERG in MeOH as the solvent, without any additional agents (Scheme 3).

One of the crucial steps in the formation of ketene aminals is the in situ formation of an imide chloride **8C** from the corresponding primary arylamines and *gem*-dihalo nitroalkene **6**. The idea to form the imide chloride **8C** in situ from *gem*-dihalo nitroalkene **6** and a primary arylamine led to the discovery of α-chlorohydrazones **9a–e**. During the reaction of imide chloride **8C**, generated in situ from **6** by treatment of primary arylamines (independent of the nucleophilicity) with additional primary arylamines containing EWGs such as nitro, cyano, and trifluoromethyl, a different reaction pathway operated instead of the aforementioned initial *N*-substitution (Scheme 3).

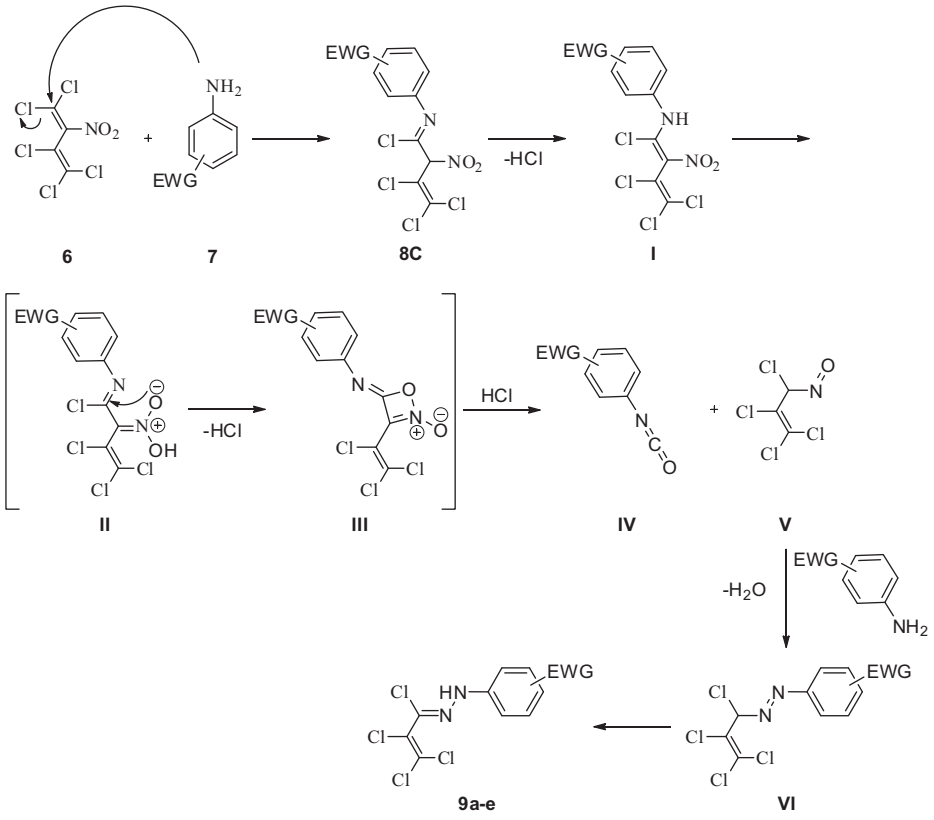
On the basis of the investigations of the reaction conditions and substrate diversity, a possible mechanism for this reaction is described in Scheme 4.[19] At the beginning, independent of the nucleophilicity of the primary amines, the first substitution reaction always takes place at the strongly δ-positive C1 of **6** leading to the corresponding imide chloride **8C**. After tautomerization of the monoaminated intermediate **I** to give the reactive imide chloride **II**, an intramolecular nitronic acid oxygen is now apparently more nucleophilic than the amine containing EWG of a second molecule. Therefore, a cyclic nitrone **III** is formed. Upon addition of HCl (liberated earlier) and the subsequent cycloreversion, two intermediates, isocyanate **IV** and nitroso compound **V** are formed. Subsequent coupling of nitroso compounds **V** with the second equivalent of the aniline containing the EWG leads to the azo compounds **VI** along with elimination of water. Subsequent isomerization gives the α-chlorohydrazones **9a–e** (Scheme 4).



Scheme 2. Tautomeric structures of enamines.



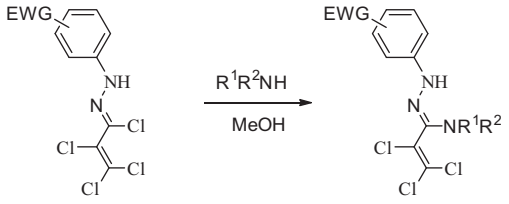
Scheme 3. Synthetic pathways for ketene aminals **8a**–**e** and α-chlorohydrazones **9a**–**e**.



Scheme 4. A plausible reaction mechanism.

The halogen atom on the first carbon in compounds **9a**–**e** is activated by the strong electron-withdrawing C=N group. This feature provides the opportunity for further selective functionalization at the halide group. Fortunately, reaction with two equivalents of an aromatic or an aliphatic amine gave the desired α-aminohydrazones **10a**–**e** in good yields (Scheme 5). Attempts to react α-chlorohydrazones with various aromatic and aliphatic thiols in basic medium (in sodium ethoxide in ethanol) did not succeed at ambient temperature, and led to decomposition upon heating to around 50 °C. The prepared library is potentially interesting for both further medicinal and synthetic evaluations.

Structure determination of the products was performed on the basis of IR, NMR, mass spectrometry, and elemental analyses. All the hydrazone compounds (**9a**–**e** and **10a**–**e**) showed strong absorptions around 1600 cm^{-1} in their IR spectra due to the C=N group. Additionally, the IR spectra of all the compounds exhibited



9a, EWG = 3-CF_3
9b, EWG = 3,5-$(CF_3)_2$
9c, EWG = 4-CN
9d, EWG = 4-CF_3

10a, EWG = 4-CN, R^1R^2 = -$(CH_2)_2S(CH_2)_2$-
10b, EWG = 4-CN, R^1R^2 = -$(CH_2)_2O(CH_2)_2$-
10c, EWG = 3-CF_3, R^1 = H, R^2 = 4-methoxyphenyl
10d, EWG = 3,5-$(CF_3)_2$, R^1 = H, R^2 = 4-methoxyphenyl
10e, EWG = 4-CF_3, R^1R^2 = -$(CH_2)_2S(CH_2)_2$-

Scheme 5. Selective functionalization of α-chlorohydrazones **10a–e**.

amine absorption bands at around 3300 cm^{-1}. In the electrospray ionization (ESI) mass spectra of the products, almost all the ketene aminals and hydrazones displayed molecular ions as base peaks. Only compound **8e** showed a different fragmentation pattern and ionic species. In the ^{13}C NMR spectra of ketene aminals **8a–e**, the C-1 carbon atoms appeared relatively downfield around 150 ppm, depending on the structure of the molecule, while the NO_2-bearing carbon atoms C-2 exhibited resonances at around 110 ppm. The individual C-3 and C-4 carbons of each molecule of the library gave chemical shift values around 130 and 120 ppm, respectively. In the ^{13}C NMR spectra of all the hydrazone derivatives (**9a–e** and **10a–e**), there were signals corresponding to the C=N carbons at around 150–155 ppm. Assignment of the exchangeable –NH proton of hydrazone **9b** was performed based on data from D_2O exchange, after the –NH peak had disappeared or decreased in intensity.

In conclusion, an efficient and straightforward route for preparing synthetically useful functionalized ketene aminals and α-chlorohydrazones from *gem*-dihalo nitroalkene **6** has been developed. The conditions are mild and good to excellent yields are obtained in the absence of any additives. Additionally, α-aminohydrazones are prepared by using α-chlorohydrazones as the precursors. Substitution with four equivalents of a primary arylamine such as aniline or its electron-rich derivatives leads to the formation of ketene aminals. In contrast, during the reaction with electron-deficient primary arylamines such as trifluoromethyl-, cyano-, or nitro-aniline, a different reaction pathway operates. We believe that the resulting functionalized products may be highly valuable for the synthesis of useful complex molecules. These experimental findings, structures, and reaction pathways should pave the way for possible new reactions. Since the multifaceted character of the *gem*-dihalo nitroalkene **6** provides significant potential for the diversity-oriented synthesis of heterocyclic frameworks, further extension of our research is now ongoing.

General procedure for the preparation of ketene aminals 8a–e

3,4,4-Trichloro-*N*,*N*′-bis(4-methoxyphenyl)-2-nitrobuta-1,3-diene-1,1-diamine (8a)

At −20 °C, a solution of 4-(methoxy)aniline (2.75 g, 22.4 mmol) in MeOH (15 mL) was added dropwise to a solution of *gem*-dihalo nitroalkene **6** (1.35 g, 5 mmol) in MeOH (15 mL) over 10 min. The resulting mixture was kept at the same temperature for an additional 1 h with stirring. After 5 h at room temperature and subsequent cooling to −5 °C, concd HCl (3.0 mL) was added. The resulting precipitate was filtered off, washed with H_2O, hexane, and cold MeOH, and dried in vacuo to give ketene aminal **8a**. Yield 1.968 g, 89%, mp 166–168 °C. IR (ATR) ν (cm^{-1}): 3476, 3417 (NH), 3057 ($CH_{aromatic}$), 2940 ($CH_{aliphatic}$), 1640, 1612 (C=C), 1508 (NO_2), 1303, 1244 (NO_2), 1097, 1031. ^1H NMR (500 MHz, DMSO-d_6) δ = 3.69 (br s, 6H, $2OCH_3$), 6.81–6.84 (dd, ^3J = 3.42, 12.69 Hz, 4H, $4CH_{aromatic}$), 7.04–7.07 (dd, ^3J = 3.42, 12.21 Hz, 4H, $4CH_{aromatic}$), 10.03 (s, 2H, 2NH). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 56.03 (OCH_3), 114.93, 124.77 ($CH_{aromatic}$), 109.05 (C2), 131.46 (C3), 126.87, 157.59 ($C_{aromatic}$), 153.75 (C1). MS (ESI+): *m*/*z* (%) 466 (100, $[M+Na]^+$). Anal. Calcd for $C_{18}H_{16}Cl_3N_3O_4$ (444.696) (%): C, 48.62; H, 3.63; N, 9.45. Found (%): C, 48.77; H, 3.77; N, 9.55.

General procedure for the preparation of α-chlorohydrazones 9a–e

2,3,3-Trichloro-*N*′-[(3-(trifluoromethyl)phenyl)]acrylohydrazonoyl chloride (9a)

Under a nitrogen atmosphere, a mixture of *gem*-dihalo nitroalkene **6** (650 mg, 2.39 mmol) and 3-(trifluoromethyl)aniline (810 mg, 5.02 mmol) in anhydrous THF (20 mL) was heated at 45–50 °C for 4 d. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (3 × 30 mL), and dried over $CaCl_2$. The product was purified via column chromatography on silica gel to give hydrazone **9a**. Yield 0.730 g, 87%. IR (ATR) ν (cm^{-1}): 3332, 3050, 1690, 1600, 1574, 1494, 1473, 1455, 1515, 1335, 1280, 1167, 1127, 1092, 1066, 929, 841, 790. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.12 (d, ^3J = 7.81 Hz, 1H, $CH_{aromatic}$), 7.17 (d, ^3J = 8.29 Hz, 1H, $CH_{aromatic}$), 7.27 (s, 1H, $CH_{aromatic}$), 7.29 (t, ^3J = 7.81 Hz, 1H, $CH_{aromatic}$), 8.06 (br s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 117.77 (CCl_2), 126.15 (CCl), 128.97 (CF_3), 116.34, 129.01, 131.06 ($CH_{aromatic}$), 134.79, 141.60 ($C_{aromatic}$), 150.53 (C=N). MS (ESI+): *m*/*z* (%) 346 (100, $[M-4H]^+$). Anal. Calcd for $C_{10}H_5Cl_4F_3N_2$ (351.967) (%): C, 34.12; H, 1.43; N, 7.96. Found (%): C, 34.33; H, 1.22; N, 7.69.

General procedure for the preparation of α-aminohydrazones 10a–e

4-[(2-(2,3,3-Trichloro-1-thiomorpholinoallylidene)]hydrazinyl)-benzonitrile (10a)

To a suspension of hydrazone **9c** (30 mg, 0.098 mmol) in MeOH (10 mL) was added with stirring a solution of the thiomorpholine (21 mg, 0.206 mmol) in MeOH (5 mL) at 0 °C over 15 min. The resulting mixture was stirred for 2 h at room temperature. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (3 × 30 mL), and dried over $CaCl_2$. The

product was purified via column chromatography on silica gel. Yield 0.028 g, 77%. IR (ATR) ν (cm^{-1}): 3262 (NH), 3015 ($CH_{aromatic}$), 2960, 2922, 2850 ($CH_{aliphatic}$), 2215 (CN), 1609, 1597, 1421, 1408, 1519, 1334, 1261, 1167, 1100, 1019, 954, 915, 802. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.64–2.73 (m, 4H, S-CH_2), 3.60 (t, ^3J = 5.37 Hz, 4H, N-CH_2), 6.88 (m, 2H, 2$CH_{aromatic}$), 6.95 (br s, 1H, NH), 7.37–7.41 (m, 2H, 2$CH_{aromatic}$). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 25.58 (S-CH_2), 47.74 (N-CH_2), 117.13 (CN), 111.49, 119.15 ($CH_{aromatic}$), 125.51 (CCl), 132.56 (CCl_2), 100.05, 147.88 ($C_{aromatic}$), 153.92 (C=N). MS (ESI+): m/z (%) 375 (100, $[M+H]^+$), 339 (54, $[M-Cl]^+$). Anal. Calcd for $C_{14}H_{13}Cl_3N_4S$ (375.704): C, 44.76; H, 3.49; N, 14.91. Found: C, 44.99; H, 3.77; N, 15.27.

Acknowledgment

The author thanks the Board of Trustees of Beykent University for supplying equipment and materials.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.02.038.

References and notes

1. (a) Kizirian, J. C. *Chem. Rev.* **2008**, *108*, 140–205; (b) Kotti, S.; Timmons, C.; Li, G. G. *Chem. Biol. Drug Des.* **2006**, *67*, 101–114; (c) Muniz, K. *New J. Chem.* **2005**, *29*, 1371–1385; (d) Lucet, D.; Le Gall, T.; Mioskowski, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 2581–2627.
2. Zapol'skii, V. A.; Vogt, E. J.; Gjikaj, M.; Kaufmann, D. E. *Heterocycles* **2012**, *86*, 1431–1447.
3. Ozpinar, G. A.; Erdem, S. S.; Meyer, C.; Kaufmann, D. E. *J. Org. Chem.* **2009**, *74*, 4727–4739.
4. (a) Das, A.; Volla, C. M. R.; Atodiresei, I.; Bettray, W.; Rueping, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 8008–8011; (b) Xu, X. F.; Zavalij, P. Y.; Hu, W. H.; Doyle, M. P. *J. Org. Chem.* **2013**, *78*, 1583–1588; (c) Shawali, A. S.; Haboub, A. J. M. *J. Heterocycl. Chem.* **2013**, *50*, 17–22; (d) Durust, Y.; Yildirim, M.; Fronczek, C. F.; Fronczek, F. R. *Monatsh. Chem.* **2012**, *143*, 127–138; (e) Zou, H. B.; Zhu, H. J.; Shao, J. A.; Wu, J. W.; Chen, W. T.; Giulianotti, M. A.; Yu, Y. P. *Tetrahedron* **2011**, *67*, 4887–4891; (f) Durust, Y.; Yildirim, M. *Monatsh. Chem.* **2010**, *141*, 961–973; (g) Altug, C.; Durust, Y.; Elliott, M. C. *Tetrahedron Lett.* **2009**, *50*, 7392–7394; (h) Esseffar, M.; El Messaoudi, M.; Azzouzi, S.; Jalal, R.; Saez, J. A.; Domingo, L. R.; Latorre, J.; Liu-Gonzalez, M. *J. Phys. Org. Chem.* **2009**, *22*, 31–41; (i) Bonini, B. F.; Franchini, M. C.; Gentili, D.; Locatelli, E.; Ricci, A. *Synlett* **2009**, 2328–2332; (j) Lee, K. J.; Choi, J. K.; Yum, E. K.; Cho, S. Y. *Tetrahedron Lett.* **2009**, *50*, 6698–6700; (k) Wagner, G.; Danks, T. N.; Vullo, V. *Tetrahedron* **2007**, *63*, 5251–5260; (l) Pinto, D. J. P.; Orwat, M. J.; Koch, S.; Rossi, K. A.; Alexander, R. S.; Smallwood, A.; Wong, P. C.; Rendina, A. R.; Luettgen, J. M.; Knabb, R. M.; He, K.; Xin, B. M.; Wexler, R. R.; Lam, P. Y. S. *J. Med. Chem.* **2007**, *50*, 5339–5356; (m) De Benassuti, L.; Garanti, L.; Molteni, G. *Tetrahedron* **2004**, *60*, 4627–4633; (n) Vullo, V.; Danks, T. N.; Wagner, G. *Eur. J. Org. Chem.* **2004**, 2046–2052; (o) Molteni, G. *Heterocycles* **2004**, *63*, 1423–1428; (p) Broggini, G.; Garanti, L.; Molteni, G.; Zecchi, G. *Heterocycles* **1997**, *45*, 1945–1953; (q) Garanti, L.; Molteni, G.; Zecchi, G. *Heterocycles* **1995**, *40*, 777–786; (r) Easton, C. J.; Hughes, C. M. M.; Savage, G. P.; Simpson, G. W. *Adv. Heterocycl. Chem.* **1994**, *6060*, 261–327.
5. (a) Rollas, S.; Kucukguzel, S. G. *Molecules* **2007**, *12*, 1910–1939; (b) Aslan, H. G.; Karacan, N. *Med. Chem. Res.* **2013**, *22*, 1330–1338; (c) Kandhavelu, M.; Paturu, L.; Mizar, A.; Mahmudov, K. T.; Kopylovich, M. N.; Karp, M.; Yli-Harja, O.; Pombeiro, A. J. L.; Ribeiro, A. S. *Pharm. Chem. J.* **2012**, *46*, 157–164; (d) Kaymakcioglu, B. K.; Rollas, S. *Farmaco* **2002**, *57*, 595–599; (e) Kucukguzel, S. G.; Rollas, S.; Kucukguzel, I.; Kiraz, M. *Eur. J. Med. Chem.* **1999**, *34*, 1093–1100; (f) Kucukguzel, S. G.; Rollas, S.; Erdeniz, H.; Kiraz, M. *Eur. J. Med. Chem.* **1999**, *34*, 153–160.
6. Sletten, E. M.; Bertozzi, C. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 6974–6998.
7. (a) Algar, W. R.; Prasuhn, D. E.; Stewart, M. H.; Jennings, T. L.; Blanco-Canosa, J. B.; Dawson, P. E.; Medintz, I. L. *Bioconjugate Chem.* **2011**, *22*, 825–858; (b) Dirksen, A.; Dirksen, S.; Hackeng, T. M.; Dawson, P. E. *J. Am. Chem. Soc.* **2006**, *128*, 15602–15603.
8. (a) Zapol'skii, V. A.; Yang, X. N.; Namyslo, J. C.; Gjikaj, M.; Kaufmann, D. E. *Synthesis* **2012**, 885–894; (b) Meyer, C.; Zapol'skii, V. A.; Adam, A. E. W.; Kaufmann, D. E. *Synthesis* **2008**, 2575–2581.
9. (a) Zapol'skii, V. A.; Namyslo, J. C.; Adam, A. E. W.; Kaufmann, D. E. *Heterocycles* **2004**, *63*, 1281–1298; (b) Vogt, E. J.; Zapol'skii, V. A.; Nutz, E.; Kaufmann, D. E. *Eur. J. Org. Chem.* **2013**, *2013*, 4285–4293.
10. Tuyun, A. F. *Heterocycles* **2013**, *87*, 2589–2598.
11. (a) Aydinli, S. G.; Ibis, C. *Eur. J. Chem.* **2010**, *7*, 1498–1506; (b) Aydinli, G.; Sayil, C.; Ibis, C. *Spectrosc. Lett.* **2010**, *43*, 44–50; (c) Ibis, C.; Yildirim, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **2009**, *184*, 369–378; (d) Ibis, C.; Sayil, C.; Ozkok, F. Z. *Naturforsch. (B)* **2006**, *61*, 1174–1179; (e) Zapolskii, V. A.; Potkin, V. I.; Nechai, N. I.; Kaberdin, R. V. *Zh. Org. Khim.* **1993**, *29*, 885–888; (f) Oldekop, Y. A.; Kaberdin, R. V.; Potkin, V. I. *Zh. Org. Khim.* **1980**, *16*, 543–547; (g) Potkin, V. I.; Knizhnikov, V. A.; Kaberdin, R. V.; Oldekop, Y. A. *Zh. Org. Khim.* **1986**, *22*, 86–89.
12. (a) Ol'dekop, Yu. A.; Kaberdin, R. V. *Zh. Org. Khim.* **1976**, *12*, 2039; (b) Ol'dekop, Yu. A.; Kaberdin, R. V.; Buslovskaya, E. E. *Zh. Org. Khim.* **1979**, *15*, 1321–1322.
13. (a) Leroyer, L.; Maraval, V.; Chauvin, R. *Chem. Rev.* **2012**, *112*, 1310–1343; (b) Kaberdin, R. V.; Potkin, V. I.; Zapolskii, V. A. *Usp. Khim.* **1999**, *68*, 845–860; (c) Kaberdin, R. V.; Potkin, V. I.; Zapolskii, V. A. *Usp. Khim.* **1997**, *66*, 919–935.
14. (a) Watkins, A. L.; Landis, C. R. *Org. Lett.* **2011**, *13*, 164–167; (b) Ananikov, V. P.; Hazipov, O. V.; Beletskaya, I. P. *Chem. Asian J.* **2011**, *6*, 306–323; (c) Onul, N.; Brimo, W. M. D.; Ibis, C. *Phosphorus, Sulfur Silicon Relat. Elem.* **2011**, *186*, 2180–2188; (d) Ibis, C.; Yildirim, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **2011**, *186*, 2236–2249; (e) Zapol'skii, V. A.; Namyslo, J. C.; Gjikaj, M.; Kaufmann, D. E. Z. *Naturforsch. (B)* **2010**, *65*, 843–860; (f) Zapol'skii, V. A.; Fischer, R.; Namyslo, J. C.; Kaufmann, D. E. *Bioorg. Med. Chem.* **2009**, *17*, 4206–4215; (g) Zapol'skii, V. A.; Namyslo, J. C.; Gjikaj, M.; Kaufmann, D. E. *Arkivoc* **2007**, *i*, 76–93; (h) Block, E.; Tries, F.; He, C. H.; Guo, C. X.; Thiruvazhi, M.; Toscano, P. J. *Org. Lett.* **2003**, *5*, 1325–1327.
15. Nechai, N. I.; Potkin, V. I.; Kurman, P. V.; Kaberdin, R. V. *Dokl. Akad. Nauk Belarusi* **1998**, *42*, 75–78.
16. (a) Ibis, C.; Tuyun, A. F. *Phosphorus, Sulfur Silicon Relat. Elem.* **2012**, *187*, 1161–1172; (b) Ibis, C.; Tuyun, A. F. *Curr. Org. Synth.* **2011**, *8*, 861–871; (c) Ibis, C.; Deniz, N. G.; Tuyun, A. F. *J. Chem. Crystallogr.* **2010**, *40*, 353–356; (d) Ibis, C.; Tuyun, A. F.; Aydinli, G. *Asian J. Chem.* **2010**, *22*, 1360–1368; (e) Ibis, C.; Tuyun, A. F.; Aydinli, G. *Phosphorus, Sulfur Silicon Relat. Elem.* **2010**, *185*, 2014–2023.
17. (a) Zapol'skii, V. A.; Namyslo, J. C.; de Meijere, A.; Kaufmann, D. E. *Beilstein J. Org. Chem.* **2012**, *8*, 621–628; (b) Vogt, E. J.; Zapol'skii, V. A.; Nutz, E.; Kaufmann, D. E. Z. *Naturforsch. (B)* **2012**, *67*, 285–294; (c) Nutz, E.; Zapol'skii, V. A.; Kaufmann, D. E. *Synthesis* **2009**, 2719–2724; (d) Zapol'skii, V. A.; Namyslo, J. C.; Altug, C.; Gjikaj, M.; Kaufmanna, D. E. *Synthesis* **2008**, 304–310; (e) Zapol'skii, V. A.; Namyslo, J. C.; Gjikaj, M.; Kaufmann, D. E. *Synlett* **2007**, 1507–1512; (f) Zapol'skii, V. A.; Namyslo, J. C.; Blaschkowski, B.; Kaufmann, D. E. *Synlett* **2006**, 3464–3468.
18. (a) Ishmaeva, E. A.; Berestovitskaya, V. M.; Litvinov, I. A.; Vereshchagina, Y. A.; Yarkova, E. G.; Fattakhova, G. R.; Krivolapov, D. B.; Makarenko, S. V.; Trukhin, E. V.; Pavlova, I. V. *Russ. J. Gen. Chem.* **2001**, *71*, 429–436; (b) Berestovitskaya, V. M.; Makarenko, S. V.; Kovalenko, K. S.; Litvinov, I. A.; Krivolapov, D. B.; Shevchenko, A. D. *Russ. J. Gen. Chem.* **2011**, *81*, 376–384.
19. Zapol'skii, V. A.; Nutz, E.; Namyslo, J. C. N.; Adam, A. E. W.; Kaufmann, D. E. *Synthesis* **2006**, 2927–2933.