Syntheses of Alkenes from Vinyl Halides

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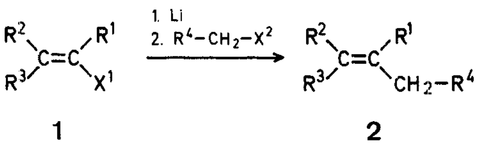
The syntheses of unsaturated systems has been studied extensively[1]. We have recently reported a new stereospecific synthesis of disubstituted alkenes via vinyllithium reagents[2]. We now report (i) a general, efficient synthesis of mono-, di-, and tri-substituted alkenes by alkylation of vinyllithium reagents with primary halides, and (ii) an efficient synthesis of trisubstituted cycloalkenes by reaction of primary lithium-alkyls with cyclic vinyl bromides.

The vinyllithium reagents for the former are prepared quantitatively from vinyl chlorides or bromides and lithium powder (containing 2% sodium) in anhydrous ether.

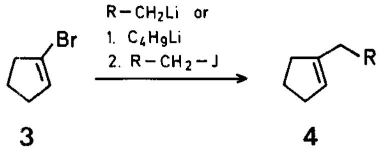
Monosubstituted alkenes can be obtained by alkylation of commercial vinyllithium in tetrahydrofuran. Di-substituted alkenes can be prepared in high yield from the monosubstituted vinyl reagents; e.g. **2**, $R^1 = R^3 = H$, $R^2 = CH_3$. Tri-substituted alkenes can be formed in high yield: *cis*- and *trans*-2-butenyllithium[3] are obtained with 94% stereospecificity from the corresponding chloro- or bromo-2-butenes; reaction of each of these with a primary alkyl halide occurred in high yield and retention of configuration[4]. For example, *n*-propyl iodide or bromide (1 equiv.) reacted to give (*E*)- and (*Z*)-3-methyl-2-hexene, respectively (90%). The organolithium reagents are known to react stereospecifically with carbonyl compounds[5] and disulfides[5] but non-stereospecifically with oxetane[7].

Reaction of *trans*-2-butenyllithium with 1 equiv of 1-bromo-4-methyl-3-pentene gave dihydromyrcene (**2**, $R^4 = -CH_2-CH{=}C(CH_3)_2$. The alkenes which have been prepared in this way are listed in the Table.



Scheme A

Vinyllithium reagents can also be obtained from vinyl bromides by halogen-metal exchange with an alkyllithium. Thus, when 1-bromocyclopentene was treated with a primary alkyllithium at −70°, 1-cyclopentenyllithium and the corresponding alkyl bromide were obtained. Upon warming, alkylation occurred in good yield[8] (87% for $R = n\text{-}C_7H_{15}$, 90% for $R = n\text{-}C_3H_7$).



Scheme B

The same result can also be obtained by reaction of cyclopentenyl bromide with 1 equivalent of butyllithium at −70°, followed by addition of 1 equivalent of alkyl iodide at −50°; 1-alkylcyclopentene was obtained in good yield (75% for $R = n\text{-}C_7H_{15}$)[9].

Pure isomeric vinyl chlorides are not readily obtainable. We have found that the chloroalkene **6** is easily prepared (50%) from commercially available 1,3-dichloro-2-butene[10] (**5**) by reaction with an alkyl Grignard reagent in refluxing diisopropyl ether. In tetrahydrofuran, the reaction followed a different path; for $R = n\text{-}C_4H_9$ a mixture of (*E*)- and (*Z*)-5-methyl-5-undecene was formed (82%).

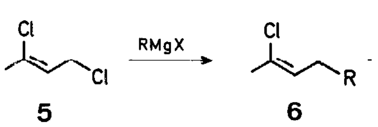
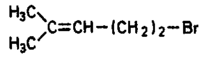


Table. Preparation of Alkenes[b] (Scheme **A**)

Vinyl halide R^1	R^2	R^3	X^1	$R^4{-}CH_2{-}X^2$	Temperature	Time	Yield (%)[a]
H	H	H	–[b]	$H_3C{-}(CH_2)_6{-}CH_2{-}J$	−28 to +10°	2 h	(92)[c]
H	H	H	–[b]	$Br{-}(CH_2)_4{-}Br$	0 to +20°	3 h	67[d]
H_3C	H	H	Br	$H_3C{-}(CH_2)_6{-}CH_2{-}J$	−50°	3 h	75 (99)
H	H_3C	H_3C	Cl	$H_3C{-}(CH_2)_6{-}CH_2{-}J$	0	1 h	79 (92)
$-(CH_2)_4-$		H	Cl	$H_3C{-}(CH_2)_6{-}CH_2{-}J$	0	1 h	65
$-(CH_2)_4-$		H	Cl	$Br{-}(CH_2)_2{-}CH_2{-}O{-}Si(CH_3)_3$	+10°	4 h	59
H_3C	H	H_3C	Br or Cl	$H_3C{-}(CH_2)_2{-}J$	−50°	3 h	(98)[c]
H_3C	H	H_3C	Br or Cl	$H_3C{-}(CH_2)_2{-}J$	+20°	0.5 h	77[e]
H_3C	H	H_3C	Br or Cl	$H_3C{-}(CH_2)_2{-}Br$	−50 to −10°	3 h	(90)[c]
H_3C	H	H_3C	Br or Cl	 $(H_3C)_2C{=}CH{-}(CH_2)_2{-}Br$	+18°	3 h	50
H_3C	H	H_3C	Br or Cl	$H_3C{-}(CH_2)_2{-}Cl$[f]	+18°	20 h	(90)[c]
H_3C	H_3C	H	Cl	$H_3C{-}(CH_2)_2{-}Br$	+18°	3 h	(84)[g]

[a] Isolated product, calculated from 1 equivalent of $R^4CH_2X^2$ with 1 equivalent of titrated vinyllithium reagent: G.L.C. yield in parentheses.

[b] Commercial vinyl lithium reagent in tetrahydrofuran was used.

[c] In this case, 2 equivalents of commercial vinyllithium were used.

[d] 15% of 1,7-octadiene was also formed.

[e] 94% *Z*, 6% *E* (compared with authenic samples), G.L.C.: SF 96, 5%.

[f] 2 equivalents of titrated lithium reagent were used.

[g] 94% *E*, 6% *Z* (compared with authentic samples), G.L.C.: SF 96, 5%.

Reaction of (*E*)-2-Bromo-2-butene to (*Z*)-3-Methyl-2-undecene:

Pure (*E*)-2-bromo-2-butene[3,5] (32 g, 0.23 mol) in ether (50 ml) was added dropwise at 25° to lithium powder (6.5 g, 0.96 g.-at), containing 2% sodium, in ether (200 ml) (4 h). After stirring for 1 h, the lithium reagent was transferred through a glass wool plug to a storage bottle and titrated. This lithium reagent (25 ml, 0.8 *N*, 20 mmol) was slowly added under nitrogen at 0° with a syringe to a solution of octyl iodide (4.8 g, 20 mmol) in tetrahydrofuran (50 ml). After 1 h at room temperature, the mixture was hydrolysed with ice and extracted with ether. After distillation, (*Z*)-3-methyl-2-undecene (94% isomeric purity) is obtained; yield: 2.60 g (77%); b.p. 108°/18 torr.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 5.18$ ppm (t, 1*H*, $J = 7.5$ Hz).

Mass spectrum: $m/e = 168$ ($M^{\oplus}$), 83, 70, 55, 41, 28.

I.R. (film): $\nu_{max} = 3030, 1670, 810\ cm^{-1}$.

Preparation of 1-Octylcyclopentene:

Octyllithium in hexane (47 ml, 0.425 *N*, 20 mmol) was added dropwise at −60° to 1-bromocyclopentene (2.94 g, 20 mmol) in tetrahydrofuran (150 ml). After 1.5 h at −60°, the reaction was allowed to warm to room temperature. After 6 h at room temperature, work-up in the usual manner gave (87% by G.L.C. with an internal standard) of 1-octylcyclopentene; yield: 70%; b.p. 109–110°/17 torr.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 5.31$ ppm (broad s, 1 H).

Mass spectrum: $m/e = 180$ ($M^{\oplus}$), 95, 82, 67, 55, 41, 29.

I.R. (film): $\nu_{max} = 3040, 1650, 1030, 820\ cm^{-1}$.

1-Bromocyclopentene (880 mg, 6 mmol) was added dropwise at −70° to butyllithium (3.3 ml, 2 *N* in hexane) and anhydrous tetrahydrofuran (10 ml). After treatment with octyl iodide and 2 h at −70°, the reaction mixture was allowed to warm slowly to room temperature (2 h). Work-up in the usual manner and distillation gave 1-octylcyclopentene; yield: 640 mg (65%); b.p. 109–110°/17 torr.

Preparation of (*E*)-2-Chloro-2-octene:

Butylmagnesium chloride in ether (12 ml, 40 mmol) was slowly added to a refluxing solution of pure 1,3 dichloro-(*E*)-2-butene (4 g, 32 mmol) in diisopropyl ether (60 ml). After refluxing for 2 h, an aliquot, hydrolysed and analysed by G.L.C., showed that all the chloride has reacted. Work-up in the usual manner and distillation gave 2-chloro-(*E*)-2-octene; yield: 2.3 g (50%); b.p. 75°/15 torr.

^{1}H-N.M.R. ($CDCl_3$): $\delta = 2.10$ (5 H), 5.40 ppm (t, 1 H, $J = 7.5$ Hz).

Mass spectrum: $m/e = 148, 146, 111, 83, 60, 55, 41, 28$.

I.R. (film): $\nu_{max} = 3080, 1715, 1665, 1070, 820, 620\ cm^{-1}$.

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