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Note

Vinylsilanes in synthesis: 2-Halo-1-cyclopentenyl alkyl/aryl ketones from 2-halo-1-trimethylsilylcyclopentenes

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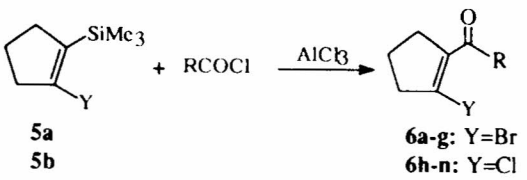
2-Bromo - and 2 - chloro - 1 - trimethylsilylcyclopent-1 -ene undergo Friedel-Crafts reaction in smoothly with a variety of acyl halides in the presence of aluminium chloride at −15°C, through the displacement of the trimethylsilyl group by acyl group to produce the corresponding 2-halocyclopentenyl alkyl/aryl ketones **6a-n**, many of which are reported for the first time. The yields vary from 62-92%. The reaction is very facile and is believed to owe its success to the well established β-silicon effect.

Halocyclopentenyl ketones **6** have found applications in the synthesis of steroid related compounds[1], anti-hypertensive pharmaceuticals[2] and heterocycles[3,4]. They have also been used in mechanistic studies[5]. There are very few procedures for the preparation of only a limited number of them starting from cyclopentanone, with moderate yields[6,7]. Cyclic vinylsilanes have been very successfully used for the synthesis of cycloalkenyl alkyl/aryl ketones by Friedel-Crafts reaction using a number of acyl halides[8-12]. We had synthesised 2-halo-1-trimethylsilylcyclopentenes **5a** and **5b** in good yields[13]. These appeared to be promising starting compounds for the preparation of halocyclopentenyl ketones **6** through the Friedel-Crafts acylation procedure. We have achieved considerable success in this attempt and the results are reported here.



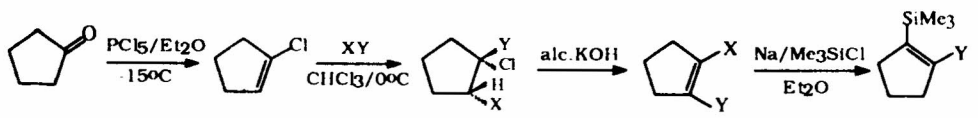
5a
5b

6a-g: Y=Br
6h-n: Y=Cl

Scheme II

Wurtz-Fittig procedure was employed for the synthesis of a variety of 1-trimethylsilylcycloalkenes starting from the corresponding 1-chloro- or 1-bromocycloalkenes[14,15]. When the same was extended. using excess reagents (sodium and chlorotrimethylsilane), to 1, 2-dihalocyclopentenes a novel homocyclic ring opening was observed, which was investigated thoroughly[13,16]. However, by careful manipulaton of the experimental conditions, success was achieved in preparing 2-chloro- and 2-bromo-1-trimethylsilylcyclopentene (Scheme I). Though 1-trimethylsilylcycloalkenes undergo Friedel-Crafts reactions smoothly, it was not known how a halogen on the adjacent vinylic position like in **5** would affect this reaction. It is satisfying to find that in these cases also the acylation, using a number of different acyl halides in presence of aluminium chloride, is smooth and it is now possible to make halocycloalkenyl ketones like **6** by a simple and efficient procedure (Scheme II). The ease of this reaction is attributable, as in other such reactions, to the β-silicon effect[17,18], and the mechanism may follow a similar path. It is fortunate that the vinylic halogen in **5** is not attacked by the Lewis acid ($AlCl_3$), probably because of the very mild reaction condition.

The yields, boiling points and elemental analyses are provided in the Table I. The UV spectra of the alkyl ketones (**6a-f** and **6h-m**) exhibited λ_{max} at 253 nm and the phenyl ketone (**6g** and **6n**) showed two λ_{max} at 253 and 214 nm. The ^1H



1 **2** **3** **4** **5**

X=Y=Br	**3a:** X=Y=Br	**4a:** X=Y=Br	**5a:** Y=Br
X=Br, Y=Cl	**3b:** X=Br, Y=Cl	**4b:** X=Br, Y=Cl	**5b:** Y=Cl
X=Y=Cl	**3c:** X=Y=Cl	**4c:** X=Y=Cl	

Scheme I

Table I—Yields and analytical data of halocyclopentenyl alkyl/aryl ketones

Starting compd	Acyl halide	Products	Yield	B.P.	Mol.	Found % (Calc.)	
						C	H
2-bromo-1-trimethylsilylcyclopentene (**5a**)	(RCOCl)	2-bromocyclopentenyl alkyl/aryl ketones	(%)	°C/Torr	formula		
	R = Me	R = Me (**6a**)	65	80/4.5	C_7H_9BrO	44.52 (44.47	4.92 4.80)
	Et	Et (**6b**)	73	65/1.5	$C_8H_{11}BrO$	47.27 (47.31	5.31 5.46)
	n-Pr	*n*-Pr (**6c**)	80	65-68/1.0	$C_9H_{13}BrO$	49.83 (49.79	5.94 6.03)
	i-Pr	*i*-Pr (**6d**)	75	75-76/2.0	$C_9H_{13}BrO$	49.94 (49.79	6.12 6.03)
	n-Bu	*n*-Bu (**6e**)	85	80-83/2.0	$C_{10}H_{15}BrO$	52.08 (51.96	6.58 6.54)
	n-Am	*n*-Am (**6f**)	92	115-120/3.0	$C_{11}H_{17}BrO$	53.96 (53.89	7.08 6.99)
	Ph	Ph (**6g**)	78	125-128/2.5	$C_{12}H_{11}BrO$	57.52 (57.39	4.57 4.42)
2-chloro-1-trimethylsilylcyclopentene(**5b**)		2-chlorocyclopentenyl alkyl/aryl ketones					
	R = Me	R = Me (**6h**)	68	72-75/5.0 (91-92/22)*			
	Et	Et (**6i**)	73	85-88/9.0 (97-98/13)*			
	n-Pr	*n*-Pr (**6j**)	80	68-70/4.0 (106-107/8)*			
	i-Pr	*i*-Pr (**6k**)	63	65-70/4.0	$C_9H_{13}ClO$	62.73 (62.61	7.67 7.59)
	n-Bu	*n*-Bu (**6l**)	75	80-82/2.5	$C_{10}H_{15}ClO$	64.18 (64.34	7.98 8.10)
	n-Am	*n*-Am (**6m**)	90	120-125/6.0	$C_{11}H_{17}ClO$	66.01 (65.82	8.59 8.54)
	Ph	Ph (**6n**)	62	115-120/1.5	$C_{12}H_{11}ClO$	69.96 (69.74	5.41 5.37)

* Literature b.p. reported in ref. 6.

NMR and mass spectral data are given in the experimental section.

Attempts were made to carry out Friedel-Crafts alkylation on **5a** and **5b** using several alkyl halides, which usually led to unidentifiable polymeric material. Variations in experimental conditions and Lewis acid catalyst also did not give any useful results. Thus whereas the acylation of **5a** and **5b** is an immensely fruitful reaction, the alkylation is not of any practical use. It should be noted that even acylation would be useless in the absence of silyl substituent.[19,20]

Experimental Section

^{1}H NMR spectra were recorded on JEOL FX-90Q and Bruker AC-250 spectrometers using $CDCl_3$ as solvent and TMS as internal standard (chemical shifts in δ, ppm), IR spectra on Carl-Zeiss 75 and Nicolet 5DXC FT-IR spectrophotometers, with films of liquid samples between NaCl plates and UV spectra on Shimadzu UV-160 spectrophotometer. GC-MS were obtained on Hewlett-Packard 5985B system attached to a Hewlett-Packard 5840A gas chromatograph. GC analyses were carried out on a Varian Vista 6000 gas chromatograph using 5% OV-101, 10% OV-101 and 15% FFAP columns with different temperature programmes.

The acid chlorides, propionyl chloride, *iso*-butyryl chloride, *n*-valeryl chloride and *n*-caproyl chloride, were prepared according to standard procedures by reacting the organic acid with about 25% excess of thionyl chloride[21]. Acetyl chloride and benzoyl chloride were commercial samples. All the acid chlorides were distilled twice before use. Dichloromethane was distilled over phosphorus pentoxide. Commercial aluminium chloride was used without further purification.

General procedure for the Friedel-Crafts reaction. All the reactions were carried out using approximately 0.5 g or 1.0 g of the vinylsilane **5a**/**5b**. Each reaction was repeated 3 to 4 times and the yields were optimised.

To a mangetically stirred mixture of 3 molar

equivalents of anhydrous $AlCl_3$ and 3 molar equivalents of acid chloride in dry CH_2Cl_2 (50 mL), cooled to −15°C on an ice-salt bath, was added the vinylsilane **5a/5b** (0.5 g or 1.0 g) in 25 mL of dry CH_2Cl_2 dropwise over a period of 1 hr. Saturated $NaHCO_3$ solution (25 mL) was then carefully added to the reaction mixture and stirred for 30 min, smultaneously allowing the reaction mixture to attain room temperature. The organic layer was separated and washed with saturated $NaHCO_3$ solution (2×25 mL), water (25 mL) and saturated NaCl solution (25 mL). After drying over Na_2SO_4, the solvent was stripped and the residue was purified by bulb to bulb distillation under reduced pressure.

2-Bromo-1-ethanoylcyclopent-1-ene 6a. IR: 2870, 2860, 1660, 1600, 1435, 1360, 1265 and 1040 cm^{-1}; ^1H NMR: 1.81 (m, 2H), 2.40 (s, 3H) and 2.75 (m, 4H); MS (relative intensity): m/z 190 (40.5), 188 (40.8) (M^+), 175 (100), 173 (93.9), 147 (3.6), 145 (4.4) ($M^+ - Ac$), 134 (3.3), 119 (11.9), 109 (12.0) ($M^+ - Br$), 94 (20.9), 79 (2.8), 66(22.7), 65 (37.3), 51 (4.4) and 43 (32.5).

2-Bromo-1-propanoylcyclopent-1-ene 6b. IR: 2870, 1640, 1580, 1425, 1345, 820 and 715 cm^{-1}; ^1H NMR: 1.08 (t, J=7.2 Hz, 3H), 2.0 (q, J=7.2 Hz, 2H), 2.73 (m, 2H) and 2.92 (t, J=7.2 Hz, 4H); MS (relative intensity): m/z 204 (18.9), 202 (19.1) (M^+), 175 (98.1), 173 (100), 147 (3.0), 145 (3.1), 119 (3.3), 117 (2.6), 107 (0.5), 94 (13.4), 77 (1.3), 66 (12.3), 65 (19.4), 51 (1.8), 39 (8.6) and 27 (4.5).

2-Bromo-1-butanoylcyclopent-1-ene 6c. IR: 2960, 1660, 1595, 1460, 1410, 1360 and 795 cm^{-1}; ^1H NMR: 0.93 (t, J=7.2 Hz, 3H), 1.65 (q, J=7.2 Hz, 2H), 1.97 (m, J= 7.2 Hz, 2H), 2.75 (m, 4H) and 2.8 (t, J=7.7 Hz, 2H);MS (relative intensity): m/z 218 (3.0), 216 (4.0) (M^+), 190 (8), 188 (7), 173 (96), 171 (100), 147 (5.0), 145 (4.5), 137 (34.0) ($M^+ - Br$), 129 (8.0), 94 (28), 77 (8), 71 (17.5), 66 (52.5), 65 (88.0).

2-Bromo-1 - (2′-methylpropanoyl)cyclopent-1-ene 6d. IR: 2860, 1660, 1590, 1420, 1340, 1060 and 865 cm^{-1}; ^1H NMR: 1.19 (d, J=7.6 Hz, 6H), 2.0 (q, J=7.6 Hz, 2H), 2.74 (m, 4H) and 2.42 (septet, J=7.6 Hz, 1H); MS (relative intensity): m/z 218 (10.3), 216 (10.9) (M^+), 203 (0.1), 190 (0.3), 175 (97), 173 (100) ($M^+ - C_3H_{78}$), 147 (2.5), 107 (0.6), 94 (11.5), 77 (1.1), 66 (13.1) and 65 (20.7).

2-Bromo-1-pentanoylcyclopent-1-ene 6e. IR: 2980, 1720, 1680, 1340, 1100, 920 and 860 cm^{-1}; ^1H NMR: 0.86 (t, J=4 Hz, 3H), 1.38 (m, 6H), 1.93 (m, 2H) and 2.63 (m, 4H); MS (relative intensity): m/z 232 (0.2), 230, (0.2) (M^+), 203 (1.4), 190 (45.9), 188 (46.4) ($M^+ - C_3H_7$ through McLafferty rearrangement), 175 (100.0), 173 (95.7), 151 [$M^+ - Br$), 119 (2.2), 109 (1.0), 94 (15.0), 77 (1.6), 66 (18.5) and 65 (26.4).

2-Bromo-1-hexanoylcyclopent-1-ene 6f. IR: 2870, 1650, 1580, 1350, 1160, 1050, 830, 800 720 cm^{-1}; ^1H NMR: 0.95 (t, J=7.2 Hz, 3H), 1.36 (m, 4H), 1.84 (t, J=6.12 Hz, 2H), 1.98 (q, J=7.2 Hz, 2H), 2.40 (m, 2H), 2.78 (m, 2H) and 2.82 (t, J=7.2 Hz, 2H); MS (relative intensity): m/z 244 (0.2), 242 (0.2) (M^+), 218 (0.2), 203 (2.1), 201 (2.0) ($M^+ - C_3H_7$), 190 (57.0), 188 (59.0) ($M^+ - C_4H_9$ through McLafferty rearrangement), 175 (95.9), 173 (100), 165 ($M^+ - Br$), 147 (2.7), 131 (0.1), 109 (3.1), 94 (11.3), 79 (3.1), 66 (13.7) and 65 (20.8).

1-Benzoyl-2-bromocyclopent-1-ene 6g. IR: 3080, 3040, 2920, 2100-1900 (weak benzenoid bands), 1600 (broad), 1460, 1360 and 830 cm^{-1}; ^1H NMR: 2.16 (m, 2H), 2.81 (m, 4H) and ca 7.3 (complex, 5H); MS (relative intensity): m/z 252 (48.5), 250 (48.8) (M^+), 171 (100) ($M^+ - Br$), 153 (9.9), 143 (50.5), 128 (37.4), 115 (16.3), 105 (84.1), 94 (9.7), 77 (75.9), 66 (19.6), 65 (32.7), 51 (27.9) and 39 (15.0).

2-Chloro-1-ethanoylcyclopent-1-ene 6h. ^1H NMR: 1.95 (quintet, J=7.2 Hz, 2H), 2.48 (s, 3H) and 2.70 (m, 4H); MS (relative intensity): m/z 146 (12.9), 144 (39.9) (M^+), 131 (32.1), 129 (100) ($M^+ - CH_3$), 109 (3.9) ($M^+ - Cl$), 103 (2.1), 101 (6.9), 93 (1.2), 81 (1.7), 73 (3.5), 66 (12.0), 65 (43.1), 51 (1.9), 43 (18.2), 39 (11.6), 27 (1.4) and 15 (1.9).

2-Chloro-1-propanoylcyclopent-1-ene 6i. IR: 2975, 2940, 1665, 1607, 1459, 1436, 1410, 1377, 1364, 1238, 1195, 1074 and 966 cm^{-1}; ^1H NMR: 1.07 (t, J=7.7 Hz, 3H), 1.92 (quintet, J=7.7 Hz, 2H), 2.55 (t, J=7.7 Hz, 2H) and 2.75 (m, 4H); MS (relative intensity): m/z 160 (3.9), 158 (12.9) (M^+), 131 (31.5), 129 (97.3) ($M^+ - C_2H_5$), 103 (4.9), 101 (17.5), 75 (5.7), 73 (11.2), 66 (16.6), 65 (100), 39 (59.3), 29 (36.7) and 27 (33.8).

1-Butanoyl-2-chlorocyclopent-1-ene 6j. IR: 2964, 2936, 2904, 2875, 1664, 1605, 1465, 1457, 1436, 1404, 1378, 1193, 1181 and 1085 cm^{-1}; ^1H NMR: 0.82 (t, J=7.7 Hz, 3H), 1.67 (t/q, J=7.7 Hz, 2H), 1.82 (quintet, J=7.7 Hz, 2H), 2.60 (complex m, 4H), and 2.69 (t, J=7.7 Hz, 2H); MS (relative intensity): m/z 174 (0.4), 72 (1.1) (M^+), 159 (0.4), 157 (1.1) ($M^+ - CH_3$), 146 (3.6), 144 (10.5) ($M^+ - C_2H_5$), 131 (33.8), 129 (100) ($M^+ - C_3H_7$), 103 (1.7), 101 (4.5), 77 (7.5), 65 (7.5), 51 (0.5), 39 (2.4), 27 (0.8) and 15 (0.1).

2-Chloro-1- (2'-methylpropanoyl)cyclopent-1-ene 6k. IR: 2973, 2936, 2891, 2876, 1736, 1731, 1712, 1664, 1600, 1467, 1384, 1239, 1196, 1167 and 1087 cm^{-1}; ^1H NMR: 1.15 (d, J=7.7 Hz, 6H), 1.00 (s, 3H), 1.87 (quintet, J=7.7 Hz, 2H), 2.62 (complex m, 4H) and 3.31 (septet, 1H); MS (relative intensity): m/z 174 (2.8), 172 (8.6) (M^+), 157 (0.1) ($M^+ - CH_3$), 144 ($M^+ - C_2H_5$), 131 (31.6), 129 (100) ($M^+ - C_3H_7$), 103 (1.0), 101 (3.2), 75 (1.0) and 65 (10.2).

2-Chloro-1-pentanoylcyclopent-1-ene 6l. IR: 2960, 2935, 2874, 1734, 1711, 1690, 1685, 1664, 1605, 1466, 1457, 1436, 1405, 1380, 1259, 1189, 1180 and 1036 cm^{-1}; ^1H NMR: 0.92 (t, J=7.7 Hz, 3H), 1.31 (m, 2H), 1.58 (m, 2H), 1.87 (quintet, 2H), 2.66 (complex m, 4H) and 2.80 (t, 2H); MS (relative intensity): m/z (M^+ peak absent), 159 (0.7), 157 (1.9) ($M^+ - C_2H_5$), 146 (15.2), 144 (44.6) ($M^+ - C_3H_7$ through McLafferty rearrangement), 131 (30.9), 129 (100) ($M^+ - C_4H_9$), 103 (1.6), 101 (4.1), 77 (1.3), 65 (16.0) and 39 (4.8).

2-Chloro-1-hexanoylcyclopent-1-ene 6m. IR: 2958, 2933, 2873, 2861, 1711, 1665, 1606, 1467, 1460, 1435, 1412, 1379, 1297, 1248, 1212, 1180, 1087 and 795 cm^{-1}; ^1H NMR: 0.88 (t, J=7.7 Hz, 3H), 1.29 (m, 4H), 1.52 (m, 2H), 1.90 (quintet, J=7.7 Hz, 2H), 2.62 (m, 4H) and 2.74 (t, J=7.7 Hz, 2H); MS (relative intensity): m/z 200 (0.2) M^+, 187 (0.2) ($M^+ - CH_3$), 172 (0.2), 165 (6.7) ($M^+ - Cl$), 157 (1.9), 146 (14.7), 144 (44.3) ($M^+ - C_4H_9$ through McLafferty rearrangement), 131 (28.6), 129 (100) ($M^+ - C_5H_{11}$), 109 (3.9), 103 (4.8), 101 (14.6), 91 (5.3), 77 (6.9), 66 (15.1), 65 (89.0), 55 (10.5), 39 (46.3) and 29 (19.7).

1-Benzoyl-2-chlorocyclopent-1-ene 6n. IR: 2956, 2954, 2952, 2939, 2718, 1700, 1685, 1663, 1653, 1646, 1597, 1449, 1315, 1277, 1258, 1249, 1214, 1001, 836 and 712 cm^{-1}; ^1H NMR: 2.02 (m, 2H), 2.60 (m, 4H), 7.47 (m, 3H) and 8.02 (m, 2H); MS (relative intensity): m/z 208 (21.3), 206 (53.4) (M^+), 171 (39.7) ($M^+ - Cl$), 115 (11.5), 105 (100), 89 (5.7), 77 (100) (C_6H_5), 65 (42.5), 51 (28.7), 39 (10.3), 27 (6.6) and 18 (10.1).

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