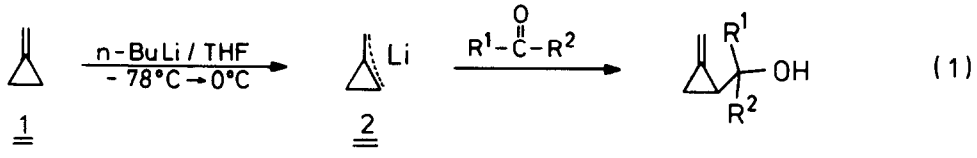
Tetrahedron Letters,Vol.26,No.3,pp 301-304,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

SYNTHESIS OF SILYLATED METHYLENECYCLOPROPANES

Ethan Sternberg and Paul Binger*
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1; D-4330 Mülheim a.d. Ruhr
Bundesrepublik Deutschland

Abstract: 2-Trimethylsilylmethylenecyclopropane (3) was synthesized by reaction of lithio methylenecyclopropane with TMSCl. The lithium salt of 3 reacts with some electrophiles by α- or γ-attack depending on the nature of the electrophile. Whereas alkenylbromides 8 and 9 or alkinylbromide 10 give exclusively α-attack, benzaldehyde reacts with γ-alkylation.

Recently some reports have been published dealing with the preparations and reactions of lithio methylenecyclopropanes 2[1-3]. Up to now only the alkylation of 2 with epoxides, aldehydes or ketones which give primary[2], secondary and tertiary alcohols[1,3] have been described.



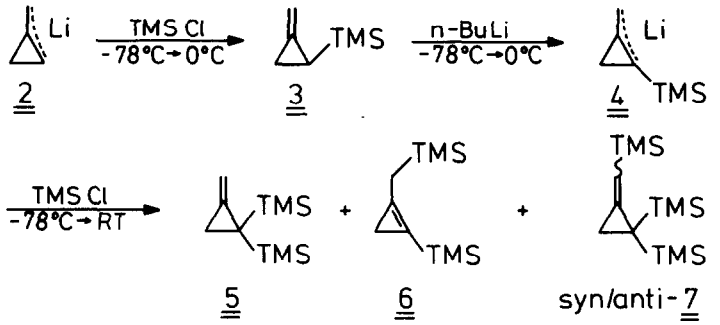
1 2 (1)

R^1 = alkyl, aryl
R^2 = H, alkyl

We hoped to develop a general method for the functionalization of methylenecyclopropanes by first silylation and then alkylation under similiar conditions as used above, so that this method could be applied to prepare new starting materials for our work in the fields of Pd(0) and Ni(0) catalyzed

cycloadditons[4].

Silylation of 2, prepared according to lit.[1], with trimethylsilylchloride (TMSCl) gives methylenecyclopropane 3 in 72% yield. Furthermore, in situ deprotonation of 3 and subsequent silylation with TMSCl proceeds to give the bisilylated methylenecyclopropanes 5 and 6 in the ratio 88:12 (74% yield) contaminated with syn/anti trisilyl derivative 7 (13% yield).

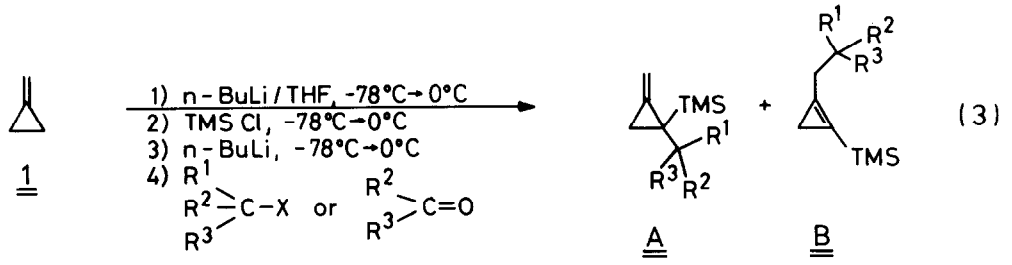


(2)

Alkylation of the anion 4 with the α,ω-alkenylbromides 8, 9, α,ω-alkinylbromide 10 and with 2-dimethoxyethylbromide 11 proceeds to give moderate to good yields of only one isomer (15-18) derived from reaction next to the TMS group (eqn.3 and table). Benzylchloride also gives the α-alkylated product 19 with a significant amount (15%) of trans-stilbene. These results differ somewhat from the known alkylation of allylsilanes in which mostly γ-alkylation occurs[6]. The reason for this seems to be the greater ring strain in cyclopropene derivatives compared with methylenecyclopropanes. The formation of the less stable 1-(trimethylsilyl)methyl-2-trimethylsilylcyclopropene 6 in eqn.2 is possibly due to steric hinderance which does not allow the anion 4 to react exclusively with TMSCl in the α-position.

As in the work of Thomas[1], we anticipated that the alkylation of 4 with an aldehyde or a ketone is likely to occur on the cyclopropane ring next to the silicon. But the reaction with benzaldehyde proceeds through a number of coloured intermediates to give exclusively the cyclopropene derived from γ-alkylation, as described with other lithiated allylsilanes[7]. In situ silylation with TMSCl gave the thermally sensitive siloxane 20 in good yields. Alkylation of 4 with acetone followed by silylation with TMSCl of

the reaction mixture gave both a cyclopropene 22 and a methylenecyclopropane 21 in a ratio of 41:59. We believe that the reaction with benzaldehyde and in part with acetone is best described by an electron transfer mechanism[7]. This would imply: formation of the benzoxyradical anion and subsequent coupling at the γ-position of the radical cation of 4.



(3)

alkylating agent	#	R^1	R^2	R^3	A	#[5]	B	#[5]	b.p. [°C/Torr]	yield
$Br(CH_2)_3CH=CH_2$	8	$(CH_2)_2CH=CH_2$	H	H	100	15	-	-	55-56/1	75%
$Br(CH_2)_4CH=CH_2$	9	$(CH_2)_3CH=CH_2$	H	H	100	16	-	-	42/0.3	81%
$Br(CH_2)_2(CH_2O)_2$	10	$CH_2(CH_2O)_2$	H	H	100	17	-	-	62-63/0.1	54%
$Br(CH_2)_4C$ CH	11	$(CH_2)_3C$ CH	H	H	100	18	-	-	60-65/0.02	65%
$C_6H_5CH_2Cl$	12	C_6H_5	H	H	100	19	-	-	60-61/0.5	46%
C_6H_5CHO	13	OTMS	C_6H_5	H	-	-	100	20	130-140/0.005	70%
$(CH_3)_2C=O$	14	OTMS	CH_3	CH_3	59	21	41	22	115-130/0.01	67%

Table 1: Regioselectivity and yields in the alkylation of 2-trimethylsilyl-methylenecyclopropyllithium.

General Procedure

To 7.25g (0.134mol) of methylenecyclopropane in 300ml of THF cooled to -78°C was added 77ml (0.134mol) of n-butyllithium in hexane over a period of 5 min. After warming to 0°C in 30 min., stirring for 20 min. and cooling again to -78°C 14.6g (0.134mol) of TMSCl was added. The reaction mixture was warmed again to 0°C as described and 77ml (0.134mol) of n-butyllithium in hexane was added in 5 min. at -78°C. The warming procedure was repeated before addition of the alkylating agent (0.14mol) dissolved in 25ml THF at -78°C and stirring at room temperature for 5h. In the case of benzaldehyde

or acetone the reaction mixture was warmed to 0°C and 16.1g (0.148mol) of TMSCl was added.

After normal workup the new methylenecyclopropanes were isolated by Kugelrohrdistillation. Preparative gas chromatography was necessary to separate compound 19 from the trans-stilbene and the isomers 21, 22; 5, 6 and syn/anti-7.

^{1}H NMR spectra:

3: [5.26, 5.18 (ddd, J= 3.5, 4 and 5 Hz; 2H)]; 1.21 (ddd, J= 4, -6.5 and 10.5 Hz; 1H); 0.86 (ddd, J= 3.5, -6.5 and 6.5 Hz; 1H); 0.58 (ddd, J= 5, 6.5 and 10.5 Hz; 1H); ca. 0 ppm (s, 9H). - 5: 6.75 (m, 1H); 5.03 (m, 1H); 0.99 (m, 2H); 0.03 ppm (s, 18H). - 6: 2.04 (s, 2H); 0.70 (s, 2H); 0.14 (s, 9H); 0.04 (s, 9H). - 15: 5.77 (ddt, J= 17, 10.5, 6.5 Hz; 1H); 5.20 (m, 1H); 5.10 (d, J= 10.5 Hz; 1H); 5.06 (d, J= 17 Hz; 1H); 4.82 (m, 1H); 1.93 (m, 2H); 1.38 (m, 4H); 1.00 (ddd, J= 1.5, 2 and -6.5 Hz; 1H); 0.74 (ddd, J= 1.5, 2 and -6.5 Hz; 1H); -0.03 ppm (s, 9H). - 17: [5.20, 5.12 (m, 2H)]; 4.69 (t, J= 4Hz; 1H); [3.47, 3.37 (m, 4H)]; 1.67 (m, 4H); 0.96 (m, J= -7.5 and ca. 1-2 Hz; 1H); 0.76 (m, J= -7.5 and ca. 1 Hz; 1H); -0.03 ppm (s, 9H). - 18: 5.29 (m, 1H); 5.19 (m, 1H); 1.91 (m, 2H); 1.72 (m, 1H); 1.30 (m, 6H); 0.98 (ddd, J= 1.5, 2 and -7.5 Hz; 1H); 0.70 (ddd, J= ca. 1, 2 and -7.5 Hz; 1H); -0.04 ppm (9H). - 20: 6.9 (m, 5H); 4.91 (t, J= 6.5 Hz; 1H); [3.02 and 2.94 (d, J= 6.5 Hz; 2H)]; 1.90 (s, 2H); 0.05 (s, 9H); -0.05 ppm (s, 9H).

*) E.W. Thomas; Tetrahedron Letters 1983, 1467.

2) G. Leandri, H. Monti and M. Bertrand; Bull. Soc. Chim. France 1974, 3015.

3) T.V. Akhachenskayo, M. Bakhbukh, Y.K. Grishin, N.A. Donskaya and Y.A. Ustynyuk; J. Org. Chem. USSR 14, 2139 (1978).

4) P. Binger, B. Cetinkaya, M.J. Doyle, A. Germer and U. Schuchardt; Fundamental Research in Homogenous Catalysis, Vol.3, 271; Plenum Press New York, London (1979).

5) All compounds were characterized by their MS, ^{1}H NMR and ^{13}C NMR spectra and elemental analysis.

6a) R.J.P. Corriu, J. Masse and D. Samate; J. Organomet. Chem. 93, 71 (1975).
b) K. Kovmaylo and T.H. Chan; Tetrahedron Letters 1984, 717.

7) P.W.K. Lau and T.H. Chan; Tetrahedron Letters 1978, 2383.

(Received in Germany 12 September 1984)