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Synthesis of (trimethylsilyl)(cyclopropyl)acetylenes and terminal cyclopropylacetylenes via an arsonium ylide under phase-transfer conditions

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Abstract

The phase-transfer reaction of 3-(trimethylsilyl)-2-propynylidenetriphenylarsorane generated from the corresponding arsonium salt and aqueous sodium hydroxide with substituted chalcones gave (trimethylsilyl)(cyclopropyl)acetylenes in 83–98% yields with high stereoselectivity. In all cases exclusively one isomer is obtained. Addition of methanol gives the desilylated terminal cyclopropylacetylenes in 85–96% yields. This methodology provides a convenient route to the (trimethylsilyl)(cyclopropyl)acetylenes and subsequently to the desilylated terminal cyclopropyl acetylenes.

Introduction

(Trimethylsilyl)(cyclopropyl)acetylenes and desilylated species have much potential in organic synthesis since they can serve as useful intermediates and are capable of undergoing many organic transformations [1]. Recently we described a method for the synthesis of (trimethylsilyl)(cyclopropyl)acetylenes, but n-butyllithium had to be used under a rather rigorous conditions (anhydrous and oxygen-free solution) [2]. Here we report a convenient route to the title compounds by use of an arsonium salt under phase-transfer conditions with high stereoselectivity.

Results and discussion

The phase-transfer reaction of 3-(trimethylsilyl)-2-propynylidenetriphenylarsorane, generated from the corresponding arsonium salt and aqueous sodium hydroxide, with chalcones such as α,β-unsaturated ketones gives (trimethylsilyl)(cyclopropyl)acetylenes in 83–98% yields with high stereoselectivity (eq. 1).

$$\underset{(1)}{(C_6H_5)_3\overset{+}{As}CH_2C{\equiv}CSi(CH_3)_3Br^-} \xrightarrow{aq.NaOH/Et_2O} \underset{(2)}{(C_6H_5)_3\overset{+}{As}\overset{-}{C}HC{\equiv}CCSi(CH_3)_3}$$

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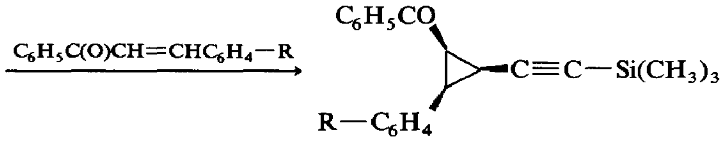
Table 1

The yields of (trimethylsilyl)(cyclopropyl)acetylenes (3) and terminal cyclopropylacetylenes (4) prepared.

R	Yield (%)	
	3	4
4-Cl	**3a** 96	**4a** 95
4-Br	**3b** 96	**4b** 96
3-Br	**3c** 98	**4c** 92
4-CH_3	**3d** 90	**4d** 87
H	**3e** 91	**4e** 85
4-CH_3O	**3f** 88	**4f** 88
4-NO_2	**3g** 83	**4g** 88

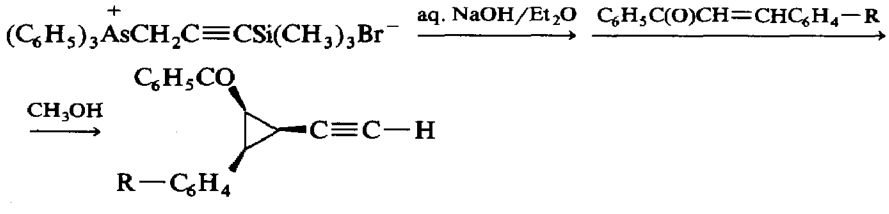


(1)

(3)

In contrast to the results reported previously [2], one isomer was obtained in all cases under phase-transfer conditions. The configurations of the products were ascertained on the basis of their NMR data by comparsion with the data reported previously [2]. Under the conditions employed here no trimethylsilyl enynes [3] were formed.

One of the methods to remove the introduced silyl group that of treatment with tetra-n-butyl ammonium fluoride in tetrahydrofuran is known. We have found that the addition of methanol to the mixture with stirring gives the desilylated terminal acetylenes (**4**) in a one-pot reaction under phase-transfer conditions (85–96% yields) (eq. 2).



(2)

(4)

The results are summarized in Table 1.

The major advantage of this phase-transfer reaction is the use of the more convenient handling of aqueous alkali than that of n-butyllithium. The characteristic feature of this phase-transfer reaction is that no added catalyst is necessary, since the reactant arsonium salt is also effective as the phase-transfer agent. In this case the proton transfer occurs at the interface followed by dissolution of the ylide in the organic medium where it then undergoes the cyclopropanation.

Experimental

All boiling and melting points are uncorrected. Infrared spectra of the solid products were obtained as KCl disks and liquid products were determined as films on a Shimadzu IR-440 Spectrometer. ^1H NMR spectra (chemical shifts in ppm from TMS) were obtained on a Varian EM-360 Spectrometer at 60 MHz or XL-200 Spectrometer at 200 MHz. Mass spectra were recorded on a Finnigan GC-MC 4021 Mass Spectrometer.

*Preparation of (trimethylsilyl)(cyclopropyl)acetylenes (**3**); general procedure*

Aqueous sodium hydroxide (20%; 2 ml) was added with stirring to a suspension containing 3-(trimethylsilyl)-2-propynyl triphenyl arsonium bromide (1) (0.497 g 1 mmol) and substituted chalcones (1 mmol) in absolute ether (10 ml) at 0 ° C. The reaction mixture was stirred at 0 ° C for 2 h and at 10 ° C for 9 h. After stirring the organic layer was removed. Evaporation of the solvent gave a residue which was purified by column chromatography on silica gel with petroleum ether (b.p. 60–90 ° C)/benzene (10 : 1) as eluent, to give triphenylarsine, and with petroleum ether/Et_2O (10 : 1) as eluent to afford product **3** in 83–98% isolated yields.

*Preparation of terminal cyclopropylacetylenes (**4**); general procedure:*

A similar procedure to that mentioned above was used, but after stirring at 10 ° C for 9 h, methanol (2ml) was added and the reaction mixture was stirred for 17 h. Compounds **4a–4g** are novel and their NMR, IR, mass spectrocopic data and elemental analyses are consistent with the assigned structures.

4a. Yield: 95%; m.p. 78-79 ° C. Analysis. Found: C, 77.12; H, 4.64. $C_{18}H_{13}ClO$ calcd.: C, 77.01; H, 4.67%. Selected IR data (KCl): 1660(s), 1020(s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{int.}$): δ 2.00 (d, 1H, $J = 2.2$); 2.60(ddd, 1H, $J = 2.2, 4.8, 9.0$); 2.98(dd, 1H, J = 5.5, 9.0); 3.28(dd, 1H, J = 4.8, 5.5); 7.25–7.61(m, 7H); 8.03 (d, 2H, $J = 9.5$). MS m/e: 280(M^+), 105 ($C_6H_5CO^+$), 77($C_6H_5^+$).

4b. Yield: 96%; m.p. 76–77 ° C. Analysis. Found: C, 66.76; H, 3.96. $C_{18}H_{13}BrO$ calcd.: C, 66.48; H, 4.03%. Selected IR data (KCl): 1660(s), 1020(s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{int.}$): δ 2.00(d, 1H, $J = 2.3$); 2.62(ddd, 1H, $J = 2.3, 5.0, 8.9$); 2.97(dd, 1H, $J = 5.5, 8.9$); 3.28(dd, 1H, $J = 5.0, 5.5$); 7.24–7.62(m, 7H); 8.02(d, 2H, $J = 8.4$). MS m/e: 324(M^+), 105 ($C_6H_5CO^+$), 77($C_6H_5^+$).

4c. Yield: 92%; b.p. 142–144 ° C/0.7 mmHg. Analysis. Found: C, 66.22; H, 3.90. $C_{18}H_{13}BrO$ calcd.: C, 66.48; H, 4.63%. Selected IR data (film): 1660(s), 1020(s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{int.}$): δ 2.00(d, 1H, $J = 2.1$); 2.58(ddd, 1H, $J = 2.1, 5.0, 8.9$); 2.97(dd, 1H, $J = 5.6, 8.9$); 3.28(dd, 1H, $J = 5.0, 5.6$); 7.16–7.60(m, 7H); 8.03(d, 2H, $J = 7.8$). MS m/e: 324(M^+), 105 ($C_6H_5CO^+$), 77($C_6H_5^+$).

4d. Yield: 87%; m.p. 86–87 ° C. Analysis. Found: C, 87.70; H, 6.23. $C_{19}H_{16}O$ calcd.: C, 87.66; H, 6.20%. Selected IR data (KCl): 1660(s), 1030(s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{int.}$): δ 1.99(d, 1H, $J = 2.3$); 2.35(s, 3H); 2.62(ddd, 1H, $J = 2.3, 4.9, 9.0$); 2.97(dd, 1H, $J = 5.5, 9.0$); 3.31(dd, 1H, $J = 4.9, 5.5$); 7.13–7.59(m, 7H); 8.00–8.05(m, 2H). MS m/e: 260 (M^+), 105($C_6H_5CO^+$), 77($C_6H_5^+$).

4e: Yield: 85%; m.p. 89–90 ° C. Analysis. Found: C, 87.72; H, 5.77. $C_{18}H_{14}O$ calcd.: C, 87.78; H, 5.73%. Selected IR data (KCl): 1660(s), 1020(s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{int.}$): δ 1.99(d, 1H, $J = 2.2$); 2.63(ddd, 1H, $J = 2.2, 5.0, 9.0$); 3.01(dd, 1H, $J = 5.5, 9.0$); 3.34(dd, 1H, $J = 5.0, 5.5$); 7.14–7.61(m, 8H); 7.96–8.08(m, 2H). MS m/e: 246(M^+), 105 ($C_6H_5CO^+$), 77($C_6H_5^+$).

4f. Yield: 88%; m.p. 61–62 ° C. Analysis. Found: C, 82.80; H, 5.92. $C_{19}H_{16}O_2$ calcd.: C, 82.58; H, 5.84%. Selected IR data (KCl): 1670(s), 1020(s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{int.}$): δ 1.93(d, 1H, $J = 2.2$); 2.56(ddd, 1H, $J = 2.2, 5.0, 8.8$); 2.94(dd, 1H, $J = 5.6, 8.8$); 3.23(dd, 1H, $J = 5.0, 5.6$); 3.80(s, 3H); 6.85–7.58(m, 7H); 8.03(d, 2H, $J = 6.7$). MS *m/e*: 276(M^+), 105($C_6H_5CO^+$), 77($C_6H_5^+$).

4g. Yield: 88%; m.p. 108–109 °C. Analysis. Found: C, 74.23, H, 4.60. $C_{18}H_{13}NO_3$ calcd.: C, 74.22, H, 4.50%. Selected IR data (KCl): 1670(s), 1020(s) cm^{-1}. ^1H NMR ($CDCl_3/TMS_{int.}$): δ 2.01(d, 1H, $J = 2.1$); 2.66(ddd, 1H, $J = 2.1, 5.0, 8.9$); 3.09(dd, 1H, $J = 5.5, 8.9$); 3.38(dd, 1H, $J = 5.0, 5.5$); 7.48–7.66(m, 5H); 8.04(d, 2H, $J = 7.0$); 8.20(d, 2H, $J = 8.7$). MS *m/e*: 291(M^+), 105($C_6H_5CO^+$), 77($C_6H_5^+$).

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