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Generation of previously unknown (alk-1-ynyl)organylthiocarbenes by the γ-elimination of HCl from 1-substituted 3-organyl-1-chloropropadienes under the action of bases

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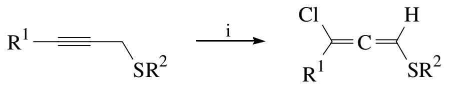
Previously unknown (alk-1-ynyl)organylthiocarbenes were generated from 1-substituted 1-chloro-3-organylthiopropadienes **1** as a result of HCl elimination under the action of potassium *tert*-butoxide.

By now, a considerable number of (alk-1-ynyl)carbenes with different substituents at the carbene centre, which were generated using various methods, were described.[1–4] In particular, (alk-1-ynyl)halocarbenes were generated under the action of bases as a result of either α-elimination of a hydrogen halide molecule from 1,1-dihaloalk-2-ynes[5] or γ-elimination of HCl from 1,1-dichloroalka-1,2-dienes.[6] Taking into account analogies in the behaviours of a halogen atom and an organylthio group in the generation of corresponding halo- and organylthiocarbenes, we attempted to obtain previously unknown (alk-1-ynyl)organylthiocarbenes in a similar manner.

We tried to prepare 1-organylthio-1-chloroalk-2-ynes, which are potential precursors of (alk-1-ynyl)organylthiocarbenes, by the action of *N*-chlorosuccinimide in CCl_4 on sulfides **1a**–**c**. However, previously unknown 1-substituted 3-organylthio-1-chloropropadienes[†] **2a**–**c** were obtained instead of the expected products (Scheme 1).



1a–**c** **2a**–**c**

a $R^1 = Bu^t$, $R^2 = Me$
b $R^1 = Bu^t$, $R^2 = p$-Tolyl
c $R^1 = Ad$, $R^2 = Me$

Scheme 1 *Reagents and conditions*: i, *N*-chlorosuccinimide, CCl_4, 20 °C.

The subsequent treatment of allenes **2a**–**c** with potassium *tert*-butoxide in hexane at –20 °C in the presence of a threefold to fivefold excess of 2,3-dimethylbut-2-ene or styrene resulted in the formation of 1-(alk-1-ynyl)-1-methylthio- and 1-(alk-1-ynyl)-1-*p*-tolylthiocyclopropanes[‡] **6a**–**d** in 18–49% yield (Scheme 2). The structures of prepared compounds **6a**–**d** were assigned on the basis of elemental analyses as well as ^{1}H and ^{13}C NMR spectra.

The fact that adducts **6a**–**d** were formed from styrene and 2,3-dimethylbut-2-ene by addition of carbenes **5a**–**c** (rather than **4a**–**c**) allows one to propose a mechanistic scheme. This scheme includes (*a*) deprotonation of allenes **2a**–**c** by Bu^tOK leading to the anions **3a**–**c**; (*b*) elimination of the chloride ion and formation of carbenes **4a**–**c** [similarly to the generation of (alk-1-ynyl)chlorocarbenes from 1,1-dichloropropadienes[6]], which do not add to ethylene derivatives under the reaction conditions; (*c*) isomerization of carbenes **4a**–**c** to more highly reactive carbenes **5a**–**c** according to the scheme proposed previously[1] for the rearrangement of alk-1-ynylcarbenes; and (*d*) formation of a three-carbon ring as a result of the addition of carbenes **5a**–**c** to ethylene derivatives.

Thus, the addition of organylthio(alk-1-ynyl)carbenes to alkenes can be applied as a direct method for the synthesis of 1-(organylthio)-1-(alk-1-ynyl)cyclopropanes. Previously, 1-(organylthio)-1-(alk-1-ynyl)cyclopropanes were prepared starting from 2,3-disubstituted oxiranes and 1-lithio-phenylthioprop-2-yne as a result of a three-step reaction[7] or from 1-(trichlorovinyl)-1-chlorocyclopropanes.[8]

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[†] *Spectroscopic data for allenes* **2a**–**c**.

For **2a**: ^{1}H NMR, δ: 1.17 (s, 9H, 3Me), 2.15 (s, 3H, SMe), 6.24 (s, 1H, =CH). ^{13}C NMR, δ: 14.2 (SMe), 28.6 (3Me), 37.7 (*C*Me$_3$), 99.6 (MeS*C*H=), 122.9 [Bu^t(Cl)*C*=], 192.5 (=C=).

For **2b**: ^{1}H NMR, δ: 0.99 (s, 9H, 3Me), 2.38 (s, 3H, Me), 6.28 (s, 1H, =CH–), 7.21 (br. d, 2H, *o*-H in cyclo-C_6H_4, *J* 8.2 Hz), 7.39 (br. d, 2H, *m*-H in cyclo-C_6H_4, *J* 8.2 Hz). ^{13}C NMR, δ: 21.0 (Me), 28.0 (3Me), 37.1 (*C*Me$_3$), 99.6 (–SCH=), 121.8 [Bu^t(Cl)*C*=], 127.7 (C-1 in cyclo-C_6H_4), 129.4, 133.5 (C-2, C-3, C-5, C-6 in cyclo-C_6H_4), 138.5 (C-4 in cyclo-C_6H_4), 193.9 (=C=).

For **2c**: ^{1}H NMR, δ: 1.63 (br. s, 6H, 3CH$_2$ in Ad), 1.70 (br. s, 6H, 3CH$_2$ in Ad), 1.98 (br. s, 3H, 3CH in Ad), 2.11 (s, 3H, SMe), 6.20 (s, 1H, =CH–). ^{13}C NMR, δ: 14.0 (SMe), 28.0 (3CH in Ad), 36.3 (3CH$_2$ in Ad), 38.5 [=(Cl)C*C* in Ad], 40.6 (3CH$_2$ in Ad), 99.7 (MeS*C*H=), 122.7 [Ad(Cl)*C*=], 192.6 (=C=).

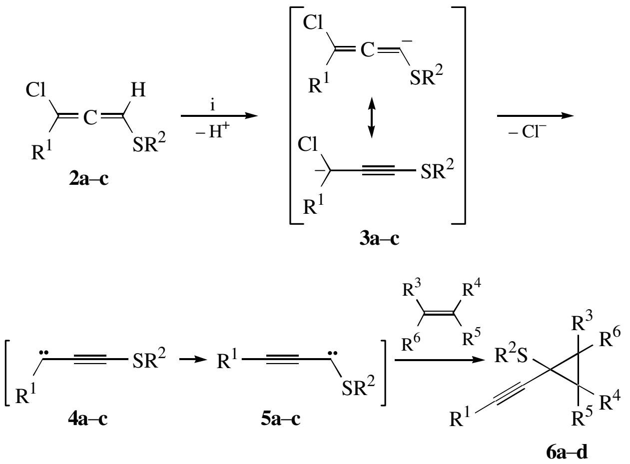
[‡] The structures of cyclopropanes **6a**–**d** were assigned on the basis of their ^{1}H and ^{13}C NMR spectra (200 and 50 MHz for ^{1}H and ^{13}C, respectively; $CDCl_3$) as well as elemental analysis.

For **6a**: 28% from chloride **2a** and 2,3-dimethylbut-2-ene. ^{1}H NMR, δ: 1.17 (s, 6H, 2Me), 1.19 (s, 6H, 2Me), 1.21 (s, 9H, 3Me in Bu^t), 2.12 (s, 3H, SMe). ^{13}C NMR, δ: 14.7 (SMe), 18.0 (2Me), 20.2 (2Me), 27.7 (*C*Me$_3$), 29.5 (2*C*Me$_2$), 31.4 (3Me in Bu^t), 34.2 (*C*SMe in cyclo-C_3), 77.8, 90.8 (C≡C). Found (%): C, 75.26; H, 10.56. Calc. for $C_{14}H_{24}S$ (%): C, 74.99; H, 10.70.

For **6b**: 49% from chloride **2b** and 2,3-dimethylbut-2-ene. ^{1}H NMR, δ: 1.19 (s, 9H, 3Me in Bu^t), 1.30 (s, 6H, 2Me), 1.33 (s, 6H, 2Me), 2.37 (s, 3H, Me in *p*-tolyl), 7.12 (br. d, 2H, *o*-H in cyclo-C_6H_4, *J* 8.3 Hz), 7.31 (br. d, 2H, *m*-H in cyclo-C_6H_4, *J* 8.3 Hz). ^{13}C NMR, δ: 18.8 (2Me), 20.4 (2Me), 21.1 (Me in *p*-tolyl), 27.6 (*C*Me$_3$), 30.5 (2*C*Me$_2$), 31.2 (3Me in Bu^t), 34.0 (*C*SMe in cyclo-C_3), 78.8, 90.7 (C≡C), 128.4, 129.1 (C-2, C-3, C-5, C-6 in cyclo-C_6H_4), 133.5, 134.7 (C-1, C-4 in cyclo-C_6H_4). Found (%): C, 80.14; H, 9.11. Calc. for $C_{20}H_{28}S$ (%): C, 79.98; H, 9.32.

For **6c** (isomer ratio = 5:1): 18% from chloride **2a** and styrene. For the major isomer: ^{1}H NMR, δ: 1.31 (s, 9H, Bu^t), 1.48 (dd, 1H, 1H from CH$_2$ in cyclo-C_3H_3, *J* 5.3 Hz, *J* 7.5 Hz), 1.63 (dd, 1H, 1H from CH$_2$ in cyclo-C_3H_3, *J* 5.3 Hz, *J* 8.6 Hz), 2.39 (s, 3H, SMe), 2.72 (dd, 1H, C*H*Ph, *J* 7.5 Hz, *J* 8.6 Hz), 7.25–7.35 (m, 5H, Ph). ^{13}C NMR, δ: 15.8 (SMe), 22.3 (CH$_2$ in cyclo-C_3H_3), 27.2 (*C*SMe in cyclo-C_3H_3), 28.5 (*C*Me$_3$), 30.9 (3Me in Bu^t), 34.1 (*C*HPh), 81.0, 86.7 (C≡C), 126.5, 127.5, 128.9 (Ph), 135.8 (C-1 in Ph). For a minor isomer: ^{1}H NMR, δ: 1.26 (s, 9H, Bu^t), 1.20–1.39 (m, 2H, CH$_2$ in cyclo-C_3H_3), 2.41 (s, 3H, SMe), 2.51 (dd, 1H, C*H*Ph, *J* 6.3 Hz, *J* 9.1 Hz), 7.25–7.35 (m, 5H, Ph). ^{13}C NMR, δ: 16.2 (SMe), 23.4 (CH$_2$ in cyclo-C_3H_3), 23.8 (*C*SMe in cyclo-C_3H_3), 28.2 (*C*Me$_3$), 30.9 (3Me), 35.2 (*C*HPh), 75.2, 88.1 (C≡C), 126.1, 127.3, 128.2 (Ph), 137.1 (C-1 in Ph). Found (%): C, 78.45; H, 8.34. Calc. for $C_{16}H_{20}S$ (%): C, 78.68; H, 8.19.

For **6d**: 39% from chloride **2c** and 2,3-dimethylbut-2-ene. ^{1}H NMR, δ: 1.17 (s, 6H, 2Me), 1.18 (s, 6H, 2Me), 1.67 (br. s, 6H, 3CH$_2$ in Ad), 1.84 (br. s, 6H, 3CH$_2$ in Ad), 1.91 (br. s, 3H, 3CH in Ad), 2.13 (s, 3H, SMe). ^{13}C NMR, δ: 14.9 (SMe), 18.0 (2Me), 20.2 (2Me), 28.1 (3CH in Ad), 29.5 (2*C*Me$_2$), 29.8 (C≡C*C* in Ad), 34.3 (*C*SMe in cyclo-C_3), 36.4 (3CH$_2$ in Ad), 43.5 (3CH$_2$ in Ad), 78.0, 90.9 (C≡C). Found (%): C, 79.64; H, 9.73. Calc. for $C_{20}H_{30}S$ (%): C, 79.47; H, 9.92.



2–5 **a** $R^1 = Bu^t$, $R^2 = Me$
b $R^1 = Bu^t$, $R^2 = p$-Tolyl
c $R^1 = Ad$, $R^2 = Me$

6 **a** $R^1 = Bu^t$, $R^2 = R^3 = R^4 = R^5 = R^6 = Me$
b $R^1 = Bu^t$, $R^2 = p$-Tolyl, $R^3 = R^4 = R^5 = R^6 = Me$
c $R^1 = Bu^t$, $R^2 = Me$, $R^3 = Ph$, $R^4 = R^5 = R^6 = H$
d $R^1 = Ad$, $R^2 = R^3 = R^4 = R^5 = R^6 = Me$

Scheme 2 *Reagents and conditions*: i, Bu^tOK, hexane, 20 °C.

References

1 M. Franck-Neumann and P. Geoffroy, *Tetrahedron Lett.*, 1983, 1779.
2 U. Mislitz and A. de Meijere, in *Methoden der Organische Chemie*, Houben-Weyl, 1989, Band E19b, Teil 1, S. 769.
3 A. de Meijere and R. R. Kostikov, *Synthesis*, 1991, 547.
4 H. Hauptman, *Tetrahedron*, 1976, **32**, 1293.
5 (*a*) 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*, 1992, 1875; (*b*) 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).
6 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).
7 F. Narjes and E. Schaumann, *Synthesis*, 1991, 1168.
8 (*a*) T. Liese and A. de Meijere, *Chem. Ber.*, 1986, **119**, 2995; (*b*) G. Bengtson, S. Keyaniyan and A. de Meijere, *Chem. Ber.*, 1986, **119**, 3607; (*c*) G. McGaffin, B. Grimm, U. Heinecke, H. Michaelsen, A. de Meijere and R. Walsh, *Eur. J. Org. Chem.*, 2001, 3559.

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