An Easy Preparation of α-Allenic Ethers and Tertiary α-Allenic Amines

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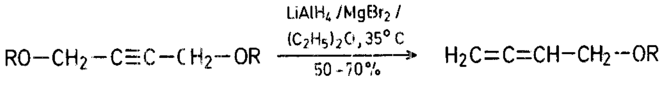
α-Allenic ethers **2** are prepared by the reaction of 1,4-dialkoxy-2-butynes **1** with lithium aluminium hydride and magnesium bromide. Tertiary α-allenic amines **4** are obtained by treating 4-dialkylamino-1-methoxy-2-butynes **3** with lithium aluminium hydride and aluminium chloride.

The reported procedures for the preparation of α-allenic ethers involve the reaction of 2,3-alkadienyl halides with alkoxides[1,2], the alkylative elimination of 1,4-dialkoxy-2-alkynes using Grignard reagents[3], and the base-induced isomerisation of 1,4-dialkoxy-2-alkynes[4,5,6]. We now report that α-allenic ethers **2** can be easily prepared in 50–70% yield from 1,4-dialkoxy-2-butynes **1** by a reductive elimination reaction using a mixture of lithium aluminium hydride and magnesium bromide in refluxing ether (Table 1).

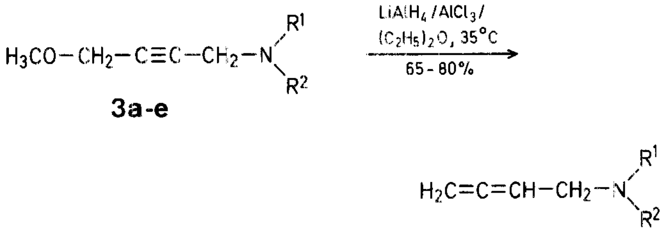


1a–g **2a–g**

1,2	R	1,2	R
a	C_2H_5	e	$H_2C=CH-CH_2-$
b	n-C_3H_7	f	$H_3C-CH=CH-CH_2-$
c	n-C_4H_9		
d	n-C_5H_{11}	g	$H_2C=C(CH_3)-CH_2-$

Tertiary α-allenic amines have been prepared by the reaction of 2,3-alkadienyl halides[7–12] or mesylates[13] with secondary amines, addition of secondary amines[8,10,14] or lithium dialkylamides[15–18] to alkenynes, addition of organometallic reagents to secondary enynamines[19,20,21], reaction of the aluminium derivative of 1-bromo-2-butyne with *gem*-aminoethers[22], reductive elimination reaction of aminoacetylenic ethers using butylmagnesium bromide and copper(I) iodide in tetrahydrofuran[13,14,23,24], and alkylative elimination of aminoacetylenic ethers using Grignard reagents[23–27].

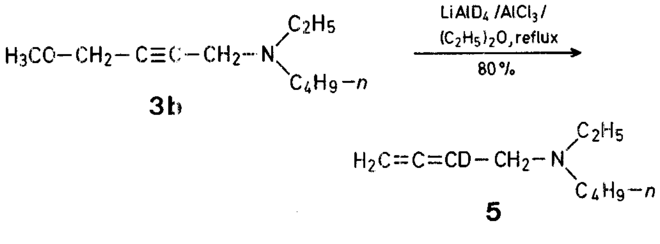
We have now found that tertiary α-allenic amines **4** are readily produced in good yield when 4-dialkylamino-1-methoxy-2-butynes **3** are reacted with a mixture of lithium aluminium hydride and aluminium chloride in refluxing ether (Table 2).



3a–e **4a–e**

3,4	R¹	R²
a	C_2H_5	C_2H_5
b	C_2H_5	n-C_4H_9
c	n-C_4H_9	n-C_4H_9
d	$-(CH_2)_5-$	
e	$-(CH_2)_2-O-(CH_2)_2-$	

The reaction of 4-(n-butyl-ethyl-amino)-1-methoxy-2-butyne (**3b**) with a mixture of lithium aluminium deuteride and aluminium chloride in refluxing ether provided the amine **5** (yield 80%) with more than 98% deuterium incorporation.



3b **5**

Table 1. α-Allenic Ethers **2** prepared

Product	b.p. [°C]/torr	Yield [%]	n_D^{20}	Molecular Formula[a]	^{1}H-N.M.R. (CCl_4/TMS_{int}) δ [ppm]
2a	106°/760	57	1.4429	$C_6H_{10}O$ (98.1)	1.1 (t, 3H, J = 7 Hz); 3.4 (q, 2H, J = 7 Hz); 3.7–4.0 (m, 2H); 4.5–4.8 (m, 2H); 4.8–5.3 (m, 1H)
2b	69°/70	65	1.4408	$C_7H_{12}O$ (112.2)	0.85 (t, 3H, J = 7 Hz); 1.2–1.8 (m, 2H); 3.3 (t, 2H, J = 7 Hz); 3.7–4.0 (m, 2H); 4.5–4.8 (m, 2H); 4.8–5.3 (m, 1H)
2c	76°/50	72	1.4433	$C_8H_{14}O$ (126.2)	0.85 (t, 3H, J = 7 Hz); 1.1–1.7 (m, 4H); 3.3 (t, 2H, J = 7 Hz); 3.7–4.0 (m, 2H); 4.5–4.8 (m, 2H); 4.8–5.3 (m, 1H)
2d	100°/58	60	1.4437	$C_9H_{16}O$ (140.2)	0.85 (t, 3H, J = 6 Hz); 1.0–1.7 (m, 6H); 3.25 (t, 2H, J = 6 Hz); 3.7–4.0 (m, 2H); 4.5–4.8 (m, 2H); 4.8–5.3 (m, 1H)
2e	65°/80	50	1.4572	$C_7H_{10}O$ (110.1)	3.8–4.1 (m, 4H); 4.5–4.9 (m, 2H); 4.9–5.4 (m, 3H); 5.5–6.2 (m, 1H)
2f	83°/52	55	1.4561	$C_8H_{12}O$ (124.2)	1.65 (m, 3H); 3.7–4.0 (m, 4H); 4.5–4.8 (m, 2H); 4.9–5.4 (m, 1H); 5.4–5.8 (m, 2H)
2g	78°/55	60	1.4569	$C_8H_{12}O$ (124.2)	1.65 (s, 3H); 3.7–4.0 (m, 4H); 4.5–5.4 (m, 5H)

[a] Satisfactory microanalyses obtained: C ±0.30, H ±0.20.

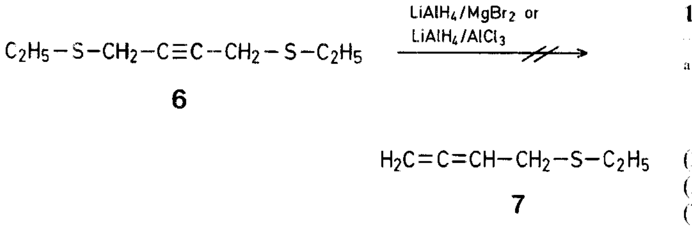
Table 2. α-Allenic Amines **4** prepared

Product	b.p. [°C]/torr	Yield [%]	n_D^{20}	Molecular Formula[a]	^{1}H-N.M.R. (CCl_4/TMS_{int}) δ [ppm]
4a	70°/53	65	1.4582	$C_8H_{15}N$ (125.2)	1.0 (t, 6H, J = 7 Hz); 2.45 (q, 4H, J = 7 Hz); 2.9–3.3 (m, 2H); 4.4–4.7 (m, 2H); 4.7–5.3 (m, 1H)
4b	80°/19	80	1.4581	$C_{10}H_{19}N$ (153.3)	0.8–1.2 (m, 6H); 1.2–1.6 (m, 4H); 2.2–2.7 (m, 4H); 2.9–3.3 (m, 2H); 4.4–4.7 (m, 2H); 4.8–5.3 (m, 1H)
4c	64°/0.1	80	1.4569	$C_{12}H_{23}N$ (181.3)	0.7–1.1 (m, 6H); 1.1–1.6 (m, 8H); 2.1–2.6 (m, 4H); 2.9–3.3 (m, 2H); 4.4–4.7 (m, 2H); 4.8–5.3 (m, 1H)
4d	72°/14	73	1.4925	$C_9H_{15}N$ (137.2)	1.3–1.8 (m, 6H); 2.2–2.5 (m, 4H); 2.7–3.0 (m, 2H); 4.4–4.7 (m, 2H); 4.8–5.3 (m, 1H)
4e	85°/16	72	1.4934	$C_8H_{13}NO$ (139.2)	2.2–2.6 (m, 4H); 2.8–3.1 (m, 2H); 3.4–3.8 (m, 4H); 4.5–4.8 (m, 2H); 4.8–5.3 (m, 1H)

[a] Satisfactory microanalyses obtained: C ±0.30, H ±0.20, N ±0.30.

The yields of the present two reductive elimination reactions are much lower when lithium aluminium hydride is used without added salt. The exact influence of these salts (magnesium bromide and aluminium chloride) is still unclear.

All attempts to prepare the α-allenic thioether **7** from 1,4-diethylthio-2-butyne (**6**)[28] with either lithium aluminium hydride/magnesium bromide or lithium aluminium hydride/aluminium chloride were unsuccessful.



$C_2H_5-S-CH_2-C\equiv C-CH_2-S-C_2H_5$

6

$H_2C=C=CH-CH_2-S-C_2H_5$

7

1,4-Diethoxy-2-butyne (**1a**)[29] (Table 3) and 4-dialkylamino-1-methoxy-2-butynes **3a,c–e**[32] were prepared according to literature procedures.

1,4-Dialkoxy-2-butynes 1b–g; General Procedure[4,30]:
Potassium hydroxide pellets (22.4 g, 0.4 mol) are added to a solution of 2-butyne-1,4-diol (8.6 g, 0.1 mol) in dimethyl sulfoxide (50 ml). The mixture is vigorously stirred for 0.5 h, when most of the potassium hydroxide dissolves. The pure alkyl bromide (0.2 mol) is then added in 20 min. The reaction is exothermic and the temperature is maintained at 50 °C by external cooling[31]. Stirring is continued for 0.5 h at 50 °C. After pouring the reaction mixture into ice/water (200 ml), the product is extracted with 1 : 1 pentane/ether (3 × 50 ml), the extract is dried with magnesium sulfate, and distilled (Table 3).

Table 3. 1,4-Dialkoxy-2-butynes **1** prepared

Product	b.p. [°C]/torr	Yield [%]	Molecular Formula[a] or Lit. b.p. [°C]/torr
1a	77°/13	75	76°/12[29]
1b	70°/2	69	101°/14[34]
1c	82°/0.1	77	120°/10[35]
1d	116°/0.3	64	$C_{14}H_{26}O_2$ (226.3)
1e	76°/0.5	79	104–6°/10[36]
1f	106°/3	78	$C_{12}H_{18}O_2$ (194.3)
1g	82°/0.1	67	$C_{12}H_{18}O_2$ (194.3)

[a] Satisfactory microanalyses obtained: C ±0.30, H ±0.20, N ±0.30.

^{1}H-N.M.R. (CCl_4/TMS_{int}): δ = 4.05 ppm (s, 4H, $\equiv C-CH_2O$) for all the 1,4-dialkoxy-2-butynes prepared.

α-Allenic Ethers 2; General Procedure:
An ether solution of magnesium bromide is prepared from magnesium (1.2 g, 0.05 mol), 1,2-dibromoethane (9.4 g, 0.05 mol), and ether (40 ml). To this solution maintained at 0 °C is added lithium aluminium hydride (1.9 g, 0.05 mol). The mixture is stirred for 0.5 h at room temperature, 1,4-dialkoxy-2-butyne **1** (0.05 mol) dissolved in an equal volume of ether is added dropwise and the mixture is refluxed for 3 h. After cooling to room temperature, triethylene glycol trimethyl ether (triglyme; 50 ml) is slowly added. Stirring is then stopped, the condenser is replaced by a short Vigreux column,

pumice-stones are added and the product is isolated by distillation (oil bath) (Table 1). A further refractionation provides the pure α-allenic ethers **2a–g**.

The triglyme used can be recovered by dropwise addition, under stirring, of water to the distillation residue maintained at 0 °C, till a granular precipitate appears. After filtration, the liquid is washed with 5 normal sodium hydroxide solution, dried with potassium carbonate, and distilled; b.p. 101–103 °C/8 torr.

4-(*n*-Butyl-ethyl-amino)-1-methoxy-2-butyne (3b):
This compound is prepared from 1-methoxy-2-propyne, polyoxymethylene glycol and ethyl-*n*-butylamine according to a previously described method[32]; yield: 80%; b.p. 115 °C/18 torr.

^{1}H-N.M.R. (CCl_4/TMS_{int}): $\delta = 0.8$–1.2 (m, 6H, CH_3); 1.2–1.6 (m, 4H, $C\underline{H}_2C\underline{H}_2CH_3$); 2.2–2.7 (m, 4H, $NC\underline{H}_2$); 3.2–3.4 (m, 5H, $OC\underline{H}_3$, $NC\underline{H}_2{-}C{\equiv}C{-}$); 4.0 ppm (t, 2H, $J = 2$ Hz, $C{\equiv}C{-}C\underline{H}_2{-}O$).

α-Allenic Amines 4; General Procedure:
A solution of anhydrous aluminium chloride (13.3 g, 0.1 mol) in ether (35 ml) is added to a suspension of lithium aluminium hydride (3.8 g, 0.1 mol) in ether (35 ml) maintained at 0 °C. After stirring for 1 h at room temperature, the 4-dialkylamino-1-methoxy-2-butyne (**3**; 0.05 mol) dissolved in an equal volume of ether is slowly added and the mixture is refluxed for 3 h. After lowering the temperature to 0–5 °C, water is added dropwise until a granular precipitate appears. The mixture is then poured into a solution of potassium sodium tartrate (150 g) in water (300 ml)[33] and stirred until the complete disappearance of the precipitate (formation of a milky solution). The product is extracted with ether (4 × 50 ml), the organic phase is washed with 5 normal sodium hydroxide solution, brine (50 ml), dried with potassium carbonate, evaporated, and the residue distilled (Table 2).

1-(*n*-Butyl-ethyl-amino)-2-deuterio-2,3-butadiene (5):
Prepared from **3b** following the above procedure except for the use of lithium aluminium deuteride; yield: 80%; b.p. 79–80 °C/20 torr; n_D^{20}: 1.4564.

^{1}H-N.M.R. (CCl_4/TMS_{int}): $\delta = 0.7$–1.2 (m, 6H, CH_3); 1.2–1.6 (m, 4H, $C\underline{H}_2C\underline{H}_2CH_3$); 2.2–2.7 (m, 4H, NCH_2); 3.0–3.2 (m, 2H, $=C{-}CH_2$); 4.5–4.7 ppm (m, 2H, $=CH_2$).

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