Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2006, 16(2), 73–76
Mendeleev Communications

1-(Alk-1-ynyl)cyclopropenes: synthesis by interaction of 1-(alk-1-ynyl)-1-halocyclopropanes with lithium *N*,*N*-dialkylamides and subsequent additions of the latter

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

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 135 5328; e-mail: vgvozdev2006@yandex.ru*
[b] *The Higher Chemical College, Russian Academy of Sciences, 125047 Moscow, Russian Federation*
[c] *D. I. Mendeleev Russian University of Chemical Technology, 125047 Moscow, Russian Federation*

DOI: 10.1070/MC2006v016n02ABEH002267

A new synthetic approach to 1-(alk-1-ynyl)cyclopropenes 2 by the reaction of 1-(alk-1-ynyl)-1-chlorocyclopropanes 1 with lithium *N*,*N*-dialkylamides has been developed. Alkynylcyclopropenes 2, obtained by this method *in situ* or isolated in individual state can add dialkylamide anions across the double bond of the cyclopropene fragment to give hitherto unknown alkynyl-(dialkylamino)cyclopropanes 3, 4.

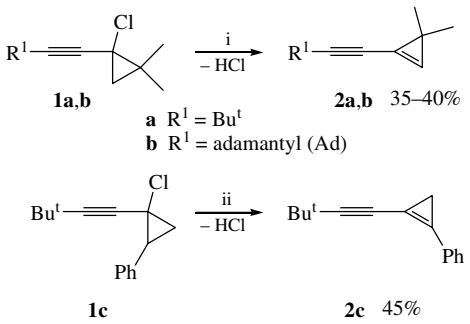
The syntheses of only a few 1-(alk-1-ynyl)cyclopropenes have been reported.[1,2] The first representative of this class of compounds, 3,3-dimethyl-2-phenyl-1-phenylethynylcyclopropene, was obtained by the photolysis of a corresponding 3*H*-pyrazole.[1] Two other alkynylcyclopropenes, 2-trimethylsilylethynyl- and 2-phenylethynyl-substituted 3,3-dimethyl-1-trimethylsilylcyclopropenes,[2] were synthesised by the reaction of (3,3-dimethyl-2-trimethylsilylcyclopropen-1-yl)zinc chloride with 1-bromo-2-trimethylsilyl- and 1-bromo-2-phenylacetylenes, respectively, in the presence of $Pd(PPh_3)_4$ as the catalyst. Alkynylcyclopropenes are of interest due to the combination of highly-reactive triple bond and unsaturated three-membered ring in one molecule. However, there are almost no data on reactions involving these compounds. An attempt to obtain the simplest representative of these compounds, 1-ethynylcyclopropene, gave just a product of its dimerisation by [2+2] cycloaddition,[3] and the reaction of 3,3-dimethyl-2-phenyl-1-phenylethynylcyclopropene with 2-diazopropane occurred as [1,3]-dipolar cycloaddition of the latter to the double bond of the cyclopropene fragment.[4]

We have previously developed general synthetic approaches to various 1-(alk-1-ynyl)-1-halocyclopropanes[5–8] **1** in yields of up to 90%. It could be expected that the reactions of these compounds with bases would occur with abstraction of a hydrogen halide molecule to give conjugated alkynylcyclopropenes **2**. Taking into account the enhanced reactivity of 1-alkynylcyclopropenes,[3] we used lithium *N*,*N*-dialkylamides, which are strong

bases with low nucleophilicity, as bases in the transformations indicated above.

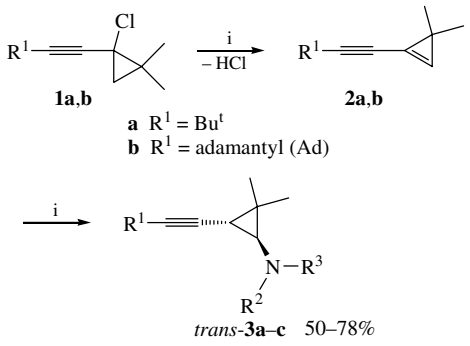
The experiments were carried out by adding the starting 1-(alk-1-ynyl)-1-chlorocyclopropanes to a threefold excess of a solution of the corresponding lithium *N*,*N*-dialkylamide in THF at –20 °C followed by warming to 20–40 °C and treatment of the reaction mixture with water. After removal of the solvent, the resulting products were isolated by chromatography on silica gel or by vacuum microdistillation.

It was found during these studies that the addition of (alk-1-ynyl)-1-chlorocyclopropanes **1a–c** to a solution of a threefold excess of a lithium *N*,*N*-dialkylamide, such as $LiNEt_2$ or $LiN(Pr^i)_2$, resulted in corresponding alkynylcyclopropenes **2a–c**† (Scheme 1), which could be isolated by column chromatography (with hexane as the eluent) in 35–45% yields and with purities exceeding 90%.



Scheme 1 *Reagents and conditions*: i, Et_2NLi, THF, –20 to 20 °C; ii, Pr^i_2NLi, THF, –20 to 20 °C.

An attempt to obtain 2,2-dimethyl-1-phenylethynylcyclopropene **2d** from 2,2-dimethyl-1-phenylethynyl-1-chlorocyclopropane **1d** in a similar manner by treatment with lithium diisopropylamide failed. That is, only high-molecular compounds, most likely transformation products of cyclopropene **2d**, were obtained rather than the expected product.



3a $R^1 = Bu^t$, $R^2 + R^3 = (CH_2)_4$
3b $R^1 = Bu^t$, $R^2 + R^3 = (CH_2)_2O(CH_2)_2$
3c R^1 = adamantyl (Ad), $R^2 + R^3 = (CH_2)_2O(CH_2)_2$

Scheme 2 *Reagents and conditions*: i, R^2_2NLi, THF, –20 to 40 °C.

† The structures of the new compounds obtained were proved by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200p spectrometer (200 MHz for ^1H, 50 MHz for ^{13}C) in $CDCl_3$ with TMS as an internal standard. Mass spectra were recorded on a Finnigan MAT INCOS-50 GL-MS spectrometer.

For **2a**: ^1H NMR, δ: 1.18 (s, 6H, 2Me), 1.27 (s, 9H, Bu^t), 7.21 (s, 1H, CH, cyclo-C_2H_1). ^{13}C NMR, δ: 22.4 (CMe_2), 27.0 (2Me), 28.7 (CMe_3), 30.8 (CMe_3), 68.1 (C≡CBu^t), 117.2 (C≡CBu^t), 118.7 (C≡C*C*, cyclo-C_3H_1), 121.9 (CH, cyclo-C_3H_1).

For **2b**: ^1H NMR, δ: 1.22 (s, 6H, 2Me), 1.72 (t, 6H, $3CH_2$ in Ad, *J* 2.9 Hz), 1.92–2.04 (m, 9H, $3CH_2$, 3CH in Ad), 7.25 (s, 1H, CH, cyclo-C_2H_1). ^{13}C NMR, δ: 22.6 (CMe_2), 27.1 (2Me), 28.0 (3CH, Ad), 31.6 (C≡*C*C, Ad), 36.4 ($3CH_2$, Ad), 42.6 ($3CH_2$, Ad), 68.2 (*C*≡CAd), 113.0 (C≡*C*Ad), 118.6 (C≡C*C*, cyclo-C_3H_1), 122.0 (CH, cyclo-C_3H_1).

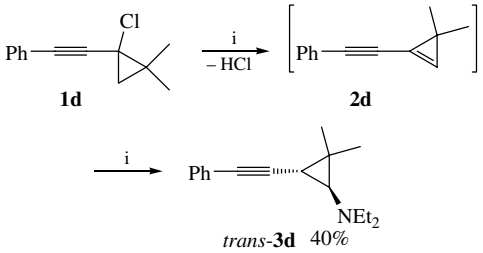
For **2c**: ^1H NMR, δ: 1.28 (s, 9H, Bu^t), 1.52 (s, 2H, CH_2), 7.15–7.35 (m, 3H, *meta*-H, *para*-H, Ph), 7.48 (br. d, 2H, *ortho*-H, Ph, *J* 7.4 Hz). ^{13}C NMR, δ: 10.4 (CH_2), 28.8 (CMe_3), 30.8 (3Me), 70.2, 95.8, 112.4, 115.9, 129.0 (C≡C, C=C, C-1 in Ph), 128.4, 128.6, 129.4 (Ph).

The resulting alkynylcyclopropenes **2a–c** were found to be unstable compounds, which underwent complete conversion into high-molecular-weight products upon storage for a few days in deuteriochloroform at room temperature. However, despite the lability of compounds **2a–c**, the addition of lithium amides (Et_2NLi, Pr^i_2NLi) to the double bonds of formed cyclopropenes **2** was not observed under the conditions used for the synthesis.

On the contrary, the reactions of alkynylchlorocyclopropanes **1a–d** with lithium derivatives of dimethylamine and cyclic amines, such as morpholine, pyrrolidine and piperazine, as well as the reaction of cyclopropane **1d** with lithium diethylamide under similar conditions did not give the corresponding cyclopropenes, but (alk-1-ynyl)dialkylaminocyclopropanes **3a–g**‡ and **4a**,**b**§ in 40–78% yields. In this case, the regio- and stereoselectivity of these reactions are determined by the nature of substituents, both in the original alkynylcyclopropanes **1** and in the lithium *N*,*N*-dialkylamides used.

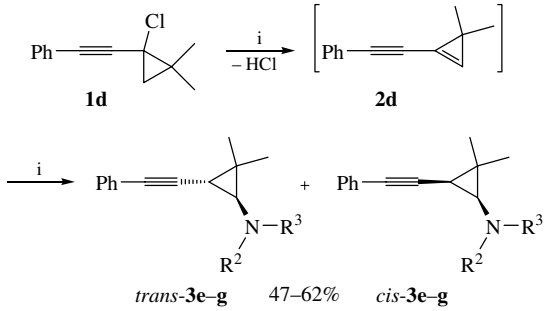
In fact, if cyclopropanes **1a** and **1b** with bulky *tert*-butyl or adamantyl substituents at the triple bond were used as the starting compounds and lithium morpholide or pyrrolidide was used as a base, the *trans* isomers of corresponding cyclopropanes **3a–c** were formed (Scheme 2).

The reaction of cyclopropane **1d** with lithium diethylamide also gave only the *trans* isomer of cyclopropane **3d** (Scheme 3).



Scheme 3 *Reagents and conditions*: i, Et_2NLi, THF, –20 to 40 °C.

The reactions of **1d** with lithium morpholide, dimethylamide and piperazide gave mixtures of *trans* and *cis* isomers of cyclopropanes **3e–g** in ratios of 2.2:1–3:1 (Scheme 4).



3e $R^2 + R^3 = (CH_2)_2O(CH_2)_2$
3f $R^2 = R^3 = Me$
3g $R^2 + R^3 = (CH_2)_2NH(CH_2)_2$

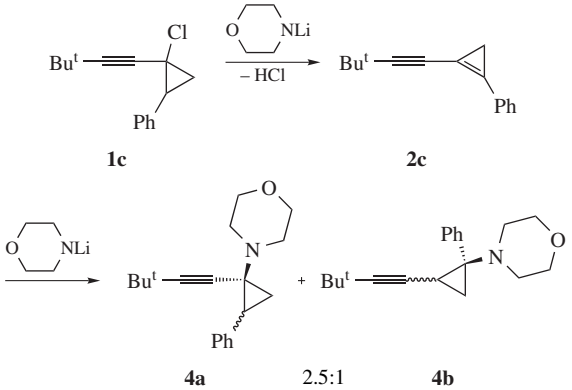
Scheme 4 *Reagents and conditions*: i, R^2_2NLi, THF, –20 to 20 °C.

In this work, we also studied the behaviour of 1-chloro-2-phenyl-1-*tret*-butylethynylcyclopropane **1c** in the test reactions. The reaction with lithium morpholide gave a mixture of two compounds in a 2.5:1 ratio and in 48% yield; the latter were identified as regioisomeric aminocyclopropanes **4a** and **4b** with different mutual arrangements of the ethynyl fragment and the morpholine ring (Scheme 5). However, the relative locations of the substituents in products **4a**,**b** could not be determined due to the absence of characteristic vicinal coupling constants in the ^1H NMR spectra of these compounds. Most likely, the formation of two regioisomers occurs due to the mutual influence of both the phenyl and *tert*-butylethynyl substituents, which have similar electronegativity, on the double bond in intermediate cyclopropene **2c**.

Based on the composition of the products, it can be assumed that aminocyclopropanes **3** and **4** formed by the abstraction–

addition mechanism *via* intermediate alkynylcyclopropenes **2a–d** due to the dehydrochlorination of chlorocyclopropanes **1** under the action of lithium dialkylamides used. The amide anions that are present in the reaction mixture add to the double bond of the cyclopropene fragment of highly reactive compounds **2a–d** to give aminocyclopropanes **3**, **4**, similarly to the addition of secondary amines to non-conjugated cyclopropenes reported previously.[9,10]

This assumption is confirmed by the fact that treatment of cyclopropenes **2a** and **2b** with an excess of lithium morpholide in THF at room temperature gave *trans*-aminocyclopropanes **3b** and **3c**, respectively, in 80–90% yields, whereas treatment of cyclopropene **2c** under the same conditions gave a mixture of products **4a** and **4b** in the same ratio as in the reaction of chlorocyclopropane **1c** with an excess of lithium morpholide. These results suggest conclusively that the formation of aminocyclopropanes **3a–g**, **4a**,**b** in the reaction of chlorocyclopropanes **1a–d** with lithium diorganylamides occurs *via* the corresponding intermediate alkynylcyclopropenes **2a–d**. In this case, the isomeric composition of products **3a–g** formed in the reaction of chlorides **1a–c** with lithium dialkylamides suggests that amide anions undergo, exclusively or preferentially, *cis* addition to intermediate cyclopropenes **2a–c**. Taking these data into account, we can conclude that the most probable configuration of regioisomeric cyclopropanes **4a** and **4b** (Scheme 5) involves a *cis* mutual arrangement of the phenyl and *tert*-butylethynyl substituents.



Scheme 5

Thus, we have proposed a new method to synthesise conjugated alkynylcyclopropenes **2** and shown that they are capable of nucleophilic addition of diorganylamide ions to the double bond of the cyclopropene ring to give hitherto unknown (alk-1-ynyl)dialkylaminocyclopropanes **3**, **4**. The regio- and stereoselectivity of addition is determined by the structure of the compounds participating in these reactions.

This work was supported by the Russian Foundation for Basic Research (grant no. 06-03-33045-a), Russian Academy of Sciences (Programme 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 M. A. Kuznetsov, Yu. V. Dorofeeva, V. V. Semenovskii, V. A. Gindin and A. N. Studenikov, *Tetrahedron*, 1992, **48**, 1269.
2 S. Untiedt and A. de Meijere, *Chem. Ber.*, 1994, **127**, 1511.
3 M. M. Haley, B. Biggs, W. A. Looney and R. D. Gilbertson, *Tetrahedron Lett.*, 1995, **36**, 3457.
4 M. A. Kuznetsov, Yu. I. D. Kuchuk and V. A. Gindin, *Zh. Obshch. Khim.*, 1993, **63**, 1627 (*Russ. J. Gen. Chem.*, 1993, **63**, 1136).
5 K. N. Shavrin, I. V. Krylova, I. B. Shvedova, G. P. Okonnishnikova, I. E. Dolgy and O. M. Nefedov, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1875.

‡ For *trans*-**3a**: ^{1}H NMR, δ: 0.99 (d, 1H, CHC≡C, *J* 3.7 Hz), 1.07 (s, 3H, Me), 1.1 (s, 3H, Me), 1.16 (s, 9H, Bu^t), 1.40 (d, 1H, CHN, cyclo-C_3H_2, *J* 3.7 Hz), 1.66–1.75 (m, 4H, CH_2CH_2, cyclo-C_4H_8N), 2.50–2.61 (m, 4H, CH_2NCH_2, cyclo-C_4H_8N). ^{13}C NMR, δ: 19.5, 20.64, 21.8 (2Me, *C*HC≡C), 23.8 (CH_2CH_2, cyclo-C_4H_8N), 24.6 (*C*Me$_2$), 27.5 (*C*Me$_3$), 31.5 (3Me), 53.7 (CH_2NCH_2, cyclo-C_4H_8N), 56.9 (CHN, cyclo-C_3H_2), 78.1, 87.1 (C≡C). MS, *m/z*: 219 [M$^+$].

For *trans*-**3b**: ^{1}H NMR, δ: 0.88 (d, 1H, CHC≡C, *J* 3.8 Hz), 1.04 (s, 3H, Me), 1.10 (s, 3H, Me), 1.11 (s, 9H, Bu^t), 1.41 (d, 1H, CHN, cyclo-C_3H_2, *J* 3.8 Hz), 2.32–2.56 (m, 4H, CH_2NCH_2, cyclo-C_4H_8NO), 3.56 (t, 4H, CH_2OCH_2, cyclo-C_4H_8N, *J* 4.6 Hz). ^{13}C NMR, δ: 19.1, 19.7, 21.7 (2Me, *C*HC≡C), 24.9 (*C*Me$_2$), 27.3 (*C*Me$_3$), 31.4 (3Me), 53.2 (CH_2NCH_2, cyclo-C_4H_8NO), 58.2 (CHN, cyclo-C_3H_2), 66.8 (CH_2OCH_2, cyclo-C_4H_8NO), 77.7, 87.2 (C≡C). MS, *m/z*: 235 [M$^+$].

For *trans*-**3c**: ^{1}H NMR, δ: 0.94 (d, 1H, CHC≡C, *J* 3.8 Hz), 1.09 (s, 3H, Me), 1.17 (s, 3H, Me), 1.45 (d, 1H, CHN, cyclo-C_3H_2, *J* 3.8 Hz), 1.60–1.70 (m, 6H, 3CH_2, Ad), 1.75–1.84 (m, 6H, 3CH_2, Ad), 1.90–1.98 (m, 3H, 3CH, Ad), 2.38–2.62 (m, 4H, CH_2NCH_2, cyclo-C_4H_8NO), 3.61 (t, 4H, CH_2OCH_2, cyclo-C_4H_8N, *J* 4.7 Hz). ^{13}C NMR, δ: 19.2, 20.1, 21.9 (2Me, *C*HC≡C), 25.0 (*C*Me$_2$), 28.1 (3CH, Ad), 29.6 (C-1, Ad), 36.5 (3CH_2), 43.5 (3CH_2), 53.4 (CH_2NCH_2, cyclo-C_4H_8NO), 58.4 (CHN, cyclo-C_3H_2), 67.0 (CH_2OCH_2, cyclo-C_4H_8NO), 78.1, 87.5 (C≡C). MS, *m/z*: 313 [M$^+$].

For *trans*-**3d**: ^{1}H NMR, δ: 1.13 [t, 6H, N(CH_2*Me*)$_2$, *J* 7.2 Hz], 1.29 (d, 1H, CHC≡C, *J* 4.2 Hz), 1.30 (s, 3H, Me), 1.31 (s, 3H, Me), 1.87 (d, 1H, C*H*NEt$_2$, *J* 4.2 Hz), 2.68 [q, 4H, N(C*H*$_2$Et)$_2$], 7.35–7.50 (m, 5H, Ph). ^{13}C NMR, δ: 11.8 (2Me, NEt$_2$), 19.8, 21.8, 22.0 (2Me, *C*HC≡C), 26.4 (*C*Me$_2$), 47.9 [N(*C*H$_2$Me)$_2$], 57.2 (*C*HNEt$_2$), 78.8, 90.3 (C≡C), 124.3 (C-1, Ph), 127.2, 128.1, 131.5 (Ph). MS, *m/z*: 241 [M$^+$].

For *trans*-**3e**: ^{1}H NMR, δ: 1.26 (d, 1H, CHC≡C, *J* 3.8 Hz), 1.28 (s, 3H, Me), 1.30 (s, 3H, Me), 1.74 (d, 1H, CHN, cyclo-C_3H_2, *J* 3.8 Hz), 2.40–2.65 (m, 4H, CH_2NCH_2, cyclo-C_4H_8NO), 3.68 (t, 4H, CH_2OCH_2, cyclo-C_4H_8NO, *J* 4.7 Hz), 7.30–7.46 (m, 5H, Ph). ^{13}C NMR, δ: 19.0, 20.5, 22.0 (2Me, *C*HC≡C), 26.4 (*C*Me$_2$), 53.1 (CH_2NCH_2, cyclo-C_4H_8NO), 58.6 (CHN, cyclo-C_3H_2), 66.8 (CH_2OCH_2, cyclo-C_4H_8NO), 78.9, 89.7 (C≡C), 124.0 (C-1, Ph), 127.2, 128.0, 131.4 (Ph). MS, *m/z*: 255 [M$^+$].

For *cis*-**3e**: ^{1}H NMR, δ: 1.11 (s, 3H, Me), 1.32 (s, 3H, Me), 1.38 (d, 1H, CHC≡C, *J* 6.9 Hz), 1.69 (d, 1H, CHN, cyclo-C_3H_2, *J* 6.9 Hz), 2.55–2.81 (m, 4H, CH_2NCH_2, cyclo-C_4H_8NO), 3.72 (t, 4H, CH_2OCH_2, cyclo-C_4H_8NO, *J* 4.7 Hz), 7.30–7.46 (m, 5H, Ph). ^{13}C NMR, δ: 14.1, 19.4, 25.8 (2Me, *C*HC≡C), 24.4 (*C*Me$_2$), 52.9 (CH_2NCH_2, cyclo-C_4H_8NO), 53.8 (CHN, cyclo-C_3H_2), 67.0 (CH_2OCH_2, cyclo-C_4H_8NO), 79.8, 88.2 (C≡C), 124.5 (C-1, Ph), 127.1, 128.0, 131.3 (Ph). MS, *m/z*: 255 [M$^+$].

For *trans*-**3f**: ^{1}H NMR, δ: 1.29 (d, 1H, CHC≡C, *J* 3.8 Hz), 1.30 (s, 3H, Me), 1.32 (s, 3H, Me), 1.66 (d, 1H, C*H*NMe$_2$, cyclo-C_3H_2, *J* 3.8 Hz), 2.35 (s, 6H, NMe$_2$), 7.35–7.46 (m, 5H, Ph). ^{13}C NMR, δ: 19.1, 21.5, 22.1 (2Me, *C*HC≡C), 26.9 (*C*Me$_2$), 45.2 (NMe$_2$), 60.4 (*C*HNMe$_2$, cyclo-C_3H_2), 78.9, 90.0 (C≡C), 124.2 (C-1, Ph), 127.2, 128.0, 131.5 (Ph). MS, *m/z*: 213 [M$^+$].

For *cis*-**3f**: ^{1}H NMR, δ: 1.13 (s, 3H, Me), 1.38 (s, 3H, Me), 1.40 (d, 1H, CHC≡C, *J* 7.0 Hz), 1.58 (d, 1H, CHN, cyclo-C_3H_2, *J* 7.0 Hz), 2.40 (s, 6H, NMe$_2$), 7.35–7.46 (m, 5H, Ph). ^{13}C NMR, δ: 15.7, 20.1, 25.9 (2Me, *C*HC≡C), 24.5 (*C*Me$_2$), 45.1 (NMe$_2$), 56.2 (*C*HNMe$_2$, cyclo-C_3H_2), 80.1, 88.3 (C≡C), 124.5 (C-1, Ph), 127.1, 127.9, 131.7 (Ph). MS, *m/z*: 213 [M$^+$].

For *trans*-**3g**: ^{1}H NMR, δ: 1.18 (d, 1H, CHC≡C, *J* 3.9 Hz), 1.20 (s, 3H, Me), 1.22 (s, 3H, Me), 1.68 (d, 1H, CHN, cyclo-C_3H_2, *J* 3.9 Hz), 2.23 (br. s, 1H, NH), 2.35–2.65 (m, 4H, CH_2NCH_2, cyclo-$C_4H_9N_2$), 2.80 (t, 4H, CH_2NCH_2, cyclo-$C_4H_9N_2$, *J* 4.8 Hz), 7.14–7.40 (m, 5H, Ph). ^{13}C NMR, δ: 19.0, 20.5, 22.0 (2Me, *C*HC≡C), 26.4 (*C*Me$_2$), 45.7, 53.9 (4CH_2, cyclo-$C_4H_9N_2$), 58.9 (CHN, cyclo-C_3H_2), 78.7, 90.0 (C≡C), 124.0 (C-1, Ph), 127.2, 128.0, 131.4 (Ph). MS, *m/z*: 254 [M$^+$].

For *cis*-**3g**: ^{1}H NMR, δ: 1.03 (s, 3H, Me), 1.27 (s, 3H, Me), 1.30 (d, 1H, CHC≡C, *J* 6.7 Hz), 1.64 (d, 1H, CHN, cyclo-C_3H_2, *J* 6.7 Hz), 2.23 (br. s, 1H, NH), 2.35–2.65 (m, 4H, CH_2NCH_2, cyclo-$C_4H_9N_2$), 2.83 (t, 4H, CH_2NCH_2, cyclo-$C_4H_9N_2$, *J* 4.8 Hz), 7.14–7.40 (m, 5H, Ph). ^{13}C NMR, δ: 15.7, 19.4, 25.8 (2Me, *C*HC≡C), 24.5 (*C*Me$_2$), 45.8, 53.7 (4CH_2, cyclo-$C_4H_9N_2$), 54.1 (CHN, cyclo-C_3H_2), 79.6, 88.4 (C≡C), 124.6 (C-1, Ph), 127.0, 128.0, 131.3 (Ph). MS, *m/z*: 254 [M$^+$].

§ For **4a**: ^{1}H NMR, δ: 1.05 (s, 9H, Bu^t), 1.30 (dd, 1H, CH*H*, cyclo-C_3H_3, *J* 7.2 Hz, *J* 4.8 Hz), 1.39 (dd, 1H, C*H*H, cyclo-C_3H_3, *J* 9.4 Hz, *J* 4.8 Hz), 2.32 (dd, 1H, PhC*H*, *J* 9.4 Hz, *J* 7.2 Hz), 2.70–2.78 (m, 4H, CH_2NCH_2), 3.69–3.76 (m, 4H, CH_2OCH_2), 7.15–7.4 (m, 5H, Ph). ^{13}C NMR, δ: 22.4 (CH_2, cyclo-C_3H_3), 27.2 (*C*Me$_3$), 30.9 (3Me), 33.0 (*C*HPh, cyclo-C_3H_3), 45.2 (C≡C*C*, cyclo-C_3H_3), 50.1 (CH_2NCH_2), 67.0 (CH_2OCH_2), 73.3, 95.3 (C≡C), 126.0, 127.5, 128.3 (Ph), 138.0 (C-1, Ph). MS, *m/z*: 283 [M$^+$].

For **4b**: ^{1}H NMR, δ: 1.00 (s, 9H, Bu^t), 1.23–1.44 (m, 2H, CH_2), 1.77 (dd, 1H, C≡CCH, *J* 9.3 Hz, *J* 5.8 Hz), 2.50–2.59 (m, 4H, CH_2NCH_2), 3.57–3.65 (m, 4H, CH_2OCH_2), 7.15–7.4 (m, 5H, Ph). ^{13}C NMR, δ: 15.9 (C≡C*C*H), 23.9 (CH_2), 27.1 (*C*Me$_3$), 30.7 (3Me), 49.7 (CH_2NCH_2), 54.6 (Ph*C*, cyclo-C_3H_3), 67.1 (CH_2OCH_2), 78.8, 89.2 (C≡C), 127.1, 127.2, 132.0 (Ph), 132.7 (C-1, Ph). MS, *m/z*: 283 [M$^+$].

6 K. N. Shavrin, I. B. Shvedova and O. M. Nefedov, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1991, 2559 (*Bull. Acad. Sci. USSR, Div. Chem. Sci*., 1991, **40**, 2235).
7 K. N. Shavrin, I. V. Krylova, I. E. Dolgy and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim*., 1992, 1128 (*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, **41**, 885).
8 K. N. Shavrin, V. D. Gvozdev and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1143 (*Russ. Chem. Bull., Int. Ed*., 2002, **51**, 1237).
9 M. Franck-Newmann, M. Miesch and H. Kempf, *Tetrahedron*, 1988, 2933.
10 E. I. Gritsenko, R. R. Khaliulin, V. V. Plemenkov and E. M. Faizullin, *Zh. Obshch. Khim.*, 1988, **58**, 2733 [*J. Gen. Chem. USSR* (*Engl. Transl*.), 1988, **58**, 2433].

Received: 2nd November 2005; Com. 05/2609