Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2008, **18**, 16–17
Mendeleev Communications

Unusual reactions of 1-(alk-1-ynyl)-1-chlorocyclopropanes with lithium monoalkylamides

Konstantin N. Shavrin,[a] Valentin D. Gvozdev,*[a] Serafim V. Yurov[b] and Oleg M. Nefedov[a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: vgvozdev2006@yandex.ru*
[b] *D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2008.01.007

Depending on the substituent at the triple bond, the reaction of 1-(alk-1-ynyl)-1-chlorocyclopropanes 1 with lithium monoalkylamides in THF gives hitherto unknown conjugated iminocyclopropenes 2 or 4-substituted 1,1-dimethylbuta-1,2-dienes 3 in up to 60% yields.

Recently,[1] we found that the reaction of 1-(alk-1-ynyl)-1-chlorocyclopropanes **1** with lithium dialkylamides in THF results in hitherto unknown 1-dialkylamino-2-alkynylcyclopropanes, which are formed by the addition of dialkylamide anions to intermediate conjugated alkynylcyclopropenes. In continuation, we studied the reactions of 1-(alk-1-ynyl)-1-chlorocyclopropanes **1** with various lithium monoalkylamides.

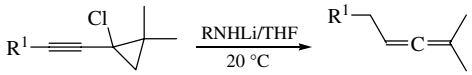
Unexpectedly, the addition of 1-chloro-2,2-dimethyl-1-phenylethynylcyclopropane **1a** to a fivefold excess of lithium monoalkylamides in THF at 20 °C gave conjugated iminocyclopropenes **2a**–**c**† in 50–60% yields rather than expected alkynyl(monoalkylamino)cyclopropanes (Scheme 1).

1a

2a R = Me
2b R = Pr
2c R = Bu

Scheme 1

However, under the same conditions, the reaction of lithium monoalkylamides with alkynylchlorocyclopropanes **1b**,**c** carrying bulky substituents such as *tert*-butyl and adamantyl at the triple bond gave 4-(*tert*-butyl)- and 4-(adamant-1-yl)-1,1-dimethylbuta-1,2-dienes **3a**,**b**,† respectively, in 40–50% yields; the latter compounds had one carbon atom less than the original ones (Scheme 2).



1b R^1 = Bu^t
1c R^1 = Ad

3a R^1 = Bu^t
3b R^1 = Ad

R = Me, Pr, Bu

Scheme 2

By analogy with the reactions of lithium dialkylamides with chlorides **1**, it can be assumed that the reactions of the latter with lithium monoalkylamides most likely proceed *via* intermediate alkynylcyclopropenes **4**. This assumption is supported, for example, by the fact that the reaction of 1-(*tert*-butylethynyl)-3,3-dimethylcyclopropene[1] **4b** with an excess of lithium propylamide results in corresponding allene **3a**. Resulting alkynylcyclopropenes **4** add monoalkylamide ions to the double bond of the cyclopropene ring to give 1-(alk-1-ynyl)-2-(alkylamino)cyclopropanes **5**; subsequent transformations of the latter under the conditions used are governed by the nature of the substituent at the triple bond. In the case of the electronegative phenyl group, the main reaction pathway involves the intramolecular addition of the amino group to the triple bond followed by its abstraction from the cyclopropane ring to give eventually corresponding iminocyclopropenes **2a**–**c**. In the case of electron-donating *tert*-butyl or adamantyl groups, a rearrangement into corresponding intermediate iminocyclopropanes **6** is most likely to occur. The latter decompose with elimination of an isonitrile to give allenes **3a**,**b**, similarly to the known precedents[2,3] (Scheme 3).

† The structures of the new compounds obtained were proved by ^{1}H and ^{13}C NMR and mass spectra. NMR spectra were measured on a Bruker AC200p spectrometer (200 and 50 MHz for ^{1}H and ^{13}C, respectively) in $CDCl_3$ solutions. Mass spectra were determined on a Finnigan MAT INCOS-50 mass spectrometer.

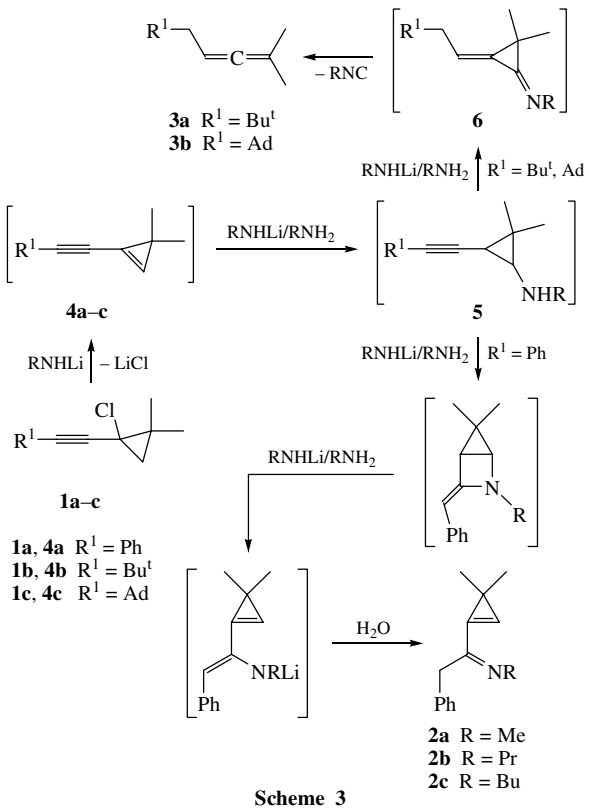
For **2a**: ^{1}H NMR, δ: 1.27 (s, 6H, 2Me), 2.50 (q, 2H, CH_2, J 1.3 Hz), 3.29 (t, 3H, NMe, J 1.3 Hz), 6.78 (s, 1H, =CH, *cyclo*-C_3H), 7.24–7.43 (m, 3H, *m*-H, *p*-H in Ph), 7.68–7.73 (m, 2H, *o*-H in Ph). ^{13}C NMR, δ: 28.7 (2Me), 40.3 (CMe$_2$), 40.8 (NMe), 43.3 (CH_2), 127.4, 127.8, 128.0 (Ph), 133.7 (C-1 in Ph), 141.2 (C=CH), 155.5 (C=CH), 176.5 (C=NMe). MS, *m*/*z*: 199 [M$^+$].

For **2b**: ^{1}H NMR, δ: 1.06 (t, 3H, Me in Pr, J 6.9 Hz), 1.29 (s, 6H, 2Me), 1.69–1.85 (m, 2H, CH_2), 2.52 (t, 2H, CH_2, J 1.2 Hz), 3.37 (tt, 2H, NCH_2, J 7.1 Hz, J 1.2 Hz), 6.80 (s, 1H, =CH, *cyclo*-C_3H), 7.25–7.45 (m, 3H, *m*-H, *p*-H in Ph), 7.75–7.82 (m, 2H, *o*-H in Ph). ^{13}C NMR, δ: 12.3 (Me in Pr), 23.0 (CH_2 in Pr), 29.0 (2Me), 40.5 (CMe$_2$), 43.7 (CH_2), 55.8 (NCH_2), 127.5, 128.0, 128.6 (Ph), 134.0 (C-1 in Ph), 141.1 (C=CH), 155.3 (C=CH), 174.3 (C=NPr). MS, *m*/*z*: 227 [M$^+$].

For **2c**: ^{1}H NMR, δ: 1.05 (t, 3H, Me in Bu, J 6.9 Hz), 1.29 (s, 6H, 2Me), 1.42–1.63 (m, 2H, CH_2), 1.70–1.85 (m, 2H, CH_2), 2.51 (t, 2H, CH_2, J 1.2 Hz), 3.42 (tt, 2H, NCH_2, J 7.1 Hz, J 1.2 Hz), 6.71 (s, 1H, =CH, *cyclo*-C_3H), 7.25–7.44 (m, 3H, *m*-H, *p*-H in Ph), 7.68–7.73 (m, 2H, *o*-H in Ph). ^{13}C NMR, δ: 14.0 (Me in Bu), 20.8 (CH_2 in Bu), 28.9 (2Me), 33.0 (CH_2 in Bu), 40.3 (CMe$_2$), 43.5 (CH_2), 53.6 (NCH_2), 127.5, 127.9, 128.4 (Ph), 133.9 (C-1 in Ph), 141.0 (C=CH), 155.1 (C=CH), 174.1 (C=NBu). MS, *m*/*z*: 241 [M$^+$].

For **3a**: ^{1}H NMR, δ: 0.89 (s, 9H, 3Me), 1.56 (d, 6H, CMe_2, J 3.0 Hz), 1.83 (d, 2H, CH_2CMe_3, J 7.8 Hz), 4.89 (t sept., 1H, CH_2CH=, J 7.8 Hz, J 3.0 Hz). ^{13}C NMR, δ: 20.7 (2Me), 29.0 (CMe_3), 31.1 (CMe_3), 44.2 (CH_2CMe_3), 85.6 (CH_2CH=), 93.2 (=CMe$_2$), 203.2 (=C=). MS, *m*/*z*: 138 [M$^+$].

For **3b**: ^{1}H NMR, δ: 1.51 (d, 6H, 2Me, J 2.8 Hz), 1.63–1.71 (m, 6H, 3CH_2 in Ad), 1.70 (d, 6H, 3CH_2 in Ad, J 2.7 Hz), 1.72 (d, 2H, CH_2Ad, J 7.9 Hz), 1.92–2.02 (m, 3H, 3CH in Ad), 4.89 (t sept., 1H, CH_2CH=, J 7.9 Hz, J 2.8 Hz). ^{13}C NMR, δ: 20.8 (2Me), 28.9 (2CH in Ad), 33.1 (C-1 in Ad), 37.3 (3CH_2 in Ad), 42.3 (3CH_2 in Ad), 44.8 (CH_2Ad), 84.2 (CH_2CH=), 93.1 (=CMe$_2$), 203.3 (=C=). MS, *m*/*z*: 216 [M$^+$].



Scheme 3

This study was supported by the Russian Foundation for Basic Research (project no. 06-03-33045-a), the Russian Academy of Sciences (project no. OKh-01) and the President of the Russian Federation (Programme for the Support of Leading Scientific Schools, grant no. NSh-6075.2006.3).

References

1 K. N. Shavrin, V. D. Gvozdev, D. V. Budanov, S. V. Yurov and O. M. Nefedov, *Mendeleev Commun.*, 2006, 73.
2 H. Quast, A. Fuss, A. Heublein, H. Jakobi and B. Seiferling, *Chem. Ber.*, 1991, **124**, 2545.
3 H. Quast and G. Meichsner, *Chem. Ber.*, 1987, **120**, 1049.

Received: 24th July 2007; Com. 07/2986