# ChemComm

Chemical Communications www.rsc.org/chemcomm



ISSN 1359-7345



#### COMMUNICATION

A. Stephen K. Hashmi, Douglas W. Stephan *et al.* B( $C_pF_5$ )<sub>3</sub> promoted cyclisation of internal propargyl esters: structural characterisation of 1,3-dioxolium compounds

## ChemComm

### COMMUNICATION

Cite this: Chem. Commun., 2014, 50, 7243

Received 21st February 2014, Accepted 1st May 2014

DOI: 10.1039/c4cc01370k

www.rsc.org/chemcomm

# B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> promoted cyclisation of internal propargyl esters: structural characterisation of 1,3-dioxolium compounds<sup>†</sup>

Max M. Hansmann, $\ddagger^a$  Rebecca L. Melen, $\ddagger^b$  Frank Rominger,<sup>a</sup> A. Stephen K. Hashmi<sup>\*ac</sup> and Douglas W. Stephan<sup>\*bc</sup>

The reactions of internal propargyl esters with  $B(C_6F_5)_3$  provide access to stable zwitterionic 1,3-dioxolium compounds which are characterised by X-ray diffraction. These  $6\pi$ -electron systems show no significant aromatic stabilisation.

The 1,2-addition of the Lewis acid B( $C_6F_5$ )<sub>3</sub> and a Lewis base to alkynes is well precedented.<sup>1,2</sup> Recently, we have extended this methodology to generate zwitterionic oxazolium borate species *via* B( $C_6F_5$ )<sub>3</sub> promoted intramolecular cyclisation reactions of a range of propargyl amides.<sup>3</sup> Related reactions with propargyl esters are thought to proceed *via* a similar initial cyclisation, however, subsequent 1,2- $C_6F_5$  group migration proceeds rapidly with concurrent ring-opening to afford a series of stable allyl-boron compounds.<sup>4</sup> These species in turn prove useful for allylation reactions with aldehydes.<sup>4</sup> In all these cases the propargyl esters employed possessed terminal alkynes.

1,3-Dithiolium and 1,3-oxathiolium compounds are known but few 1,3-dioxolium compounds have been isolated.<sup>5</sup> The enhanced stability of the S-analogues has been ascribed to the increased covalency in the  $\sigma$ -bonds and increased delocalisation of the  $\pi$ electrons within the ring affording a more stable heterocyclic system.<sup>6</sup> On the other hand, 1,3-dioxolium ions exhibit substantially more polar localised bonding and are highly reactive, particularly with respect to attack by nucleophiles including water at the C(1) position.<sup>7</sup> In addition to their instability, the synthesis involves highly reactive species such as acyl triflates and alkenyldiazo compounds.<sup>7</sup> 1,3-Dioxolium compounds have been proposed as highly reactive intermediates in some transformations.<sup>8</sup> The first 1,3-dioxolium salts



CHEMISTRY

**View Article Online** 

reported were characterised in solution by Olah et al. and Meier et al. via protonation of the corresponding cyclic carbonates in a superacidic medium,9 although none have been structurally characterised. In these cases, additional stabilisation has been afforded by the incorporation of either conjugated heteroatoms (Fig. 1),<sup>9,10</sup> which aid the delocalisation of the positive charge, or a benzo-fused ring, affording the more stable 1,3-benzodioxolium derivatives (Fig. 1).<sup>11</sup> Examples of electro-neutral zwitterionic 1,3-dioxolium salts have not been isolated and have only inferred via cycloaddition trapping reactions.<sup>12</sup> Herein, we report a facile one-pot synthesis of zwitterionic 1,3-dioxolium compounds which do not contain charge stabilising heteroatoms. These 1,3-dioxolium species are formed from a multistep reaction involving the reaction of internal propargyl esters with  $B(C_6F_5)_3$ . Three such species are fully characterized and the first X-ray crystallographic studies of 1,3-dioxolium compounds allows an investigation of the bonding within these 1,3-dioxolium products.

The reaction of **1** with  $B(C_6F_5)_3$  in a 1 : 1 ratio in toluene resulted in the formation of the 1,3-dioxolium compound **4** (Scheme 1). While exclusion of water was paramount to its isolation, the compound proved to be remarkable stable towards temperature and moisture, presumably a result of its zwitterionic character. Compound **4** was



Scheme 1 Synthesis of 1,3-dioxolium compounds.

<sup>&</sup>lt;sup>a</sup> Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg,

Im Neuenheimer Feld 270, 69120 Heidelberg, Germany. E-mail: hashmi@hashmi.de <sup>b</sup> Department of Chemistry, 80 St. George Street, University of Toronto, Toronto,

Ontario, Canada M5S 3H6. E-mail: dstephan@chem.utoronto.ca

<sup>&</sup>lt;sup>c</sup> Chemistry Department, Faculty of Science, King Abdulaziz University (KAU), Jeddah 21589, Saudi Arabia

<sup>†</sup> Electronic supplementary information (ESI) available: NMR data, DFT calculations and details of the crystal structure determination. CCDC 987406 (4) and 987407 (5). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc01370k.

<sup>‡</sup> These authors contributed equally.



**Fig. 2** POV-ray depiction of the molecular structure of **4** (top) and **5** (bottom). C: black, H: white, O: red, B: yellow-green, F: pink. Hydrogen atoms are omitted for clarity.

fully characterised by multinuclear NMR spectroscopy (<sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B and <sup>19</sup>F), elemental analysis and mass spectrometry. Importantly, the <sup>11</sup>B NMR spectrum showed a sharp singlet at  $\delta = -14.3$  ppm typical for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> bonded to an sp<sup>3</sup> hybridised carbon atom.<sup>2</sup>

On standing for 4 days, a solution of 4 afforded small colourless crystals of 4 which were isolated in 41% yield. An X-ray diffraction analysis confirmed the structure of the 1,3-dioxolium compound 4 (Fig. 2, top). In a similar fashion, the internal propargyl esters derived from 3-hexyne-1-ol (R = p-tol 2, tBu 3) react in a 1:1 ratio with  $B(C_6F_5)_3$ to yield the analogous 1,3-dioxolium compounds (R = p-tol, 4 tBu 6) which were isolated in high yields of 85% and 78% respectively (Scheme 1). These reactions of both propargyl esters (2 and 3) are very clean and proceed quantitatively based on in situ NMR studies in 12 h at 50 °C. It is also interesting to note that the combination of the propargyl ester *p*-tolCO<sub>2</sub>CH<sub>2</sub>CCtBu and  $B(C_6F_5)_3$  resulted in no reaction, even on heating to 50 °C for 24 h. This latter observation demonstrates a steric limit on the  $\pi$ -activation and cyclisation reaction affording the 1,3-dioxolium species. In the case of the 1,3-dioxolium compound 5, single crystals suitable for X-ray diffraction could be obtained by slow vapour diffusion of pentane into a saturated solution of 5 in dichloromethane at -20 °C (Fig. 2, bottom).

In the structural studies of 4 and 5, the five-membered heterocycles are essentially planar as evidenced by the maximum deviation from planarity of 0.003 Å (4) and <0.002 Å (5) and the phenyl ring at the C(1) position lies essentially in the same plane as the dioxolium ring; the angle between the phenyl and dioxolium ring planes is only  $5.21^{\circ}$  (4) and  $1.18^{\circ}$  (5). The co-planarity of the two rings offers some potential for stabilisation of the positive charge by delocalisation,

Table 1 Experimental and calculated metrics in 4 and 5

|                         | Obs. (4)                   | Obs. (5)       | $\operatorname{Calc.}^{a}(4)$ | Calc.b (4) |
|-------------------------|----------------------------|----------------|-------------------------------|------------|
| Bond length             | /Å                         |                |                               |            |
| $C_2-C_3$               | 1.331(2)                   | 1.328(3)       | 1.354                         | 1.355      |
| $C_2 - O_2$             | 1.417(2)                   | 1.420(3)       | 1.414                         | 1.412      |
| $C_3 - O_1$             | 1.425(2)                   | 1.418(3)       | 1.411                         | 1.413      |
| $O_1 - C_1$             | 1.300(2)                   | 1.304(3)       | 1.300                         | 1.301      |
| $O_2$ - $C_1$           | 1.301(2)                   | 1.294(3)       | 1.308                         | 1.306      |
| Bond angle/             | >                          |                |                               |            |
| $O_2 - C_2 - C_3$       | 107.4(2)                   | 107.4(2)       | 107.5                         | 107.3      |
| $C_2 - C_3 - O_1$       | 106.3(2)                   | 106.4(2)       | 105.4                         | 105.5      |
| $C_3 - O_1 - C_1$       | 107.4(1)                   | 107.4(2)       | 108.8                         | 108.4      |
| $O_1 - C_1 - O_2$       | 111.8(1)                   | 111.9(2)       | 111.2                         | 111.5      |
| $C_1 - O_2 - C_2$       | 107.1(1)                   | 107.0(2)       | 107.1                         | 107.2      |
| <sup>a</sup> B3LYP/6-31 | G* level. <sup>b</sup> B3L | YP/cc-pVDZ lev | vels of theory.               |            |

consistent with a shorter C–C single bond length between these rings of 1.427(3) Å (4) and 1.4343(2) Å (5). Within the dioxolium ring, the C(2)–C(3) bond length amounts to 1.331(2) Å (4) and 1.328(3) Å (5) which are typical for a C—C double bond<sup>13</sup> (Table 1). The C(1)–O(1) and C(1)–O(2) bond lengths (Table 1) are the same within experimental error and considerably shorter than the C(2)–O(2) and C(3)–O(1) bonds indicating some delocalisation across the OCO fragment. These observed distances in 4 and 5 are similar to those in the known species [RCO<sub>2</sub>C<sub>2</sub>Me<sub>4</sub>]X (R = Ph, X = ICl<sub>2</sub>;<sup>14</sup> R = Me, X = ClO<sub>4</sub><sup>15</sup>) and [PhCO<sub>2</sub>CH<sub>2</sub>C—CHB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>4</sup> and significantly shorter than those typical of 1,3-dioxolanes.<sup>14</sup>

The mechanism of these reactions are thought to involve the initial activation of alkyne unit of the propargyl ester by  $B(C_6F_5)_3$ . This prompts an intramolecular 5-exo-1,2-addition reaction across the alkyne unit to afford the cyclic anti-oxyboration intermediate I (Scheme 2). Analogous reactivity was observed in the cyclisation of propargyl amides and terminal propargyl esters with  $B(C_6F_5)_3$ .<sup>3,4</sup> In situ <sup>11</sup>B NMR studies show that reaction of  $B(C_6F_5)_3$  with 2 proceed via a transient species which gives rise to a resonance at -16.0 ppm. This is attributed to species I which undergoes ring-opening to give the carbocation II. Subsequent ring-closure yields III which then undergoes a 1,3-boron allyl shift to afford the 1,3-dioxolium product 4. Similar 1,3-boron allyl shifts have been observed previously in the rearrangement of allyl boranes to isomers where the boron atom is situated on the least substituted carbon atom.4 This mechanism closely resembles that observed for the reactions of transition metals with propargyl esters which rapidly undergo ring opening.<sup>16</sup> It is noteworthy that when the starting propargyl ester contains a terminal alkyne, ring-opening of I proceeds with concurrent 1,2-C<sub>6</sub>F<sub>5</sub> shift to form IV which is followed by a 1,3-boron allyl shift to give the sixmembered intramolecular chelate (V) (Scheme 2).

The nature of the bonding within 4 was examined by DFT calculations (B3LYP/6-31G\* and cc-pVDZ) and an NBO analysis. The calculated structure showed good agreement with the experimental findings having similar bond lengths and angles (Table 1). In principle, the 5-membered dioxolium ring system could be considered aromatic (VI, Fig. 3) since it possesses  $6\pi$ -electrons, although this is the subject of some debate.<sup>7,9b,c</sup> NBO analysis of the gas-phase geometry-optimised structure of the present compounds revealed no significant delocalisation



Scheme 2 Proposed mechanisms of reactions of propargyl esters with  $B(C_6F_5)_{3\cdot}$ 



within the dioxolium ring. Bond orders and partial charges indicated that the description as a carbenium ion stabilised by two oxygen atoms along with an endocyclic C==C double bond is appropriate (VII, Fig. 3). This view is consistent with the computed partial positive charge of +0.82 at C(1) and partial negative charges of -0.41 and -0.43 at the adjacent oxygen atoms. A second order perturbation analysis of the NBO data reveal donation of the oxygen lone pairs from O(1) and O(2) and the  $\pi$ -electron density from the aryl substituent stabilise the carbocation centre at C(1). The C(2)–C(3) bond within the ring is thus considered an isolated double bond. Whilst the HOMO is based on the perfluoroaryl group, the LUMO is delocalised over the dioxolium and tolyl groups. Notably the largest coefficient is at C(1) consistent with the tendency for nucleophilic attack at this position.

The present reactivity of internal propargyl esters with  $B(C_6F_5)_3$  reveals a different reaction pathway to that observed for the analogous propargyl derivatives bearing a terminal alkyne fragment. The internal alkyne derivatives give rise to stable dioxolium compounds affording the first structural characterisation of such 1,3 dioxolium species. These data together with DFT calculations reveal that

these five-membered rings are not aromatic but best described as an isolated C—C double bond along with a carbenium ion stabilised by two oxygen atoms.

NSERC of Canada is thanked for financial support. D.W.S. is grateful for the award of a Canada Research Chair. M.M.H. is grateful to the Fonds der Chemischen Industrie for a Chemiefonds scholarship and the Studienstiftung des deutschen Volkes. We thank Dr Matthias Rudolph (Heidelberg) for helpful discussions.

#### Notes and references

- For a general overview, see: (a) R. L. Melen, Chem. Commun., 2014, 50, 1161; for the unique properties of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, see the following reviews: (b) W. E. Piers and T. Chivers, Chem. Soc. Rev., 1997, 26, 345; (c) W. E. Piers, Adv. Organomet. Chem., 2004, 52, 1; (d) G. Erker, Dalton Trans., 2005, 1883; (e) W. E. Piers, A. J. V. Marwitz and L. G. Mercier, Inorg. Chem., 2011, 50, 12252.
- 2 (a) J. S. J. McCahill, G. C. Welch and D. W. Stephan, Angew. Chem., Int. Ed., 2007, 46, 4968; (b) A. Fukazawa, H. Yamada and S. Yamaguchi, Angew. Chem., Int. Ed., 2008, 47, 5582; (c) M. A. Dureen and D. W. Stephan, J. Am. Chem. Soc., 2009, 131, 8396; (d) M. A. Dureen, C. C. Brown and D. W. Stephan, Organometallics, 2010, 29, 6422; (e) C. Jiang, O. Blacque and H. Berke, Organometallics, 2010, 29, 125; (f) T. Voss, C. Chen, G. Kehr, E. Nauha, G. Erker and D. W. Stephan, G. Erker, J., 2010, 16, 3005; (g) C. Chen, R. Fröhlich, G. Kehr and G. Erker, Organometallics, 2011, 30, 5222; (i) T. Voss, T. Mahdi, E. Otten, R. Fröhlich, G. Kehr, D. W. Stephan and G. Erker, Organometallics, 2011, 30, 5222; (i) T. Voss, T. Mahdi, E. Otten, R. Fröhlich, G. Kehr, D. W. Stephan and G. Erker, Organometallics, 2012, 31, 2367.
- 3 R. L. Melen, M. M. Hansmann, A. J. Lough, A. S. K. Hashmi and D. W. Stephan, *Chem. – Eur. J.*, 2013, **19**, 11928.
- 4 M. M. Hansmann, R. L. Melen, F. Rominger, A. S. K. Hashmi and D. W. Stephan, *J. Am. Chem. Soc.*, 2014, **136**, 777.
- 5 H. Perst, Sci. Synth., 2001, 11, 13.
- 6 W. Kosmus and K. Kalcher, J. Crystallogr. Spectrosc. Res., 1983, 13, 143.
  7 The only current example of 1,3-dioxolium compounds without charge stabilising atoms at C-2 is limited to: W. Lorenz and G. Maas, J. Org. Chem., 1987, 52, 375.
- 8 (a) A. D. Allen, T. Kitamura, R. A. McClelland, P. J. Stang and T. T. Tidwell, *J. Am. Chem. Soc.*, 1990, **112**, 8873; (b) T. Schwier, A. W. Sromek, D. M. L. Yap, D. Chernyak and V. Gevorgyan, *J. Am. Chem. Soc.*, 2007, **129**, 9868.
- 9 (a) G. A. Olah and A. M. White, J. Am. Chem. Soc., 1968, 90, 1884;
  (b) G. A. Olah and J. L. Grant, J. Org. Chem., 1977, 42, 2237;
  (c) U. Timm, U. Plücken, H. Petersen and H. Meier, J. Heterocycl. Chem., 1979, 16, 1303; (d) H. Mayr and U. von der Brüggen, Chem. Ber., 1988, 121, 339.
- 10 (a) P. R. Moses, J. Q. Chambers, J. O. Sutherland and D. R. Williams, J. Electrochem. Soc., 1975, **122**, 608; (b) R. D. Braun and D. C. Green, J. Electroanal. Chem., 1977, **79**, 381; (c) G. Maas and B. Singer, Chem. Ber., 1983, **116**, 3639.
- (a) H. Gross and J. Rusche, Angew. Chem., Int. Ed., 1964, 3, 511;
   (b) K. Dimroth, P. Heinrich and K. Schromm, Angew. Chem., Int. Ed., 1965, 4, 873; (c) H. Volz and G. Zimmermann, Tetrahedron Lett., 1970, 3597.
- 12 (a) M. Hamaguchi and T. Nagai, J. Chem. Soc., Chem. Commun., 1985, 190; (b) M. Hamaguchi and T. Nagai, J. Chem. Soc., Chem. Commun., 1985, 1319.
- 13 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans.* 2, 1987, S1.
- 14 (a) M. R. Caira and J. F. de Wet, Acta Crystallogr., 1981, B37, 709;
  (b) R. F. Childs, R. M. Orgias, C. J. L. Lock and M. Mahendran, Can. J. Chem., 1993, 71, 836; (c) R. F. Childs, C. S. Frampton, G. J. Kang and T. A. Wark, J. Am. Chem. Soc., 1994, 116, 8499.
- (a) H. Paulsen and R. Dammeyer, *Chem. Ber.*, 1973, 106, 2324;
  (b) H. Paulsen and R. Dammeyer, *Chem. Ber.*, 1976, 109, 1837.
- 16 See: P. Mauleon and F. D. Toste, Gold-Catalyzed Reactions of Propargyl Esters, Propargyl Alcohols, and Related Compounds, in *Modern Gold Catalyzed Synthesis*, ed. A. S. K. Hashmi and F. D. Toste, 2012, Wiley-VCH Verlag GmbH & Co, KGaA, Weinheim, Germany, and references therein.