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SYNTHESIS OF SILYLCYCLOPROPANES VIA ARSONIUM YLIDES[1]

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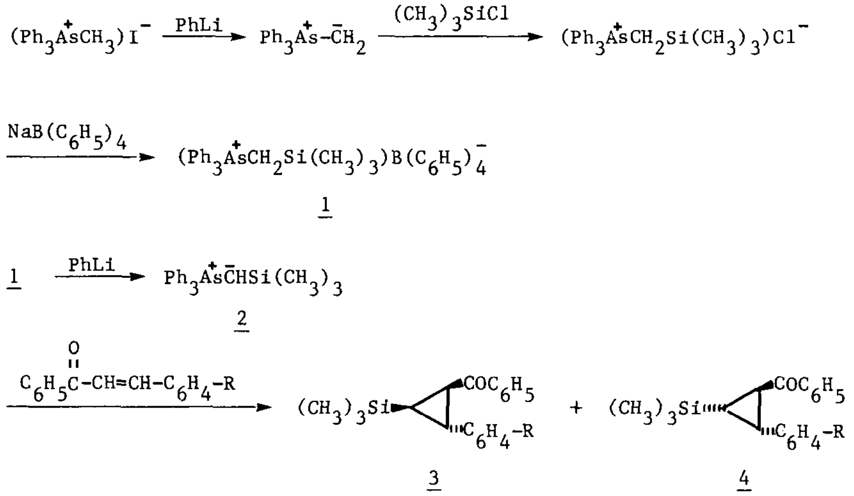
Summary. Silylcyclopropanes were synthesized from trimethylsilylmethylenetriphenylarsorane and substituted chalcones.

Since the widespread upsurge of interest in organosilicon reagents, the silylcyclopropane has begun to be considered as a useful reagent for a variety of applications. The silicon substituent can be efficiently replaced by both electrophiles and nucleophiles, therefore silylcyclopropanes will find their place as highly serviceable organic intermediates[4]. Recently, Cooke and Magnus[5] reported that trimethylsilylmethylenesulfurane reacted with α,β-unsaturated ketones especially cyclic species to give silylcyclopropanes, but with chalcone to give vinyl sulfide. Although silylated arsonium ylides have been described but virtually no details of their reactions with organic substrates were disclosed[6]. We now report that trimethylsilylmethylenetriphenylarsorane, in contrast to trimethylsilylmethylenesulfurane, could react with substituted chalcones to give silylcyclopropanes (Scheme A).



$$(Ph_3\overset{+}{A}sCH_3)I^- \xrightarrow{PhLi} Ph_3\overset{+}{A}s\text{-}\bar{C}H_2 \xrightarrow{(CH_3)_3SiCl} (Ph_3\overset{+}{A}sCH_2Si(CH_3)_3)Cl^-$$

$$\xrightarrow{NaB(C_6H_5)_4} (Ph_3\overset{+}{A}sCH_2Si(CH_3)_3)B(C_6H_5)_4^-$$

1

$$\underline{1} \xrightarrow{PhLi} Ph_3\overset{+}{A}s\bar{C}HSi(CH_3)_3$$

2

$$\xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}\text{-}CH{=}CH\text{-}C_6H_4\text{-}R}$$

3

4

Scheme A

The results are summarized in Table 1.

Table 1 Silylcyclopropanes 3a-f and 4a-f

Product	R	Mp(Bp) (^{o}C/torr)	Room Temp.		-70^{o}C	
			Yield (%)	Ratio (3:4)	Yield (%)	Ratio (3:4)
3a	p-CH_3O	91-92	40	45:55	47	31:69
4a		93-94				
3b	p-CH_3	39-40	36	50:50	40	17:83
4b		85-86				
3c	p-Br	135-137/0.6	36	42:58	34	27:73
4c		93-94				
3d	p-Cl	157-159/2	30	45:55	33	20:80
4d		81-82				
3e	H	130-132/0.8	25	50:50	30	17:83
4e		150-152/1				
3f	m-Br	166-168/1	23	50:50	30	23:77
4f		128-130/0.7				

At lower temperature (-70^{o}C), the yields of the products were better than that at higher temperature and the ratios of two isomers (3:4) were changed from ca. 1:1 down to 1:4. The structures of all products were ascertained by MS, IR and NMR spectra[7]. All micro-analyses were consistent with the calculated values.

It is worth noting that trimethylsilylmethylenesulfurane used as silylcyclopropanation reagent had to be generated with secondary butyllithium. If tertiary butyllithium or normal butyllithium is used no silylcyclopropanation results[5]. The experimental procedure of our method is simple, the conditions are mild and the yields are moderate. Thus this new silylcyclopropanation reagent provides a facile synthesis of the title compounds.

The typical procedure was as follows:

Trimethylsilylmethyltriphenyl arsonium tetraphenylborate (1):

To an ether solution of methylenetriphenylarsorane prepared from 11.2g (25 mmol) of methyltriphenyl arsonium iodide and 25 mmol of phenyllithium in a total of ca. 230 ml of absolute ether, there was added 4.1g of chlorotrimethylsilane in 40 ml of absolute ether at -70°C under nitrogen. A white precipitate formed immediately. The reaction mixture was allowed to stir at -70°C for 1 h and at room temperature for another 2 h. The precipitate was filtered under nitrogen, washed several times with ether, dissolved in 30 ml of methanol and 8.5g (25 mmol) of sodium tetraphenylborate in 20 ml of methanol was added. The crude product was separated, recrystallized from ethylene dichloride/ethyl acetate/ether to give trimethylsilylmethyltriphenyl arsonium tetraphenylborate (1), yield: 12.1g (68%); m.p. 174-176°C.

Trans and cis-3-trimethylsilyl-trans-2-benzoyl-1-p-methoxyphenylcyclopropane (3a and 4a):

To an ether solution of trimethylsilylmethylenearsorane prepared from 4.3g (6 mmol) of trimethylsilylmethyltriphenyl arsonium tetraphenylborate and 5.7 mmol of phenyllithium in a total of 170 ml of absolute ether, there was added 0.7g (3 mmol) of p-methoxybenzylideneacetophenone in 70 ml of absolute ether at room temperature under nitrogen. The mixture after stirring at room temperature for 3 h and removal of the solvent under vacuum and column chromatography on silica gel gave 3a (0.172g; 18%) and 4a (0.212g; 22%).

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References and Notes

1. This paper is the 28th report on the studies of the application of elemento-organic compounds of fifth and sixth groups in organic syntheses.
2. Department of Chemistry, Shanghai University of Science and Technology, Shanghai, China.
3. Formerly spelled as Yao-Tseng Huang.
4. L. A. Paquentte, Israel J. Chem. 1981, 21, 128.
5. F. Cooke, P. Magnus, J. Chem. Soc. Chem. Commun. 1978, 714.
6. D. Seyferth, H. M. Cohen, J. Inorg. and Nuclear Chem. 1961, 20, 73; N. E. Miller, Inorg. Chem. 1965, 4, 1458; K. A. O. Starzewski, W. Richter, H. Schmidbaur, Chem. Ber. 1976, 109, 473.
7. All new compounds gave satisfactory spectral and analytical properties. For ^{1}H-NMR, TMS was used as an external reference.

1: ^{1}H-NMR (CD_2Cl_2): δ, -0.04(s,9H); 1.99(s,2H); 6.22-7.89(m,35H); IR (ν,cm^{-1}): 1240(s); 835(s); MS m/e: 393, 306, 73.

3a: ^{1}H-NMR (CCl_4): δ,0.02(s,9H); 0.48-0.87(m,1H); 2.32-3.02(m,2H); 3.68(s,3H); 6.60-7.70(m,7H); 7.78-8.15(m,2H); IR (ν,cm^{-1}): 1670(s); 1260(s); 1020(s); 830(s); MS m/e: 324 (M^+), 309, 105, 73.

4a: ^{1}H-NMR (CCl_4): δ, -0.36(s,9H); 0.64-1.04(m,1H); 2.71-2.91(m,2H); 3.58(s,3H); 6.50-7.50(m,7H); 7.74-8.08(m,2H); IR (ν,cm^{-1}): 1660(s); 1260(s); 1000(s); 830(s); MS m/e: 324(M^+), 309, 105, 73.

3b: ^{1}H-NMR (CCl_4): δ, 0.03(s,9H); 0.50-0.90(m,1H); 2.20(s,3H); 2.38-2.95(m,2H); 6.80-7.50(m,7H); 7.75-8.08(m,2H); IR (ν,cm^{-1}): 1670(s); 1250(s); 1020(s); 840 (s); MS m/e: 308 (M^+), 105, 73.

4b: ^{1}H-NMR (CCl_4): δ, -0.30(s,9H); 0.73-1.10(m,1H); 2.17(s,3H); 2.81-3.01(m,2H); 6.77-7.50(m,7H); 7.83-8.14(m,2H); IR (ν,cm^{-1}): 1660(s); 1250(s); 1010(s); 840(s); MS m/e: 308(M^+), 105, 73.

3c: ^{1}H-NMR (CCl_4): δ, -0.02(s,9H); 0.52-0.84(m,1H); 2.43-2.97(m,2H); 6.90-7.60 (m,7H); 7.85-8.10(m,2H); IR (ν,cm^{-1}): 1680(s); 1250(s); 1010(s); 840(s); MS m/e: 372(M^+), 105, 73.

4c: ^{1}H-NMR (CCl_4): δ, -0.26(s,9H); 0.73-1.10(m,1H); 2.80-3.00(m,2H); 6.80-7.65 (m,7H); 7.80-8.13(m,2H); IR (ν,cm^{-1}): 1660(s); 1250(s); 1000(s); 840(s); MS m/e: 372(M^+), 105, 73.

3d: ^{1}H-NMR (CCl_4): δ, 0.00(s,9H); 0.53-0.90(m,1H); 2.40-3.00(m,2H); 7.00-7.66 (m,7H); 7.90-8.20(m,2H); IR (ν,cm^{-1}): 1670(s); 1240(s); 1000(s); 840(s); MS m/e: 328(M^+), 105, 73.

4d: ^{1}H-NMR (CCl_4): δ, -0.24(s,9H); 0.79-1.17(m,1H); 2.87-3.08(m,2H); 7.20-7.70 (m,7H); 7.97-8.23(m,2H); IR (ν,cm^{-1}): 1670(s); 1260(s); 1000(s); 830(s); MS m/e: 328(M^+), 105, 73.

3e: ^{1}H-NMR (CCl_4): δ, 0.00(s,9H); 0.52-0.90(m,1H); 2.37-2.91(m,2H); 6.80-7.40 (m,8H); 7.55-7.87(m,2H); IR (ν,cm^{-1}): 1670(s); 1240(s); 1010(s); 840(s); MS m/e: 294(M^+), 279, 105, 73.

4e: ^{1}H-NMR (CCl_4): δ, -0.32(s,9H); 0.79-1.16(m,1H); 2.82-3.03(m,2H); 6.90-7.45 (m,8H); 7.70-8.00(m,2H); IR (ν,cm^{-1}): 1670(s); 1250(s); 1000(s); 830(s); MS m/e: 294(M^+), 279, 105, 73.

3f: ^{1}H-NMR (CCl_4): δ, 0.07(s,9H); 0.59-1.00(m,1H); 2.50-3.06(m,2H); 6.95-7.58 (m,7H); 7.79-8.07(m,2H); IR (ν,cm^{-1}): 1670(s); 1250(s); 1020(s); 840(s); MS m/e: 372(M^+), 105, 73.

4f: ^{1}H-NMR (CCl_4): δ, -0.17(s,9H); 0.80-1.20(m,1H); 3.88-4.08(m,2H); 6.95-7.60 (m,7H); 7.82-8.11(m,2H); IR (ν,cm^{-1}): 1670(s); 1250(s); 1010(s); 840(s); MS m/e: 372(M^+), 105, 73.

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