CHEMISTRY LETTERS, pp. 1029-1030, 1982.

A SIMPLE ROUTE TO FURANS BY ORGANOALUMINUM REAGENTS

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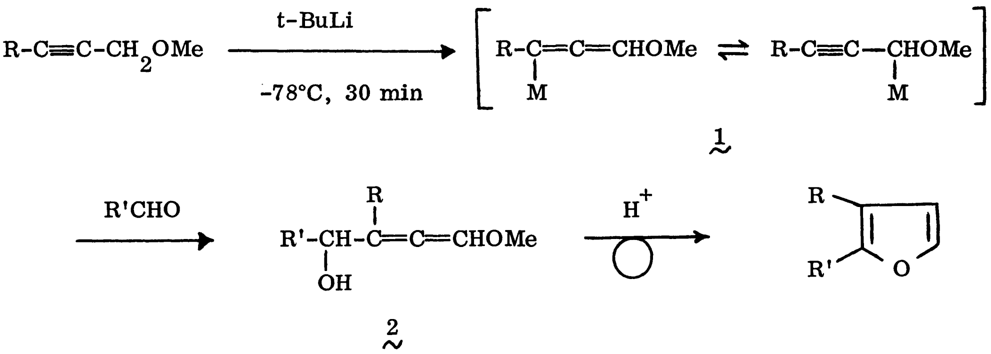
2,3-Disubstituted furans are synthesized from the reaction of aldehydes with allenylaluminum reagents derived from propargylic ethers.

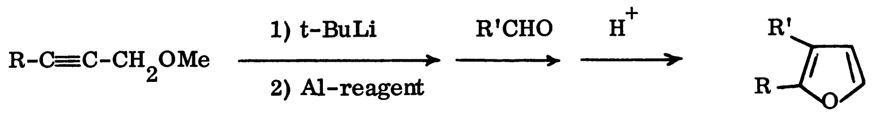
We report here a facile route to α-methoxy-β-hydroxy allenes, precursors of 2,3-disubstituted furans.[1] The process is illustrated in Scheme 1. The propargylic/allenic reagent 1 shows the ambident property as nucleophile.[2] Although β-acetylenic alcohols were the major products from the reactions of Li-1 or Mg-1 with aldehydes, the aluminum reagents of 1 produced the α-allenic alcohol 2,[3] which was cyclized to furans under mild acidic conditions.[4]

Scheme 1



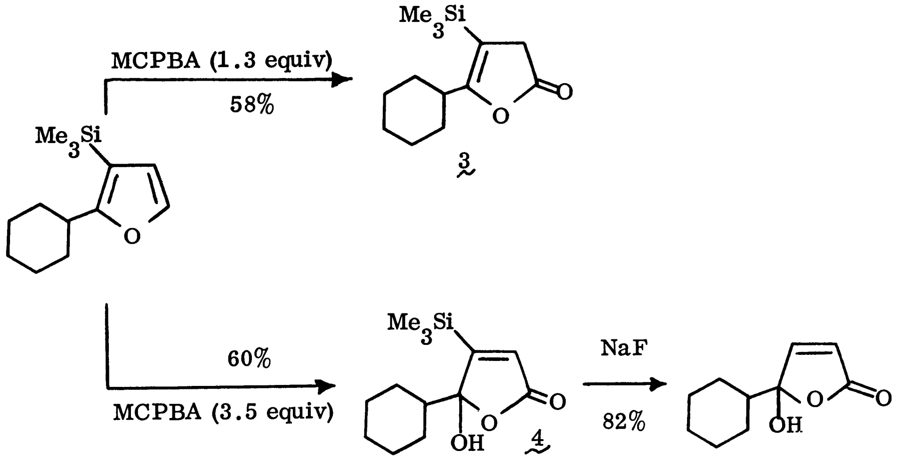
tert-Butyllithium in pentane (1.8 M, 0.83 ml, 1.5 mmol) was added dropwise to a solution of 1-methoxy-2-butyne (0.136 g, 1.5 mmol)[5] in dry THF (4 ml) with stirring under argon at -78°C. After 40 min at -78°C, diethylaluminum chloride in hexane (1.0 M, 3.0 ml, 3.0 mmol) was added dropwise to the resulting orange solution of the anion, and the slightly darkened solution was stirred there for 10 min. Freshly distilled cyclohexanecarbaldehyde (0.16 ml, 1.3 mmol) was added over a period of 5 min at -78°C and the mixture was stirred at -78°C for 30 min and then 20°C for 30 min. The reaction mixture was poured into ice-cold 1 N-hydrochloric acid and the product was extracted with ether repeatedly. The combined ethereal layers was dried and concentrated in vacuo to give a pale yellow oil, which was dissolved in dry methanol (5 ml) at 0°C. Two drops of hydrochloric acid was added and the mixture was stirred at 20°C for 1 h.[6] After the formation of furan being analysed by TLC assay, the reaction was terminated by the addition of excess sodium bicarbonate. Concentration of the suspension in vacuo and the slurry was subjected to column chromatography on silica gel to afford 2-cyclohexyl-3-methylfuran (175 mg, 82% yield). Additional experimental results are summarized in Table 1.

Table 1.



R	R'	Al-reagent (equiv)	Yield (%)
Me	Cyclohexyl	none	34
Me	Cyclohexyl	$i\text{-}Bu_3Al$ (1)	70
Me	Cyclohexyl	Et_2AlCl (2)	82
Me	$n\text{-}C_5H_{11}$	Et_2AlCl (1)	48
Me	$n\text{-}C_5H_{11}$	Et_2AlCl (2)	71
Me	$n\text{-}C_9H_{19}$	$i\text{-}Bu_3Al$ (1)	73
Me	$n\text{-}C_9H_{19}$	Et_2AlCl (2)	66
Me	Geranyl	$i\text{-}Bu_3Al$ (1)	62
Me	Geranyl	Et_2AlCl (2)	89
Me	Phenyl	$i\text{-}Bu_3Al$ (1)	70
Me	Phenyl	Et_2AlCl (2)	85
Me_3Si	Cyclohexyl	none	30
Me_3Si	Cyclohexyl	Et_2AlCl (2)	67
Me_3Si	Phenyl	Et_2AlCl (2)	54
Me_3Si	$n\text{-}C_9H_{19}$	Et_2AlCl (2)	62

3-Trimethylsilylfurans derived from 3-trimethylsilyl-1-methoxypropyne[7] were useful synthetic intermediates for butenolides.[8] Thus, 3-trimethylsilyl-2-cyclohexylfuran was treated with 1.3 equiv of m-chloroperbenzoic acid in CH_2Cl_2 at 10°C for 5 h to give the butenolide 3 in 58% yield. Treatment of the same furan with excess peracid furnished the unsaturated lactone 4 in 60% yield. Desilylation was effected by the exposure of 4 with sodium fluoride in methanol at 50°C for 3 h.



References

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(Received May 12, 1982)