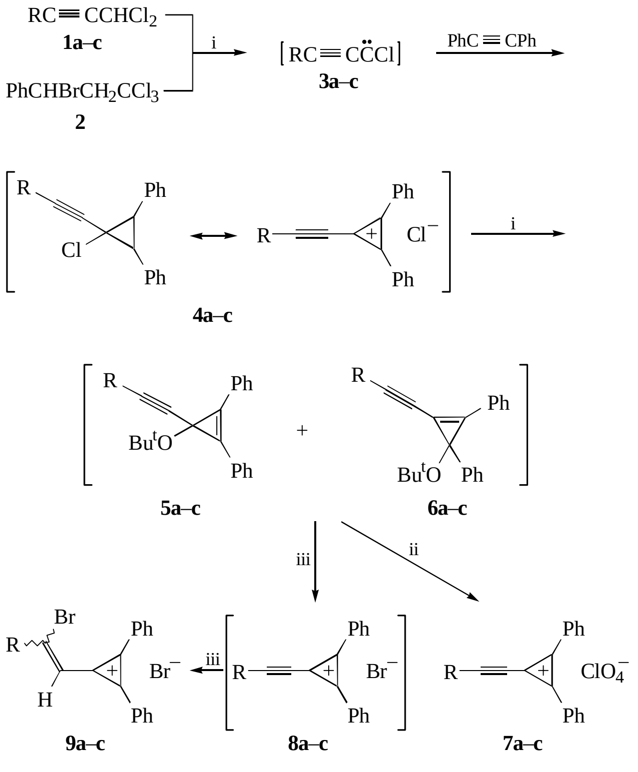
Synthesis of (alk-1-ynyl)cyclopropenium salts *via* the reaction of (alk-1-ynyl)chlorocarbenes with diphenylacetylene

Konstantin N. Shavrin,* Valentin D. Gvozdev and Oleg M. Nefedov

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 117913 Moscow, Russian Federation. Fax: +7 095 135 5328; e-mail: gvozdev@ufn.ioc.ac.ru

1-(Alk-1-ynyl)-2,3-diphenylcyclopropenium perchlorates **7** have been prepared *via* the generation of (alk-1-ynyl)chlorocarbenes **3** from 1,1-dichloroalk-2-ynes **1** or 3-bromo-1,1,1-trichloro-3-phenylpropane **2** by the interaction with Bu^{t}OK in the presence of tolan followed by the treatment of the reaction mixture with perchloric acid, whereas the treatment of the reaction mixture with HBr resulted in (2-bromoalk-1-enyl)cyclopropenium bromides **9**.

Previously we have discovered a new class of carbenic species, (alk-1-ynyl)halocarbenes, and their ability to add to double bonds of alkenes with the formation of corresponding 1-(alk-1-ynyl)halocyclopropanes.[1–5] At the same time, any data on the ability of these carbenes to react with alkynes are not available. Special interest in these reactions can be explained by the possibility of formation, analogously to halo(phenyl)carbenes,[6] of (alk-1-ynyl)-substituted cyclopropenium salts, previously unknown acetylenic compounds with the conjugation between the carbon–carbon triple bond and the cyclopropenium cation.



a R = Bu^t
b R = Ph
c R = *p*-tolyl

Scheme 1 *Reagents and conditions*: i, Bu^{t}OK, benzene, 20 °C; ii, 75% aqueous $HClO_4$ (method A), benzene, 20 °C; iii, gaseous HBr (method B) or 48% aqueous HBr (method C), benzene, 20 °C.

We have found that the reaction of Bu^{t}OK with 1,1-dichloroalk-2-ynes **1a–c** or 3-bromo-1,1,1-trichloro-3-phenylpropane **2** in benzene in the presence of a three-fold molar excess of tolan at ~20 °C (Scheme 1) followed by the treatment of the reaction mixture (passed trough SiO_2 or washed with water) with 75% perchloric acid (method A) results in solid (alk-1-ynyl)cyclopropenium perchlorates **7**† in 24–38% yields. Under the treatment of the reaction mixture with gaseous HBr (method B) or a 48% aqueous HBr solution (method C), (2-bromoalk-1-enyl)cyclopropenium bromides **9a–c**‡ were isolated in 23–37% yields. Cyclopropenium bromide **9a** was identified as a *Z*-isomer, and cyclopropenium bromides **9b** and **9c**, as mixtures of *Z*- and *E*-isomers. The configuration of double bonds in salts **9a–c** was determined by a comparative analysis of the chemical shifts of *ortho*-protons in phenyl groups attached to the three-membered ring.

---

† NMR spectra were measured on a Bruker AC200p spectrometer (200 and 50 MHz for ^{1}H and ^{13}C spectra, respectively) using solutions of the test compounds in CD_3CN. IR spectra were recorded on a Bruker IFS-113V spectrometer.

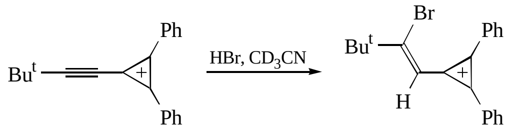
All new compounds **7a–c** gave expected spectral data. For **7a**: 38% yield from 4,4-dimethyl-1,1-dichloropent-2-yne **1a**, method A; mp 70–71 °C. ^{1}H NMR, δ: 1.54 (s, 9H, Bu^t), 7.86 (br. dd, 4H, *meta*-H, 2Ph, *J* 7.8 Hz, *J* 7.8 Hz), 8.04 (br. t, 2H, *para*-H, 2Ph, *J* 7.8 Hz), 8.43 (br. d, 4H, *ortho*-H, 2Ph, *J* 7.8 Hz). ^{13}C NMR, δ: 28.6 (3Me), 30.2 (*C*Me$_3$), 63.9 (Bu^{t}C≡*C*), 119.4 (*ipso*-C, 2Ph), 130.4, 136.1 and 139.2 (2Ph), 138.4 (Bu^t*C*≡C), 144.2 (*C*C≡C, cyclo-C_3^+), 155.3 (2*C*Ph, cyclo-C_3^+). IR (powder, ν/cm^{-1}): 1408 (cyclo-C_3^+), 2210 (C≡C).

For **7b**: 35% yield from 1,1-dichloro-3-phenylprop-2-yne **1b**, method A; mp 66–68 °C. ^{1}H NMR, δ: 7.69 (br. dd, 2H, *meta*-H, PhC≡, *J* 7.5 Hz, *J* 7.5 Hz), 7.80 (br. t, 1H, *para*-H, PhC≡, *J* 7.5 Hz), 7.93 (br. dd, 4H, *meta*-H, 2Ph, *J* 7.7 Hz, *J* 7.7 Hz), 8.0–8.15 (m, 4H, *para*-H, 2Ph, *ortho*-H, PhC≡), 8.53 (br. d, 4H, *ortho*-H, 2Ph, *J* 7.7 Hz). ^{13}C NMR δ: 73.5 (PhC≡*C*), 118.2 and 119.5 (*ipso*-C, 2Ph, *Ph*C≡), 129.5, 134.4 and 134.9 (*Ph*C≡), 130.4, 136.2 and 139.2 (2Ph), 125.7 (Ph*C*≡C), 142.4 (*C*C≡C, cyclo-C_3^+), 154.5 (2*C*Ph, cyclo-C_3^+). IR (powder, ν/cm^{-1}): 1408 (cyclo-C_3^+), 2191 (C≡C). Perchlorate **7b** was also obtained in 25% yield by method A from 3-bromo-3-phenyl-1,1,1-trichloropropane **2**, which, according to ref. 4, generates (phenylethynyl)chlorocarbene under the action of Bu^{t}OK.

For **7c**: 24% yield from 1,1-dichloro-3-(*p*-tolyl)prop-2-yne **1c**, method A; mp 163–164 °C. ^{1}H NMR δ: 2.49 (s, 3H, Me), 7.48 (br. d, 2H, *meta*-H, *p*-tolyl, *J* 8.0 Hz), 7.91 (br. dd, 4H, *meta*-H, 2Ph, *J* 7.6 Hz, *J* 7.6 Hz), 7.92 (br. d, 2H, *ortho*-H, *p*-tolyl, *J* 8.0 Hz), 8.08 (br. t, 2H, *para*-H, 2Ph, *J* 7.6 Hz), 8.51 (br. d, 4H, *ortho*-H, 2Ph, *J* 7.6 Hz). ^{13}C NMR δ: 21.3 (Me), 73.9 (*p*-tolylC≡*C*), 115.1 and 119.6 (*ipso*-C, 2Ph, *p*-tolyl); 130.3, 130.5, 135.1, 136.1 and 139.1 (2Ph, *p*-tolyl), 127.2 (*p*-tolyl*C*≡C), 142.2 (*C*C≡C, cyclo-C_3^+), 146.5 (*C*Me, *p*-tolyl), 153.9 (2*C*Ph, cyclo-C_3^+).

‡ For the *Z*-isomer of **9a**: 38% yield from 1,1-dichloro-4,4-dimethylpent-2-yne **1a**, method B; mp 75–76 °C. ^{1}H NMR δ: 1.49 (s, 9H, Bu^t), 7.87 (br. dd, 4H, *meta*-H, 2Ph, *J* 7.8 Hz, *J* 7.8 Hz), 7.93 (s, 1H, CH=), 8.02 (br. t, 2H, *para*-H, 2Ph, *J* 7.8 Hz), 8.52 (br. d, 4H, *ortho*-H, 2Ph, *J* 7.8 Hz). ^{13}C NMR (without decoupling) δ: 28.6 (q. sept., 3Me, *J* 129 Hz, *J* 5 Hz), 43.0 (m, *C*Me$_3$), 111.8 (d, CH=, *J* 172 Hz), 119.9 (t, *ipso*-C, Ph, *J* 9 Hz), 129.9 (dd, *ortho*-C, Ph, *J* 166 Hz, *J* 8 Hz), 136.2 (dd, *meta*-C, Ph, *J* 165 Hz, *J* 7 Hz, *J* 7 Hz), 138.1 (dt, *para*-C, Ph, *J* 165 Hz, *J* 7 Hz), 153.2 (d, *C*–CH=, cyclo-C_3^+, *J* 2 Hz), 156.6 (d, CBr=, *J* 5 Hz), 171.2 (s, 2*C*Ph, cyclo-C_3^+). IR (powder, ν/cm^{-1}): 1416 (cyclo-C_3^+).

For **9b**: 23% yield from 1,1-dichloro-3-(*p*-tolyl)prop-2-yne **1c**, method B; mixture of *Z*- and *E*-isomers (*Z*/*E* ratio 1.4:1). *Z*-isomer: ^{1}H NMR δ: 2.50 (s, 3H, Me), 7.46 (d, 2H, *meta*-H, *p*-tolyl, *J* 7.9 Hz), 7.69 (d, 2H, *ortho*-H, *p*-tolyl, *J* 7.9 Hz), 7.89 (br. dd, 4H, *meta*-H, 2Ph, *J* 7.6 Hz, *J* 7.6 Hz), 7.98–8.15 (m, 2H, *para*-H, 2Ph), 8.40 (s, 1H, CH–), 8.55 (br. d, 4H, *ortho*-H, 2Ph, *J* 7.6 Hz). *E*-isomer: ^{1}H NMR δ: 2.22 (s, 3H, Me), 7.21 (d, 2H, *meta*-H, *p*-tolyl, *J* 7.9 Hz), 7.53 (d, 2H, *ortho*-H, *p*-tolyl, *J* 7.9 Hz), 7.88 (br. dd, 4H, *meta*-H, 2Ph, *J* 7.6 Hz, *J* 7.6 Hz), 7.98–8.15 (m, 7H, *para*-H and *ortho*-H, 2Ph, CH=). IR (powder, ν/cm^{-1}): 1404 (cyclo-C_3^+).



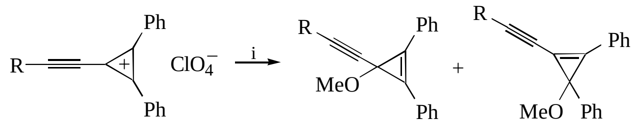
10 **11**

Scheme 2

The formation of cyclopropenium salts **7a**–**c** and **9a**–**c** proceeds, according to Scheme 1. (Alk-1-ynyl)halocarbenes[1–4] **3** generated by the reaction of halides **1a**–**c** or **2** with Bu^{t}OK add to the triple bond of tolan to form chlorides **4a**–**c**, which react with Bu^{t}OK under the reaction conditions with the formation of corresponding isomeric ethers **5a**–**c** and **6a**–**c**. These ethers give (alk-1-ynyl)cyclopropenium perchlorates **7a**–**c** on the treatment with $HClO_4$ and (2-bromoalk-1-enyl)cyclopropenium bromides **9a**–**c** under the action of HBr. The latter are likely obtained as a result of the HBr addition to the triple bond of (alk-1-ynyl)cyclopropenium bromides **8a**–**c** initially formed in the reaction. This fact is confirmed by obtaining (2-bromo-3,3-dimethylbut-1-enyl)diphenylcyclopropenium cation **11** from (3,3-dimethylbut-1-ynyl)diphenylcyclopropenium cation **10** in nearly quantitative yield (according to NMR data) under the treatment of a solution of cyclopropenium perchlorate **7a** in CD_3CN with HBr (Scheme 2).

In the reaction mixtures formed both by the interaction of 4,4-dimethyl-1,1-dichloropent-2-yne **1a** with Bu^{t}OK in the presence of diphenylacetylene and under the treatment of (3,3-dimethylbut-1-ynyl)diphenylcyclopropenium perchlorate **7a** with Bu^{t}OK, identical products were detected. According to the ^{1}H and ^{13}C NMR spectrometry data, these products were identified as isomeric ethers **5a** and **6a**. This fact suggests that the above reactions proceed *via* the intermediate formation of ethers **5** and **6**. We have also found that in the reactions of perchlorates **7a**,**b** with MeONa in methanol at about –20 °C mixtures of corresponding isomeric cyclopropenic ethers **12a**,**b** and **13a**,**b**[§] are formed with 58–67% yields (Scheme 3).

Note that the ^{13}C NMR signals due to β-carbon atoms at the triple bond of perchlorates **7a**–**c** are downfield (126–138 ppm) with respect to the corresponding signals of other acetylenes, for example, (alk-1-ynyl)halocyclopropanes (75–95 ppm).[4–5] These results suggest the conjugation between the triple bond and the cyclopropenium cation in salts **7a**–**c**.



7a,**b** **12a**,**b** **13a**,**b**

a R = Bu^t
b R = Ph

Scheme 3 *Reagents and conditions*: i, MeONa, MeOH, –20 °C.

This work was supported in part by the Russian Foundation for Basic Research (grant nos. 96-03-32907a and 96-15-97323).

§ For a mixture of **12a** and **13a** (**12a**:**13a** ratio 1:1.3): overall yield 67% from perchlorate **7a**. ^{1}H NMR, δ: for **12a**, 1.27 (s, 9H, Bu^t), 3.52 (s, 3H, MeO), 7.2–7.6 (m, 6H, *meta*- and *para*-H, 2Ph), 7.83 (br. d, 4H, *ortho*-H, 2Ph, *J* 7.8 Hz); for **13a**, 1.34 (s, 9H, Bu^t), 3.33 (s, 3H, MeO), 7.2–7.6 (m, 10H, 2Ph). ^{13}C NMR, δ: for **12a** and **13a**, 27.2 and 28.6 (CMe_3), 29.9 and 30.5 (CMe_3), 53.2 and 54.6 (MeO), 65.4, 66.8, 76.3, 90.3, 106.4 and 114.6 (*C*OMe, C≡C), 114.5, 120.6, 124.2, 126.4, 128.9 and 141.4 (C=C, *ipso*-C, Ph), 125.8, 126.6, 128.2, 129.0, 129.1, 129.5, 129.7 and 130.0 (Ph). IR (thin film, ν/cm^{-1}): 2210 (C≡C).

For a mixture of **12b** and **13b** (**12b**:**13b** ratio 1:1.2): overall yield 58% from perchlorate **7b**. ^{1}H NMR, δ: for **12b**, 3.63 (s, 3H, MeO), 7.2–7.7 (m, 11H, 3Ph), 7.89 (br. d, 4H, *ortho*-H, 2PhC=, *J* 7.8 Hz); for **13b**, 3.39 (s, 3H, MeO), 7.2–7.7 (m, 15H, 3Ph). ^{13}C NMR, δ: for **12b** and **13b**, 53.3 and 55.1 (MeO), 67.2, 77.0, 81.4, 87.8, 104.1 and 105.3 (*C*OMe, C≡C), 120.1, 121.9, 122.8, 126.4, 126.9, 128.5 and 141.2 (C=C, *ipso*-C, Ph), 125.9, 126.3, 126.8, 128.1, 128.3, 128.4, 128.6, 129.1, 129.2, 129.3, 129.5, 129.7, 130.0, 130.5, 131.4, 131.6 (Ph). IR (thin film, ν/cm^{-1}): 2198, 2214 (C≡C).

References

1 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).

2 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.

3 K. N. Shavrin, I. B. Shvedova and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 1991, 2559 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40**, 2235).

4 K. N. Shavrin, V. D. Gvozdev and O. M. Nefedov, *Mendeleev Commun.*, 1997, 144.

5 K. N. Shavrin, V. D. Gvozdev and O. M. Nefedov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 2079 (*Russ. Chem. Bull.*, 1997, **46**, 1973).

6 R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, 1961, **83**, 2367.

Received: 5th February 1999; Com. 99/1439