NJC

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: N. Singh and K. Banert, *New J. Chem.*, 2017, DOI: 10.1039/C6NJ03835B.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/njc

View Article Online
DOI: 10.1039/C6NJ03835B

NJC

Letter

Usual and unusual reactions of cyclohexane-1,2-dione with aryl azides and amines: a structural corrigendum†‡

Received 00th December 2016,
Accepted 00th December 2016

DOI: 10.1039/x0xx00000x

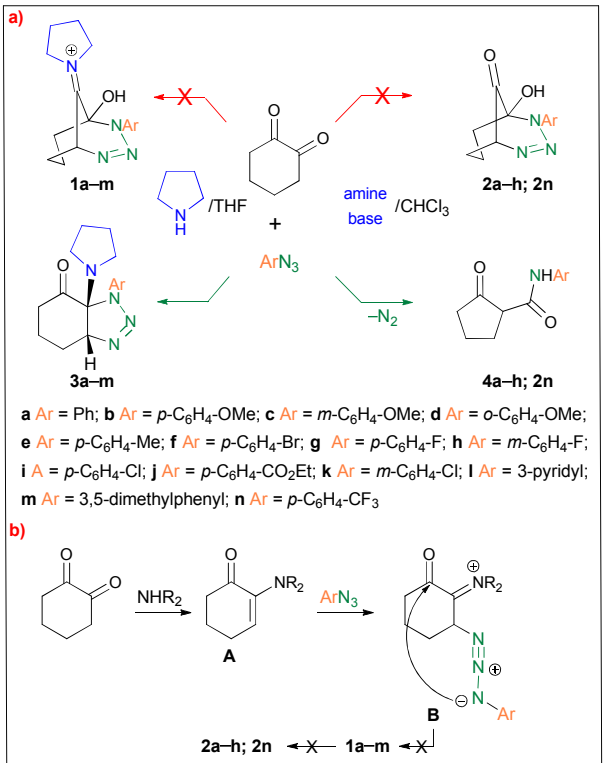
www.rsc.org/

Neeraj Singh and Klaus Banert*

The reported syntheses of alleged functionalised 1,2,3-triazines from cyclohexane-1,2-dione and aryl azides, in the presence of pyrrolidine and other amines, were repeated. The products do not contain the bicyclic triazine and bicyclic ketone moieties, instead, cyclohexane-fused 4,5-dihydro-1,2,3-triazoles and monocyclic *β*-ketoamides were obtained, respectively. These corrections are well supported by careful analyses of NMR spectra, IR spectra, elemental analysis and comparision with data which were previously published in literature. Suitable mechanisms are discussed for the synthesis of the observed compounds.

The azido group, although absent in natural products, is one of the most versatile entities, which has found immense application, not only in synthetic organic chemistry,[1] but also in chemical biology[2] and material science.[3] Particularly, the synthesis of triazoles by a cycloaddition reaction between azides and a C=C/C≡C bond, first observed by A. Michael in 1893,[4] intensively investigated and propagated with the concept of 1,3-dipolar cycloadditions by R. Huisgen,[5] and finally revolutionised by copper(I)-catalysed click chemistry,[6] is one of the most utilised reactions in present research.

As part of our current interests in the unusual reactions of azido compounds,[7] we became interested in a report by W. Li *et al.*, wherein the synthesis of bicyclic 1,2,3-triazines **1a–m** and **2a–h**, **2n** were described, although these compounds were named as "highly substituted 1,2,3-triazoles" throughout the paper including the title (Scheme 1a).[8] The products **1a–m** were claimed to be formed from aryl azides, cyclohexane-1,2-dione and pyrrolidine in THF with 54–95% yield. In the whole article and in the corresponding Electronic Supplementary Information, heterocycles **1a–m** are always depicted and addressed without any anion. This gives the impression that positively charged iminium species were isolated (without anion!). Adducts **2a–h** and **2n** were said to result from cyclohexane-1,2-dione, aryl azides and diethylamine in chloroform with 51–72% yield. Lower yields of such 1,2,3-triazines were supposedly observed, when the substrates were reacted in the presence of other bases, instead of diethylamine, such as DABCO or DBU, which cannot generate enamines with ketones. The products **1a–m**, **2a–h** and **2n** were isolated as yellow oils or yellow solids and characterised by ^{1}H NMR, ^{13}C NMR as well as by HR-MS. The authors explained the



Scheme 1 a) Claimed[8] and now revised structures resulting from the reaction of cyclohexane-1,2-dione with pyrrolidine and diethylamine; b) mechanism suggested by the authors[8] to explain the incorrect structures **1** and **2**.

Chemnitz University of Technology, Organic Chemistry, Strasse der Nationen 62, 09111 Chemnitz, Germany. Email: klaus.banert@chemie.tu-chemnitz.de

‡ Dedicated to Prof. Dr. Virendra Singh, University of Lucknow, Lucknow, India.

† Electronic Supplementary Information (ESI) available: Experimental procedures, spectroscopic data, and copies of NMR spectra. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C6NJ03835B

formation of compounds **1a–m** through formation of enamine **A** and subsequent attack of the carbon nucleophile **A** at the terminal nitrogen of the azide to give intermediate **B**, which then undergoes intramolecular cyclisation (Scheme 1b). Formation of ketones **2a–h** and **2n** was claimed to be a result of the hydrolysis of the corresponding compounds of type **1**. However, no such experiment was described to transform the iminium (salts?) **1** into the ketones **2**.

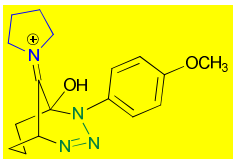
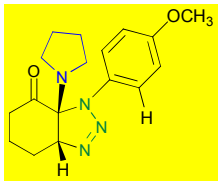
We had serious doubts about the asserted structures for compounds **1a–m**, **2a–h** and **2n** owing to various contradictions. Firstly, the mechanism invoked[8] is not in harmony with the general principles of reactivity: N_α of the azide fragment in intermediate **B** should attack the more electrophilic iminium carbon instead of the entropically disfavoured carbonyl group. Additionally, it is well established that organic azides regioselectively cycloadd at enamines to yield 5-amino-4,5-dihydro-1,2,3-triazoles.[9] Even the 1,3-dipolar cycloaddition of phenyl azide at a 2-aminocyclohex-2-en-1-one, which is very similar to intermediate **A**, was reported to lead to the corresponding five-membered heterocycle.[10]

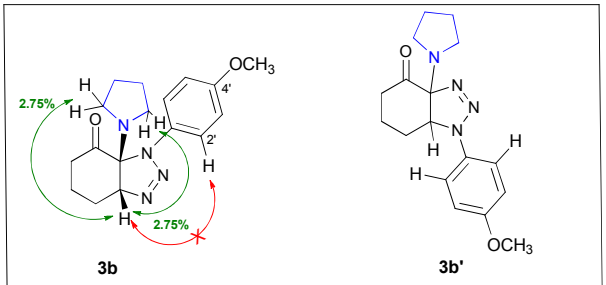
Secondly, if compounds **1a–m** exist as iminium salts, the corresponding anion is completely unclear, and it is unlikely that such polar substances can be purified by silica gel chromatography as described in the paper[8] of W. Li *et al*. Furthermore, the fixed geometry of the pyrrolidinium unit in the asymmetrical product **1** should be responsible for four different ^{13}C NMR signals (instead of only two signals).[11] Therefore, the number of ^{13}C NMR signals turned out to be incorrect in all 13 cases of the 1,2,3-triazines **1a–m**. Finally, the OH proton signal is missing in all the ^{1}H NMR spectra of these compounds.

Thirdly, in case of bicyclic ketones **2a–h** and **2n**, the ^{13}C NMR signal of the C–OH bridgehead carbon atom should resonate at $\delta \approx 80–100$ ppm.[12] However, the ^{13}C NMR data, which were reported to characterise these triazines,[8] did not include any signal with the expected chemical shift. On the other hand, a ^{13}C NMR signal at $\delta \approx 164–165$ ppm was observed for all products with the claimed structure of the heterocycle **2**.[8] But such a signal is incompatible with this structure and can, for example, be assigned to a carboxamide unit. Moreover, a broad singlet at $\delta \approx 8.7$ ppm was found in all ^{1}H NMR spectra of alleged products **2a–h** and **2n**, and this signal can only be attributed to an OH or NH group. However, the chemical shift is unusual for an alcohol and more likely for the NH proton of a carboxamide unit.

In order to clarify the structures of compounds **1a–m**, **2a–h** and **2n**, we first re-investigated the reaction of cyclohexane-1,2-dione, pyrrolidine and 1-azido-4-methoxybenzene in THF. After chromatography with silica gel using a 1:1 mixture of diethyl ether and pentane, the identical substance with the same NMR data was obtained (Table 1). We also found thirteen ^{13}C NMR signals, which is not compatible with the structure of **1b**. Therefore, the real product cannot include an unsymmetrical pyrrolidine ring that leads to four ^{13}C NMR signals. Furthermore, our IR spectrum of the product indicated a ketone (1726 cm^{-1}), but a signal of a hydroxy group was absent. This excludes the structure of **1b** as well. On the other

Table 1. Comparision of the data of putative triazine **1b** and triazole **3b**.

Supposed product **1b**[8] from cyclohexane-1,2-dione, pyrrolidine and 1-azido-4-methoxybenzene	Product **3b** from cyclohexane-1,2-dione, pyrrolidine and 1-azido-4-methoxybenzene
	
Yellow solid; yield (87%); mp N.A.	Yellow solid; yield (41%); mp 103–104 °C; purified by flash chromatography (R_f = 0.41; SiO_2; Et_2O : *n*-pentane 1:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.46–1.51 (m, 1H), 1.61–1.76 (m, 6H), 2.18–2.34 (m, 3H), 2.40–2.44 (m, 2H), 2.62–2.64 (m, 2H), 3.76 (s, 3H), 4.79–4.81 (m, 1H), 6.83 (d, J = 10 Hz, 2H), 7.43 (d, J = 10 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ = 17.1, 24.0, 26.4, 37.3, 45.8, 55.4, 80.6, 83.0, 114.4, 118.7, 133.0, 156.5, 204.0	**^{1}H NMR (400 MHz, $CDCl_3$):** δ = 1.41–1.52 (m, 1H), 1.59–1.76 (m, 6H), 2.16–2.36 (m, 3H), 2.38–2.44 (m, 2H), 2.59–2.64 (m, 2H), 3.75 (s, 3H), 4.78 (m, 1H), 6.81 (d, ^{3}J = 9.2 Hz), 7.41 (d, ^{3}J = 9.2 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 17.01 (t, $CHCH_2$), 23.94 (t, NCH_2CH_2, 2 x CH_2), 26.34 (t, $COCH_2CH_2$), 37.24 (t, $COCH_2$), 45.66 (t, NCH_2, 2 x CH_2), 55.34 (q, OCH_3), 80.52 (d, CH), 82.94 (s, NCN), 114.32 (d, *C*–2'), 118.61 (d, *C*–3'), 132.90 (s, *C*–1'), 156.41 (s, *C*–4'), 203.91 (s, *C*=O).
IR: N.A. **HR-MS (ESI):** m/z calcd. for $C_{17}H_{23}N_4O_2$ $[M]^+$ 315.1816; found: 315.1815	**IR (CCl_4, cm^{-1}):** 1726 (C=O). **HR-MS (ESI):** m/z calcd. for $C_{17}H_{23}N_4O_2$ $[M + H]^+$ 315.1816; found: 315.1792



Scheme 2 1D NOESY experiment result to verify the formation of regioisomer **3b** and to exclude **3b'**.

hand, all data are in excellent agreement with the structure of 4,5-dihydro-1*H*-1,2,3-triazole **3b**. Such a compound bears a C_2-symmetric pyrrolidine ring if we assume that rapid inversion of the nitrogen atom and rotation around the bridgehead-carbon/nitrogen axis occur. Consequently, only two ^{13}C NMR signals result from the pyrrolidine unit of **3b**; however, the four corresponding protons at C-2 and C-5 give two different signals in the ^{1}H NMR spectrum (δ = 2.38–2.44, δ = 2.59–2,64) because of the asymmetric (chiral) bicyclic moiety of the molecule. Our structure assignment was further confirmed by gCOSY, gHSQCAD and CIGAR (8–3 Hz) NMR experiments.[13] Moreover, the ^{1}H NMR spectrum of the compound **3b** was highly compatible with that of a similar cycloaddition product, which resulted from treatment of 2-morpholinocyclohex-2-enone with phenyl azide.[10] Finally, we conducted 1D NOESY experiments to confirm the regioselectivity in the formation of **3b** and the *cis* stereochemistry of the bicyclic substructure. No nuclear Overhauser effect was observed between the

View Article Online
DOI: 10.1039/C6NJ03835B

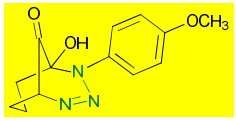
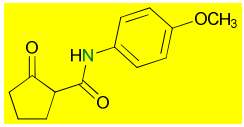
bridgehead proton and 2-H' of the aryl group, which excludes the alternative structure **3b'** (Scheme 2). On the other hand, the strong effect between the pyrrolidine protons (2-H/5-H) and the bridgehead proton provides evidence of the *cis*-fused bicyclic structure of **3b**.

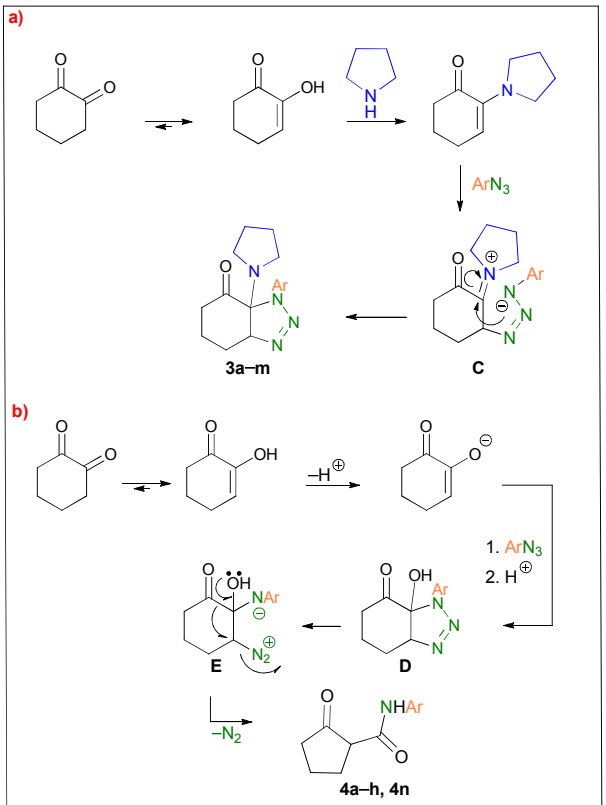
Aditionally, we also studied the reaction of cyclohexane-1,2-dione with *p*-tolyl azide in the presence of pyrrolidine/THF and isolated the product **3e** instead of **1e**.[13] A possible mechanism for the formation of **3a–m** is detailed in Scheme 3a. It is well known in the literature that cyclohexane-1,2-dione and secondary amines lead to 2-aminocyclohex-2-enones.[14] Subsequent 1,3-dipolar cycloaddition to yield **3a-m** may include intermediate **C** or proceed in a synchronous mechanism.

Moreover, the described[8] reaction of cyclohexane-1,2-dione with 1-azido-4-methoxybenzene and diethylamine in chloroform was also repeated. Again, we isolated the same substance, which showed identical NMR data when compared to the previous report (Table 2).[8] However, our additional IR spectrum indicated the carbonyl groups of a ketone (1728 cm^{-1}) and an amide (1679 cm^{-1}), and an NH signal at 3341 cm^{-1} can also be assigned to an amide. These substructures are supported by the ^{1}H NMR data, which include a broad exchangeable NH Proton at δ = 8.63, and by two carbonyl carbon signals in the ^{13}C NMR spectrum (ketone δ = 217.11, amide δ = 164.23). Most importantly, the HR-MS data and the elemental analysis excluded the claimed[8] formula $C_{13}H_{15}N_3O_3$ (or $C_{13}H_{16}N_3O_3$ for M+H) and provided evidence for the real formula $C_{13}H_{15}NO_3$. Therefore, it is obvious that the formation of the product is accompanied by loss of dinitrogen, and the structure **2b** is wrong. We came to the conclusion that this structure has to be corrected to the *β*-ketoamide **4b**, which is a known[15b,e] compound. Our data of **4b** are identical with those that were previously published (Table 2).[15b,e] Especially, the triplet signal of 2-H (δ = 3.14, J = 9.4 Hz) is highly characteristic in all ^{1}H NMR spectra of products of type **4**. We also synthesised compound **4e** from cyclohexane-1,2-dione and *p*-tolyl azide in the presence of diethylamine in chloroform.[13] Furthermore, we prepared **4e** for comparision, additionally, from ethyl 2-oxocyclopentanecarboxylate and *p*-toluidine.[13]

A quick literature search for compounds like **4b** revealed that all the compounds **4a**–**h** are known in literature,[15] only **4n** is unknown.[16] The ^{1}H NMR and ^{13}C NMR spectra of these literature-known compounds are in perfect harmony with our own results and with the data which were reported[8] for the alleged 1,2,3-triazines **2**. However, we cannot easily explain

Table 2. Comparision of the data of supposed ketone **2b** and ketoamide **4b**.

Supposed product **2b**[8a] from cyclohexane-1,2-dione, diethylamine and 1-azido-4-methoxybenzene	Product **4b**[15b]	Product **4b** from cyclohexane-1,2-dione, diethylamine and 1-azido-4-methoxybenzene
		
Yellow solid; yield (71%); mp N.A.	mp 139 °C[15e]	Yellow solid; yield (47%); mp 137 °C; purified by flash chromatography (R_f = 0.41; SiO_2; Et_2O).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.83–1.89 (m, 1H), 2.06–2.11 (m, 1H), 2.31–2.44 (m, 4H), 3.13 (t, J = 10 Hz, 1H), 3.78 (s, 3H), 6.85 (d, J = 10 Hz, 2H), 7.44 (d, J = 10 Hz, 2H), 8.60 (br., 1H).	**^{1}H NMR (400 MHz, $CDCl_3$):** δ = 1.80–1.95 (m, 1H), 2.05–2.15 (m, 1H), 2.30–2.50 (m, 4H), 3.18 (t, 1H), 3.80 (s, 3H), 6.82 (d, 2H), 7.42 (d, 2H), 8.64 (s, 1H).	**^{1}H NMR (400 MHz, $CDCl_3$):** δ = 1.81–1.92 (m, 1H), 2.05–2.14 (m, 1H), 2.30–2.45 (m, 4H), 3.14 (t, ^3J = 9.4 Hz), 3.79 (s, 3H), 6.85 (d, ^3J = 8.8 Hz, 2H, 7.44 (d, ^3J = 8.8 Hz), 8.63 (br. s, 1H, NH).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.2, 25.7, 39.1, 54.5, 55.5, 114.1, 121.5, 130.9, 156.3, 164.2, 217.0	N.A.	**^{13}C NMR (100 MHz, $CDCl_3$):** δ = 20.21 (t, CH_2), 25.73 (t, CH_2), 39.11 (t, CH_2), 54.48 (d, *C*H), 55.44 (q, OCH_3), 114.05 (d, *C*–2' or *C*–3'), 121.50 (d, *C*–2' or *C*–3'), 130.83 (s, C_{quat}), 156.30 (s, C_{quat}), 164.23 (s, *C*ONH), 217.11 (*C*=O).
Anal. calcd. for N.A.	**Anal.**[15e] **calcd. for** $C_{13}H_{15}NO_3$: C 66.94, H 6.48, N 6.00; found: C 67.3, H 6.3, N 6.9	**Anal. calcd. for** $C_{13}H_{15}NO_3$: C 66.94, H 6.48, N 6.00; found: C 66.31, H 6.39, N 5.97
IR: N.A.	N.A.	**IR ($CHCl_3$, cm^{-1}):** 1728 (C=O), 1679 (CONH), 3341 (NH).
HR-MS (ESI): m/z calcd. for $C_{13}H_{16}N_3O_3$ [M]+ 262.1192; found: 262.1196		**HR-MS (ESI):** m/z calcd. for $C_{13}H_{15}NNaO_3$ [M + Na]$^+$ 256.0944; found: 256.0934



Scheme 3 a) Mechanism of formation of triazoles **3a–m**; b) formation of keto-amides **4a–h** and **4n**.

View Article Online
DOI: 10.1039/C6NJ03835B

the strong difference in the HR-MS data of the real products **4** and the claimed substances **2**. Perhaps, the substances of the authors[8] include impurities with higher molecular masses.

Scheme 3b represents the possible mechanism leading to the formation of β-ketoamides **4a**–**h** and **4n**.[17] Amine-induced deprotonation of cyclohexane-1,2-dione,[18] which mainly exists as 2-hydroxycyclohex-2-enone, and subsequent regioselective stepwise or synchronous 1,3-dipolar cycloaddition followed by reprotonation lead to triazole **D**. The cleavage of the weak N–N bond generates the zwitterion **E**, that loses dinitrogen with simultaneous ring contraction to form β-ketoamides **4a–h** and **4n**. Thus formation of an enamine is not necessary. This is compatible with the fact that **4** is also produced in the presence of other bases, such as DABCO or DBU, which cannot react with ketones to give enamines.

In summary, we have undoubtedly demonstrated that the reaction of cyclohexane-1,2-dione and aryl azides in the presence of secondary amines does not lead to bicyclic 1,2,3-triazines **1** and **2**. Instead, we isolated the cyclohexane-fused 5-amino-4,5-dihydro-1*H*-1,2,3-triazoles **3** and the 2-oxocyclopentanecarboxamides **4**, respectively. The corrected structures of **3** and **4** are in complete agreement with our spectroscopic data, and in case of known compounds **4**, these data are identical with those of published[15] product characterisations. The formation of **3** corresponds to the well known 1,3-dipolar cycloaddition chemistry of enamines and organic azides,[9] whereas surprising generation of **4** includes the decay of a bicyclic 4,5-dihydro-1*H*-1,2,3-triazole intermediate with carbocyclic ring contraction by migration of an acyl group. Compounds of type **4** can more easily be prepared by treatment of alkyl 2-oxocyclopentanecarboxylates with anilines,[19] in other cases, however, the new ring-contraction reaction of cycloalkane-1,2-diones and azides may be useful in organic synthesis.

Acknowledgements

The authors would like to thank Dr. Manfred Hagedorn for the measurement of CIGAR and 1D NOESY NMR spectra, and Ms. Jana Buschmann for providing the starting compounds.

Notes and references

1. (a) *Organic Azides, Syntheses and Applications*, ed. S. Bräse and K. Banert, Wiley, Chichester, 2010; (b) H. Tanimoto and K. Kakiuchi, *Nat. Prod. Commun.*, 2013, **8**, 1021–1034; (c) S. Bräse, C. Gil, K. Knepper and V. Zimmermann, *Angew. Chem. Int. Ed.*, 2005, **44**, 5188–5240; (d) E. F. V. Scriven and K. Turnbull, *Chem. Rev*., 1988, **88**, 297–368.

2. X. Zhang and Y. Zhang, *Molecules*, 2013, **18**, 7145–7159.

3. J.-F. Lutz, *Angew. Chem. Int. Ed*., 2007, **46**, 1018–1025.

4. A. Michael, *J. Prakt. Chem*. 1893, **48**, 94–95.

5. (a) R. Huisgen, *Angew. Chem. Int. Ed. Engl*., 1963, **2**, 565–598; (b) R. Huisgen, *Angew. Chem. Int. Ed. Engl*., 1963, **2**, 633–645.

6. (a) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem. Int. Ed*., 2001, **40**, 2004–2021; (b) V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem. Int. Ed*., 2002, **41**, 2597–2599; (c) C. W. Tornøe, C. Christensen and M. Meldal, *J. Org. Chem*. 2002, **67**, 3057–3064.

7. (a) K. Weigand, N. Singh, M. Hagedorn and K. Banert, *Org. Chem. Front*. 10.1039/c6qo00625f; (b) K. Banert, M. Hagedorn, C. Hemeltjen, A. Ihle, K. Weigand and H. Priebe, *ARKIVOC*, 2016, **v**, 338–361; (c) K. Banert, *Synthesis*, 2016, **48**, 2361–2375.

8. (a) X. Xu, Z. Shi and W. Li, *New. J. Chem*., 2016, **40**, 6559–6563; (b) Z. Shi, W. Li, X. Xu and X. Zhou, *Faming Zhuanli Shenqing*, 2016, CN 105646455 A 20160608.

9. (a) R. Fusco, G. Bianchetti and D. Pocar, *Gazz. Chim. Ital.* 1961, **91**, 849–865; (b) R. Fusco, G. Bianchetti, D. Pocar and R. Ugo, *Chem. Ber*., 1963, **96**, 802–812; (c) G. Bianchetti, D. Pocar, P. D. Croce and A. Vigevani, *Chem. Ber*., 1965, **98**, 2715–2724; (d) R. Huisgen, G. Szeimies and L. Möbius, *Chem. Ber*. 1967, **100**, 2494–2507; (e) G. Bianchetti, P. D. Croce and D. Pocar, *Tetrahedron Lett*., 1965, 2039–2041.

10. G. I. Polozov and I. G. Tishchenko, *Vestn. Akad. Nauk Bel. SSR, Ser. Khim. Nauk*, 1978, 62–69.

11. For NMR data of other comparable iminium salts, see: (a) H. Guan, M. Iimura, M. P. Magee, J. R. Norton and G. Zhu, *J. Am. Chem. Soc*., 2005, **127**, 7805–7814; (b) C. Rabiller, J. P. Renou and G. J. Martin, *J. Chem. Soc., Perkin Trans. 2*., 1977, 536–541.

12. For ^{13}C NMR data of comparable heterocycles with N and O atoms, see: K. Banert, J. Lehmann, H. Quast, G. Meichsner, D. Regnat and B. Seiferling, *J. Chem. Soc., Perkin Trans. 2*., 2002, 126–134.

13. See Electronic Supporting Information (ESI) for further details.

14. (a) Y. Matsumoto, R. Tsuzuki, A. Matsuhisa, K. Takayama, T. Yoden, W. Uchida, M. Asano, S. Fujita, I. Yanagisawa and T. Fujikura, *Chem. Pharm. Bull*., 1996, **44**, 103–114; (b) U. Kuckländer and B. Schneider, *Chem. Ber*., 1986, **119**, 3487–3491; (c) H. Ottinger, T. Soldo and T. Hofmann, *J. Agric. Food Chem*., 2001, **49**, 5383–5390; (d) N. S. Kozlov and V. N. Kovaleva, *Zh. Org. Khim*., 1973, **9**, 2254–2256.

15. For an alternative synthesis of **4a**, see: (a) M. Presset, Y. Coquerel and J. Rodriguez, *J. Org. Chem.*, 2009, **74**, 415–418; for **4b**: (b) T. L. Andreana, S. S. Y. Cho, J. M. Graham, T. F. Gregory, H. R. Howard, Jr., B. E. Kornberg, S. S. Nikam and D. A. Pflum, *PCT Int. Appl*., 2004, WO 2004026864; for **4c**: (c) M. M. Sanchez Duque, O. Baslé, N. Isambert, A. Gaudel-Siri, Y. Génisson, J.-C. Plaquevent, J. Rodriguez and T. Constantieux, *Org. Lett*., 2011, **13**, 3296–3299; for **4d**: (d) H. C. Barany and M. Pianka, *J. Chem. Soc*., 1947, 1420–1421; for **4b**, **4e** and **4f**: (e) R. J. Brown, F. W. S. Carver and B. L. Hollingsworth, *J. Chem. Soc.*, 1961, 4295–4298; for **4g**: (f) F. D. Popp, W. R. Schleigh, P. M. Froehlich, R. J. Dubois and A. C. Casey, *J. Org. Chem*., 1968, **33**, 833–834; for **4h**: (g) S. Jaroch, H. Rehwinkel, P. Hölscher, D. Sülzle, M. Hillmann, G. A. Burton and F. M. McDonald, *PCT Int. Appl*., 1999, WO 9941240.

16. For a related compound, see: K. Mohanan, Y. Coquerel and J. Rodriguez, *Org. Lett*., 2012, **14**, 4686–4689.

17. We would also like to suggest that compounds **4a**–**h** and **4n**, should be stable in their *anti* conformation with an

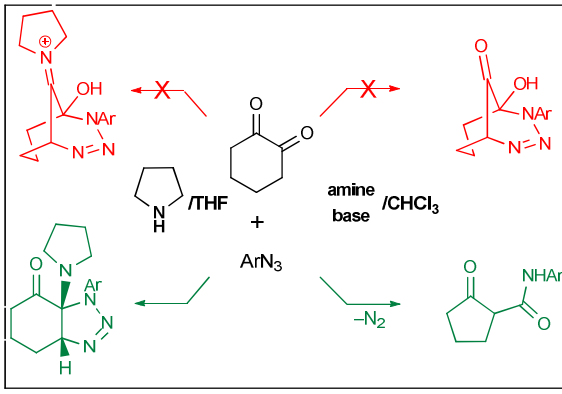
View Article Online
DOI: 10.1039/C6NJ03835B

intramolecular H-bond; for other examples, see: D. Mailhol, M. M. Sanchez Duque, W. Raimondi, D. Bonne, T. Constantieux, Y. Coquerel and J. Rodriguez, *Adv. Synth. Catal*., 2012, **354**, 3523−3532.

18. A. Feigenbaum, J.-P. Pete and A. Poquet-Dhimane, *Tetrahedron Lett.*, 1988, **29**, 73−74.

19. (a) D. H. Johnson, *J. Chem. Soc*., 1958, 1624−1628; (b) B. K. Blount, W. H. Perkin, Jr. and S. G. P. Plant, *J. Chem. Soc*., 1929, 1975−1987.

View Article Online
DOI: 10.1039/C6NJ03835B



The products, generated from cyclohexane-1,2-dione, amines and aryl azides, do not contain bicyclic 1,2,3-triazine structures because cyclohexane-fused 4,5-dihydro-1,2,3-triazoles and moncyclic β-ketoamides are formed instead.

Neeraj Singh, Klaus Banert*