Alka-2,3-dienes from Crotonaldehyde

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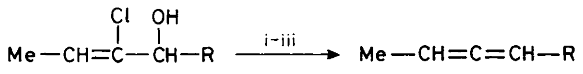
Unsaturated chlorohydrins (**1**) (readily obtained from crotonaldehyde) are converted, by methylation and *in situ* lithiation at room temperature, into alka-2,3-dienes (**2**).

Most methods for the preparation of cumulenes involve elimination from mono- or di-halogenated olefins or allylic alcohols and usually give alkynes and conjugated dienes as by-products.[1] In relation to our studies on sp^2-hybridized β-substituted organoalkaline dianions[2] of type (**5**) we now report an easy preparation of cumulenes from crotonaldehyde *via* the unsaturated chlorohydrins (**1**).†

The chlorination of crotonaldehyde (Cl_2–NaOH) followed by addition of a Grignard reagent leads, after hydrolysis, to the chlorohydrin (**1**).[2] When (**1**) was treated successively with BuLi and MeI and then lithiated *in situ* with Li powder at room temperature the corresponding cumulene (**2**) was isolated, after hydrolysis (Table 1, entries 1,4,6, and 8).‡

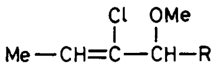


$$\mathrm{Me{-}CH{=}\overset{\overset{\large Cl}{|}}{C}{-}\overset{\overset{\large OH}{|}}{C}H{-}R} \xrightarrow{\text{i–iii}} \mathrm{Me{-}CH{=}C{=}CH{-}R}$$

(**1**) (**2**)

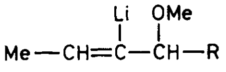
a; R = n-C_4H_9
b; R = i-C_4H_9
c; R = n-C_7H_{15}
d; R = n-C_8H_{17}

Scheme 1. *Reagents:* i, BuLi; ii, MeI; iii, Li.



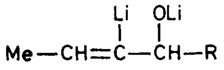
$$\mathrm{Me{-}CH{=}\overset{\overset{\large Cl}{|}}{C}{-}\overset{\overset{\large OMe}{|}}{C}H{-}R}$$

(**3**)



$$\mathrm{Me{-}CH{=}\overset{\overset{\large Li}{|}}{C}{-}\overset{\overset{\large OMe}{|}}{C}H{-}R}$$

(**4**)



$$\mathrm{Me{-}CH{=}\overset{\overset{\large Li}{|}}{C}{-}\overset{\overset{\large OLi}{|}}{C}H{-}R}$$

(**5**)

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† A method to obtain cumulenes by reaction of *O*-silylated bromohydrins [$R_2C{=}C(Br)CHR'(OSiMe_3)$] with Bu^{t}Li at −90 to −100 °C has been reported recently (ref. 3).

‡ In a typical procedure a diethyl ether solution of Bu^{n}Li (22 mmol) was added to a solution of the corresponding chlorohydrin (**1**) (20 mmol) in diethyl ether (20 ml) under argon at 0 °C. Stirring was continued for 30 min as the mixture warmed to room temperature. The solvent was removed (0.1 mmHg) and THF (40 ml) was added to the resulting residue. This solution was treated with MeI (25 mmol) and the mixture was refluxed for 48 h. After cooling Li powder (60 mmol) was added at 0 °C and the mixture stirred overnight. The resulting suspension was hydrolysed with water, extracted with diethyl ether, the ethereal layer washed with water and dried (Na_2SO_4). The solvents were evaporated (15 mmHg) and the residue condensed or distilled at reduced pressure (0.1 mmHg).

Table 1. Preparation of cumulenes (**2**).

Entry	Starting material	Cumulene				Selected spectroscopic data	
		R		Yield (%)[a]	B.p. (°C)/0.1 Torr	ν(C=C=C) (cm^{-1})	δ_C (C=C=C)
1	(**1a**)[b]	n-C_4H_9	(**2a**)	58[c]	[f]	1980	84.4, 89.4, 192.3
2	(**3a**)[d]			89[e]			
3	(**3a**)[d]			65[e,g]			
4	(**1b**)[h]	i-C_4H_9	(**2b**)	52[c]	[f]	1965	84.1, 88.3, 191.5
5	(**1b**)[h]			40[c,g]			
6	(**1c**)[i]	n-C_7H_{15}	(**2c**)	55[c]	31—33	1985	84.5, 89.6, 192.25
7	(**3c**)[j]			97[e]			
8	(**1d**)[k]	n-C_8H_{17}	(**2d**)	60	37—40	1980	84.4, 89.5, 192.3

[a] Isolated yield. [b] See ref. 2. [c] Based on compound (**1**). [d] Obtained from (**1a**) in 70% yield; b.p. 58—60 °C/0.1 Torr. [e] Based on compound (**3**). [f] Condensed at 0.1 Torr at room temp. [g] The metallation was carried out with lithium naphthalenide at −78 °C. [h] Obtained from α-chlorocrotonaldehyde in 79% yield; b.p. 65—68 °C/0.1 Torr. [i] Obtained from α-chlorocrotonaldehyde in 84% yield; b.p. 91—94 °C/0.1 Torr. [j] Obtained from (**1c**) in 60% yield; b.p. 83—85 °C/0.1 Torr. [k] Obtained from α-chlorocrotonaldehyde in 83% yield; b.p. 94—97 °C/0.1 Torr.

The reaction pathway involves the *O*-methylated chlorohydrin (**3**) in the first step; (**3**) can be isolated if the hydrolysis of the reaction mixture is carried out after the addition of MeI (Table 1, footnotes d and j). The further lithiation of compounds (**3**) afforded the expected cumulenes in excellent yield (Table 1, entries 2 and 7).

We attempted the preparation of sp^2-hybridized β-alkoxy organolithium compounds (**4**) by carrying out the lithiation at −78 °C with lithium naphthalenide.[4] Under these conditions intermediates (**4a**) [obtained from (**3a**)] and (**4b**) [from (**1b**)] suffer β-elimination leading to the expected cumulenes (**2a**) and (**2b**), respectively (Table 1, entries 3 and 5). It is noteworthy that the presence of a negative charge on the oxygen atom in β-oxy organolithium compounds (**5**) means that these intermediates are stable even under reflux in tetrahydrofuran (THF)[2] whereas the species (**4**) undergo β-elimination at −78 °C.[5]

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References

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4 J. Barluenga, J. Flórez, and M. Yus., *J. Chem. Soc., Perkin Trans. 1*, 1983, 3019.

5 For the application of β-elimination from substituted organolithium compounds see for instance: J. Barluenga, M. Yus, J. M. Concellón, and P. Bernad, *J. Org. Chem.*, 1983, **48**, 3116 and references therein.