(Alk-1-ynyl)diphenylcyclopropenium perchlorates as a new class of cyclopropenium salts

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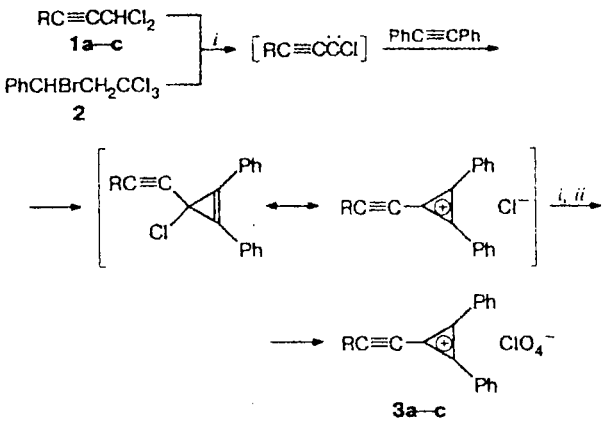
We found that generation of (alk-1-ynyl)halocarbenes by treatment of 1,1-dichloroalk-2-ynes[1–3] (**1a—c**) or 3-bromo-1,1,1-trichloro-3-phenylpropane[4] (**2**) with Bu^{t}OK in benzene at ~20 °C in the presence of a threefold excess of tolane followed by treatment of the reaction mixture, having been passed through a layer of SiO_2, with 75% perchloric acid gives (alk-1-ynyl)diphenylcyclopropenium perchlorates (**3**), previously unknown compounds of the acetylene series, as solid precipitates in 24—38% yields.



R = Bu^t (**a**), Ph (**b**), *p*-MeC$_6$H$_4$ (**c**)

Reagents and conditions. *i.* Bu^{t}OK, benzene, 20 °C. *ii.* 75% aqueous $HClO_4$, benzene, 20 °C.

We used this procedure to transform 1,1-dichloro-4,4-dimethylpent-2-yne (**1a**) into 1-(3,3-dimethylbut-1-ynyl)-2,3-diphenylcyclopropenium perchlorate (**3a**) in 38% yield, m.p. 70—71 °C. ^{1}H NMR, δ: 1.54 (s, 9 H, Bu^t); 7.86 (br.dd, 4 H, *m*-H, 2 Ph, $J_1 = J_2 = 7.8$ Hz); 8.04 (br.t, 2 H, *p*-H, 2 Ph, $J = 7.8$ Hz); 8.43 (br.d, 4 H, *o*-H, 2 Ph, $J = 7.8$ Hz). ^{13}C NMR, δ: 28.6 (3 CH_3); 30.2 ($\underline{C}(CH_3)_3$); 63.9 (Bu^{t}C≡$\underline{C}$); 119.4 (*ipso*-C, 2 Ph); 130.4, 136.1, 139.2 (2 Ph); 138.4 (Bu$^t\underline{C}$≡C); 144.2 ($\underline{C}C$≡C, *cyclo*-C_3^+); 155.3 (2 $\underline{C}$Ph, *cyclo*-C_3^+). IR, ν/cm^{-1}: 1408 (*cyclo*-C_3^+); 2210 (C≡C).

The transformation of 1,1-dichloro-3-phenylprop-2-yne (**1b**) gave 1-(phenylethynyl)-2,3-diphenylcyclopropenium perchlorate (**3b**) in 35% yield, m.p. 66—68 °C. ^{1}H NMR, δ: 7.69 (br.dd, 2 H, *m*-H, PhC≡, $J_1 = J_2 = 7.5$ Hz); 7.80 (br.t, 1 H, *p*-H, PhC≡, $J = 7.5$ Hz); 7.93 (br.dd, 4 H, *m*-H, 2 Ph, $J_1 = J_2 = 7.7$ Hz); 8.00—8.15 (m, 4 H, *p*-H, 2 Ph, *o*-H, PhC≡); 8.53 (br.d, 4 H, *o*-H, 2 Ph, $J = 7.7$ Hz). ^{13}C NMR, δ: 73.5 (PhC≡$\underline{C}$); 118.2, 119.5 (*ipso*-C, 2 Ph, PhC≡); 129.5, 134.4, 134.9 (PhC≡); 130.4, 136.2, 139.2 (2 Ph); 125.7 (Ph$\underline{C}$≡C); 142.4 ($\underline{C}C$≡C, *cyclo*-C_3^+); 154.5 (2 $\underline{C}$Ph, *cyclo*-C_3^+). IR, ν/cm^{-1}: 1408 (*cyclo*-C_3^+); 2191 (C≡C).

Perchlorate **3b** was also prepared in 25% yield from 3-bromo-1,1,1-trichloro-3-phenylpropane (**2**), which, according to published data,[4] generates (phenylethynyl)chlorocarbenes on treatment with Bu^{t}OK.

1,1-Dichloro-3-(*p*-tolyl)prop-2-yne (**1c**) was converted into 1-(*p*-tolylethynyl)-2,3-diphenylcyclopropenium perchlorate (**3c**) in 24% yield, m.p. 163—164 °C. ^{1}H NMR, δ: 2.49 (s, 3 H, Me); 7.48 (br.d, 2 H, *m*-H, *p*-Tol, $J = 8.0$ Hz); 7.91 (br.dd, 4 H, *m*-H, 2 Ph, $J_1 = J_2 = 7.6$ Hz); 7.92 (br.d, 2 H, *o*-H, *p*-Tol, $J = 8.0$ Hz); 8.08 (br.t, 4 H, *p*-H, 2 Ph, $J = 7.6$ Hz); 8.51 (br.d, 4 H, *o*-H, 2 Ph, $J = 7.6$ Hz). ^{13}C NMR, δ: 21.3 (Me); 73.9 (*p*-TolC≡$\underline{C}$); 115.1, 119.6 (*ipso*-C, 2 Ph, *p*-Tol); 130.3, 130.5, 135.1, 136.1, 139.1 (2 Ph, *p*-Tol); 127.2 (*p*-Tol$\underline{C}$≡C); 142.2 ($\underline{C}C$≡C, *cyclo*-C_3^+); 146.5 ($\underline{C}$Me, *p*-Tol); 153.9 (2 $\underline{C}$Ph, *cyclo*-C_3^+).

Typically, the signals of the β-carbon atom of the triple bond in the ^{13}C NMR spectra of perchlorates **3a—c** occur in the region of 126—138 ppm, *i.e.*, in a substantially lower field than the similar signals in the spectra of other acetylene derivatives, for example, *gem*-(alk-1-ynyl)halocyclopropanes (75—95 ppm).[4,5] This shift is due most likely to the presence of effective conjugation between the triple bond and the cyclopropenium cation in salts **3a—c**.

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