

Alka-2,3-dienes from Crotonaldehyde

José Barluenga, José R. Fernández, and Miguel Yus

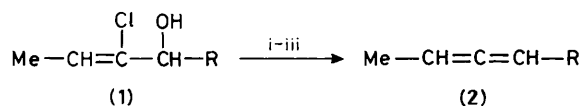
Departamento de Química Orgánica, Facultad de Química, Universidad de Oviedo, Spain

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 dianions² of type (**5**) we now report an easy preparation of cumulenes from crotonaldehyde via the unsaturated chlorohydrins (**1**).[†]

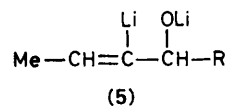
The chlorination of crotonaldehyde (Cl_2 -NaOH) followed by addition of a Grignard reagent leads, after hydrolysis, to the chlorohydrin (**1**).² When (**1**) was treated successively with

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).[‡]



- a; R = n-C₄H₉
 b; R = i-C₄H₉
 c; R = n-C₇H₁₅
 d; R = n-C₈H₁₇

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



[‡] In a typical procedure a diethyl ether solution of BuⁿLi (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 (Na₂SO₄). The solvents were evaporated (15 mmHg) and the residue condensed or distilled at reduced pressure (0.1 mmHg).

[†] A method to obtain cumulenes by reaction of *O*-silylated bromohydrins [R₂C=C(Br)CHR'(OSiMe₃)] with BuⁿLi at -90 to -100 °C has been reported recently (ref. 3).

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

| Entry | Starting material | Cumulene | | | Selected spectroscopic data | | |
|-------|----------------------------|----------------------------------|-------------|------------------------|-----------------------------|---|---|
| | | R | | Yield (%) ^a | B.p. (°C)/0.1 Torr | $\nu(\text{C}=\text{C}=\text{C})$ (cm^{-1}) | $\delta_{\text{C}}(\text{C}=\text{C}=\text{C})$ |
| 1 | (1a) ^b | n-C ₄ H 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 ₄ H ₉ | (2b) | 52 ^c | f | 1965 | 84.1, 88.3, 191.5 |
| 5 | (1b) ^h | | | 40 ^{e,g} | | | |
| 6 | (1c) ⁱ | n-C ₇ H ₁₅ | (2c) | 55 ^c | 31—33 | 1985 | 84.5, 89.6, 192.25 |
| 7 | (3c) ^j | | | 97 ^e | | | |
| 8 | (1d) ^k | n-C ₈ H 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 sp²-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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- 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.