A Facile Synthesis of (Trimethylsilylethynyl)cyclopropanes via an Arsonium Ylide

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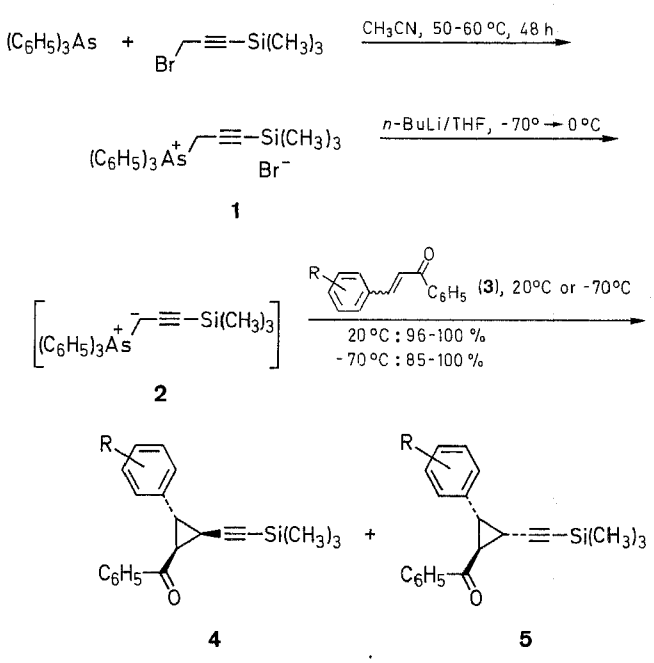
The reaction of 3-(trimethylsilyl)-2-propynylidenetriphenylarsorane, generated *in situ* from the corresponding arsonium salt and butyllithium, with chalcones (as α,β-unsaturated ketones) gives (trimethylsilylethynyl)cyclopropanes in 96–100% yield and with high stereoselectivity.

Some natural products with a cyclopropane moiety show biological activity.[1] Silylcyclopropanes are useful intermediates in organic synthesis since they capable of undergoing many transformations.[2] To the best of our knowledge, no simple methods are known for the synthesis of (trimethylsilylethynyl)cyclopropanes. Therefore, an efficient method for the synthesis of these compounds would be of interest. Corey et al.[3] reported that 3-(trimethylsilyl)-2-propynylidenetriphenylphosphorane reacts with aldehydes to give terminal 1-trimethylsilyl-3-alken-1-ynes; reactions with α,β-unsaturated ketones were not disclosed. We now report that the reaction of 3-(trimethylsilyl)-2-propynylidene)triphenylarsorane, generated

in situ from 3-(trimethylsilyl)-2-propynyltriphenylarsonium bromide (**1**) and butyllithium, with chalcones **3** as α,β-unsaturated ketones gives high yields (at 20 °C, ~ 96–100 %; at − 70 °C, ~ 85–100 %) of (trimethylsilylethynyl)cyclopropanes (**4** + **5**) with high stereoselectivity.



The reaction of phosphonium ylides with electron-deficient C=C double bonds is a well known method for the synthesis of cyclopropanes; however, the reaction usually proceeds with low stereoselectivity and the yields are only moderate.[5] Our method gives excellent yields with high stereoselectivity, even at room temperature (20 °C); in five out of eight investigated cases, the isomer **4** was obtained exclusively. The configuration of the products were ascertained on the basis of their NMR data by comparison with data reported previously[6] and by shift-reagent [Eu(fod)$_3$] studies.

3-(Trimethylsilyl)-2-propynyltriphenylarsonium bromide (**1**) is easily prepared from triphenylarsine and 3-bromo-1-(trimethylsilyl)propyne in acetonitrile.[4]

All products were characterized by microanalyses, mass, IR, and NMR spectra.

Table 2. Spectral Data of Compounds **4** and **5**

Product	IR (KBr)[a] ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS_{ext})[b] δ, J (Hz)
4a	2160 (w), 1660 (s), 1250 (s), 1020 (s), 850 (s)	0.02 (s, 9H); 2.57 (dd, 1H, J = 5.0, 9.0); 2.89 (dd, 1H, J = 5.6, 9.0); 3.00 (dd, 1H, J = 5.0, 5.6); 7.23–7.56 (m, 7H); 7.94–7.96 (m, 2H)
4b	2160 (w), 1650 (s), 1240 (s), 1020 (s), 850 (s)	0.00 (s, 9H); 2.46 (dd, 1H, J = 4.8, 9.0); 2.79 (dd, 1H, J = 5.4, 9.0); 3.09 (dd, 1H, J = 4.8, 5.4); 7.15–7.49 (m, 7H); 7.89–7.94 (m, 2H)
4c	2160 (w), 1670 (s), 1250 (s), 1020 (s), 850 (s)	0.04 (s, 9H); 2.44 (dd, 1H, J = 4.8, 9.0); 2.78 (dd, 1H, J = 5.4, 9.0); 3.07 (dd, 1H, J = 4.8, 5.4); 7.14–7.54 (m, 7H); 7.80–8.04 (m, 2H)
4d	2160 (w), 1660 (s), 1250 (s), 1020 (s), 850 (s)	0.00 (s, 9H); 2.22 (s, 3H); 2.40 (dd, 1H, J = 4.8, 9.0); 2.75 (dd, 1H, J = 5.4, 9.0); 3.04 (dd, 1H, J = 4.8, 5.4); 6.85–7.50 (m, 7H); 7.80–8.00 (m, 2H)
4e	2170 (w), 1660 (s), 1250 (s), 1030 (s), 850 (s)	0.00 (s, 9H); 2.45 (dd, 1H, J = 4.8, 9.0); 2.86 (dd, 1H, J = 5.4, 9.0); 3.14 (dd, 1H, J = 4.8, 5.4); 7.00–7.15 (m, 8H); 7.80–8.10 (m, 2H)
4f	2160 (w), 1670 (s), 1250 (s), 1030 (s), 850 (s)	0.00 (s, 9H); 2.50 (dd, 1H, J = 4.8, 9.0); 2.90 (dd, 1H, J = 5.4, 9.0); 3.17 (dd, 1H, J = 4.8, 5.4); 7.30–8.22 (m, 9H)
5f	2180 (w), 1660 (s), 1250 (s), 1030 (s), 850 (s)	0.00 (s, 9H); 2.41 (dd, 1H, J = 6.4, 8.8); 3.26 (dd, 1H, J = 6.0, 6.4); 3.33 (dd, 1H, J = 6.0, 8.8); 7.21–7.31 (m, 2H); 7.40–8.17 (m, 7H)
4g	2170 (w), 1670 (s), 1240 (s), 1030 (s), 850 (s)	−0.02 (s, 9H); 2.54 (dd, 1H, J = 4.8, 9.0); 2.84 (dd, 1H, J = 5.4, 9.0); 3.16 (dd, 1H, J = 4.8, 5.4); 3.43 (s, 3H); 6.77 (d, 2H, J = 8.6); 7.37–7.48 (m, 5H); 7.92 (d, 2H, J = 8.2)
5g	2170 (w), 1670 (s), 1240 (s), 1030 (s), 850 (s)	0.06 (s, 9H); 2.36 (dd, 1H, J = 6.6, 8.8); 3.18 (dd, 1H, J = 6.0, 6.4); 3.23 (dd, 1H, J = 6.0, 8.8); 6.81–6.85 (m, 2H); 7.09–7.58 (m, 5H); 8.01–8.05 (m, 2H)
4h	2160 (w), 1660 (s), 1250 (s), 1020 (s), 850 (s)	0.00 (s, 9H); 2.54 (dd, 1H, J = 4.8, 9.0); 2.80 (dd, 1H, J = 5.4, 9.0); 2.86 (s, 6H); 3.12 (dd, 1H, J = 4.8, 5.4); 6.59–7.54 (m, 7H); 7.90–7.94 (m, 2H)
5h	2160 (w), 1660 (s), 1250 (s), 1020 (s), 850 (s)	−0.10 (s, 9H); 1.97 (dd, 1H, J = 6.4, 8.8); 2.68 (dd, 1H, J = 6.0, 6.4); 2.72 (s, 6H); 2.83 (dd, 1H, J = 6.0, 8.8); 6.30–7.93 (m, 9H)

[a] The IR spectra were recorded on a Schmadzu IR-440 spectrometer.
[b] The NMR spectra were recorded with a Varian EM-360 or XL-200 spectrometer.

Table 1. Trimethylsilylethynylcyclopropanes **4** and **5** prepared

Product	R	Reaction at: 20 °C Yield (%)	20 °C Ratio (4:5)	− 70 °C Yield (%)	− 70 °C Ratio (4:5)	mp (°C)	Molecular Formula[a]	MS (70 eV)[b] m/z
4a	4-Cl	96	100:0	94	100:0	63–64	$C_{21}H_{21}ClOSi$ (352.9)	352 (M^+), 317, 105, 73
4b	4-Br	96	100:0	98	100:0	77–78	$C_{21}H_{21}BrOSi$ (397.4)	396 (M^+), 105, 73
4c	3-Br	99	100:0	100	100:0	(bp 160–162/0.9 mbar)	$C_{21}H_{21}BrOSi$ (397.4)	396 (M^+), 105, 73
4d	4-CH_3	98	100:0	97	100:0	69–70	$C_{22}H_{24}OSi$ (332.5)	332 (M^+), 317, 105, 73
4e	H	96	100:0	85	100:0	57–58	$C_{21}H_{22}OSi$ (318.5)	318 (M^+), 105, 73
4f	4-NO_2	96	94:6	93	95:5	85–86	$C_{21}H_{21}NO_3Si$ (363.5)	363 (M^+), 105, 73
5f						123–124	$C_{21}H_{21}NO_3Si$ (363.5)	363 (M^+), 105, 73
4g	4-OCH_3	99	88:12	99	92:8	48–49	$C_{22}H_{24}O_2Si$ (348.5)	348 (M^+), 333, 317, 105, 73
5g						90–91	$C_{22}H_{24}O_2Si$ (348.5)	348 (M^+), 333, 317, 105, 73
4h	4-$N(CH_3)_2$	100	78:22	100	80:20	70–71	$C_{23}H_{27}NOSi$ (361.6)	361 (M^+), 256, 105, 73
5h						81–82	$C_{23}H_{27}NOSi$ (361.6)	361 (M^+), 256, 105, 73

[a] Satisfactory microanalyses obtained: C ± 0.38, H ± 0.25.
[b] Recorded on a Finnigan 4021 mass spectrometer.

Trimethylsilylethynylcyclopropanes (4 + 5); General Procedure:
Butyllithium (4.0 mmol in 2.6 mL of hexane) is added dropwise over 30 min to a stirred suspension of 3-(trimethylsilyl)-2-propynyl- triphenylarsonium bromide (**1**; 4.0 mmol) in dry THF (18 mL) at −70 °C under N_2. The mixture is warmed to 20 °C, then stirred for 30 min, the α,β-unsaturated ketone **3** (3.0 mmol) is added (or the mixture is recooled to −70 °C, and **3** then added), and stirring is continued for 30 min. The solvent is then evaporated and the residue is purified by column chromatography on silica gel eluting with petroleum ether (bp 60–90 °C)/benzene (10:1) to give triphenylarsine and eluting with petroleum ether/Et_2O (10:1) to afford product **4** or **4** + **5**.

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