SHORT PAPER

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Selective synthesis of conjugated enynes from α-arylalkynols using LiCl-Acidic Al_2O_3 under solvent-free conditions†

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α-Arylalkynols were converted into conjugated enynes (in a selective manner under solvent-free conditions) using the LiCl-acidic Al_2O_3 couple as catalyst and support.

Keywords: α-arylalkynol, conjugated enyne, dehydration, acidic alumina

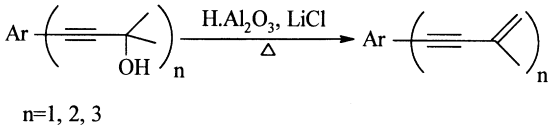
Organic reactions on solid supports have been widely used and there are several reviews on the use of solid supports in organic synthesis.[1] Improvements in the reactivity and selectivity of reagents in organic reactions and the cleaner processes on solid supports comprise a number of the advantages for such reactions. In the context of organic syntheses, alumina is one of the most efficient inorganic supports that has been applied to a wide variety of organic reactions.[2]

1,3-Enynes are conjugated systems that can be specially used in the synthesis of natural products,[3] polymers[4] and in the selective construction of aromatic frameworks.[5] There are many synthetic approaches to these compounds, most of which include coupling of terminal alkynes with vinyl halides or triflates and vinyl organometallic compounds,[6] homocoupling or cross-coupling of acetylenes using metal catalysts such as Pd[7] and Ru complexes,[8] or dehydration of α-alkynols using reagents such as dicobalthexacarbonyl complexes,[9] acidic zeolites,[10] and polyphosphoric acid trimethylsilyl ester.[11] Although all these methods have their own advantages, the scope of many of these reactions has been limited by the nature of the reactants or the procedure employed. Thus, the development of novel reagents for the synthesis of 1,3-enynes is of importance.

In acidic conditions α-arylalkynols can be converted into both α,β-unsaturated carbonyl compounds (via Meyer-Schuster rearrangement) and 1,3-enynes[12] (Scheme 1). Therefore, the selective conversion of α-alkynols into each of these compounds, is important from synthetic view point.

To achieve a simple and selective approach to conjugated enynes, we found that the pair LiCl-acidic Al_2O_3 (LiCl-$H.Al_2O_3$) can be used in order to produce 1,3-enynes selectively from α-arylalkynols. In our procedure, the LiCl-$H.Al_2O_3$ was used as a catalyst-support and the reactions were done in a homogeneous medium.

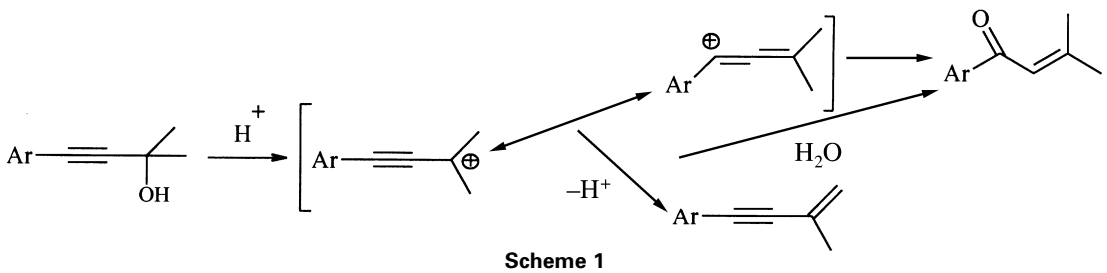
First, the α-arylalkynols, **1A–9A**, were prepared using Sonogashira conditions[6c, 13] through the reaction between suitable arylhalides and 2-methylbut-3-yn-2-ol (MEBYNOL) in Et_3N or Et_2NH as solvent and base in the presence of $Pd(PPh_3)_2Cl_2$ and CuI as catalyst.[14] Then, the enynes were obtained through dehydration of the corresponding α-arylalkynols on the LiCl-$H.Al_2O_3$, (Scheme 2). The results are given in Table 1.



Scheme 2

It seems that the observed catalytic effect of Lewis-acidic lithium ion on the α-arylalkynol dehydration reaction is related to the lithium ion ability to coordinate with the alkynol oxygen resulting in the facilitation of the dehydration under mild acidic conditions. Comparison of different catalyst-supports ($H.Al_2O_3$, LiCl-neutral Al_2O_3, LiCl-$H.Al_2O_3$, *p*-TsOH-neutral Al_2O_3, $ZnCl_2$-Al_2O_3, montmorillonites-K10) demonstrated that the catalyst and support composition plays an important role in obtaining high yields of the 1,3-enyne compounds. As can be seen in Table 2, $H.Al_2O_3$ in the absence of LiCl give the enynes with low yields as LiCl on neutral Al_2O_3. On the other hand, the reagents such as $ZnCl_2$-Al_2O_3 and K10 give a mixture of products that contains only a few percent of the corresponding enyne. However, the relatively weak acid of the $H.Al_2O_3$ (chromatography grade) coupled with LiCl caused the dehydration process in good yields.

In conclusion the present paper describes a convenient and selective method for the synthesis of conjugated enynes in good yields via dehydration of α-arylalkynols using the LiCl-$H.Al_2O_3$ couple as a catalyst-support.



Scheme 1

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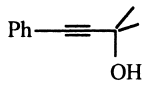
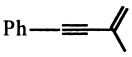
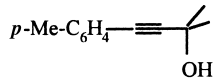
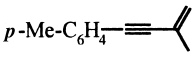
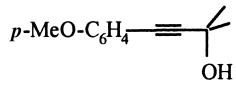
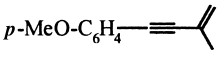
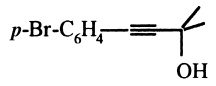
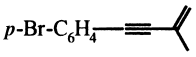
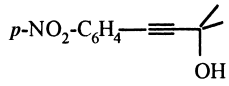
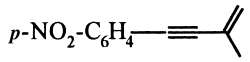
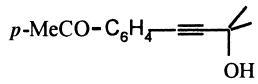
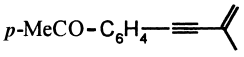
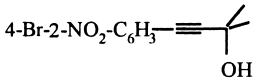
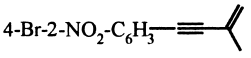
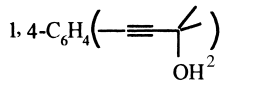
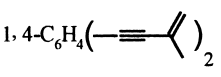
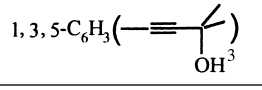
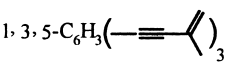
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Conversion of α-arylalkynols into conjugated enynes using LiCl/H.Al_2O_3

Entry	α-Arylalkynol **(A)**	Enyne **(B)**	Temp. /°C	Time /min	Yield[a] /%	LiCl /g	H.Al_2O_3 /g
1			105	90	85	0.12	2
2			105	55	85	0.12	2
3			100	90	80	0.12	2
4			105	70	80	0.12	2
5			115	90	80	0.15	2
6			115	90	70	0.15	2
7			130	90	65	0.20	2
8			115	60	80	0.25	3
9			130	90	65	0.40	3

[a]Yield of pure and isolated products.

Table 2 The effect of different catalyst-supports in the dehydration of α-arylalkynols.

Enyne (B)[a]	H.Al_2O_3[b]	LiCl-Al_2O_3[b,c]	*p*-TsOH-Al_2O_3	$ZnCl_2$-Al_2O_3[c]	K10[c]
	Yield/%				
1	35	20	30	<10	<10
2	40	20	30	<10	<10
3	45	20	35	<10	<10
4	35	15	25	<10	<10
5	30	15	30	<10	<10
6	30	15	30	<10	<10
7	25	10	25	<10	<10
8	40	20	30	<10	<10
9	35	15	25	<10	<10

[a]based on Table 1. [b]based on conversion of the α-arylalkynol. [c]TLC yield.

Experimental

The acidic Al_2O_3 used was Aluminium Oxide 90 active acidic (Merck-1078). Column-chromatographic separations were performed on silica gel 60 (Merck-9385). Thin-layer chromatography (TLC) was performed on silica gel 60 (Merck-7748) plates and visualisation was effected with short wavelength UV light (254 nm). IR spectra were recorded on a Mattson-1000 FTIR spectrophotometer. NMR spectra were recorded on a Bruker DRX-500 Avance or AC-80 spectrometer. Chemical shifts are expressed in ppm relative to TMS. Mass spectra were obtained on a Hewlett-Packard 5973 MSD. High-resolution mass spectra were obtained on a Varian MAT 311 instrument. Elemental analyses (C, H, N) were performed on a Heraeus CHN-O-Rapid analyser. Melting points were obtained on a Buchi B-540 melting point apparatus and are uncorrected.

General procedure for synthesis of conjugated enynes: LiCl and H.Al_2O_3 (see Table 1) were well mixed, then α-arylalkynol (1 mmol) was introduced to the mixture by grinding. The mixture was taken in a 25-ml round-bottomed flask and placed in a preheated oil bath at the desired temperature (see Table 1). The solid mixture was vigorously stirred for the period of time indicated in Table 1. For the α-arylalkynol of **4A** the build up of substance from the support was returned to the reaction mixture occasionally by use of a spatula. After the allotted time period, the oil bath was removed and the mixture was cooled to room temperature. The product was extracted with ethyl acetate and the solvent was then removed in vacuo to afford a crude product that was purified by thin layer chromatography on silica plates using hexane/ethylacetate (95/5) as eluent to give the desired enyne.

2-Methyl-4-phenylbut-1-en-3-yne (**1B**): Yield 85%, colourless liquid (Lit. colourless liquid);[4d] IR (neat, cm^{-1}), 3062, 2969, 2208, 1615, 1492, 1446, 1377, 1315, 1076, 900, 761; ^{1}HNMR ($CDCl_3$, 80 MHz), δ (ppm) 1.91 (s, 3H), 5.2 (d, 1H, *J*=2.7 Hz), 5.33 (d, 1H, *J*=2.7 Hz), 7.28 (m, 5H); ^{13}CNMR ($CDCl_3$, 20.15 MHz), δ (ppm) 23.80, 88.71, 91.02, 122.23, 123.25, 126.80, 128.15, 128.22, 131.84; MS *m/e* 142, 141, 127, 115, 77.

2-Methyl-4-(4′-tolyl)but-1-ene-3-yne (**2B**): Yield 85%, pale yellow liquid; IR (neat, cm^{-1}), 3055, 2965, 2207, 1615, 1515, 1460, 1315, 1070, 900, 823; ^{1}HNMR ($CDCl_3$, 500 MHz), δ (ppm) 2.11 (s, 3H), 2.42 (s, 3H), 5.39 (d, 1H, *J*=1.8 Hz), 5.51 (d, 1H, *J*=1.8 Hz), 7.2 (d, 2H, *J*=8Hz), 7.45 (d, 2H, *J*=8Hz); ^{13}CNMR ($CDCl_3$, 125 MHz), δ (ppm) 21.85, 23.99, 89.21, 90.47, 120.77, 121.10, 127.50, 129.54, 131.96, 138.65; MS *m/e* 156, 155, 141, 128, 115, 77; Anal. calcd for $C_{12}H_{12}$: C, 92.31; H, 7.69, found: C, 92.46; H, 7.55.

2-Methyl-4-(4′-methoxyphenyl)but-1-en-3-yne (**3B**): Yield 80%, pale yellow liquid; IR(neat, cm^{-1}), 3070, 2954, 2839, 2208, 1608, 1515, 1460, 1254, 1182, 1038, 908, 838; ^{1}HNMR ($CDCl_3$, 500 MHz), δ (ppm) 2.04 (s, 3H), 3.81 (s, 3H), 5.31 (d, 1H, *J*=1.4 Hz), 5.42 (d, 1H, *J*=1.4 Hz), 6.87 (dd, 2H, *J*=6.8, 2.08 Hz), 7.43 (dd, 2H, *J*=6.8, 2.09 Hz); ^{13}CNMR ($CDCl_3$, 125 MHz), δ (ppm) 24.01, 55.66, 88.92, 89.76, 114.37, 115.80, 121.65, 127.49, 133.44, 159.99; MS *m/e* 172, 157, 141, 128, 127, 102, 77; Anal. calcd for $C_{12}H_{12}O$: C, 83.72; H, 6.98, found: C, 83.52; H, 7.00.

2-Methyl-4-(4′-bromophenyl)but-1-en-3-yne (**4B**): Yield 80%, white solid; m.p. 30°C; IR (neat, cm^{-1}), 3050, 2960, 2205, 1615, 1485, 1315, 1077, 1015, 900, 823; ^{1}HNMR ($CDCl_3$, 500 MHz), δ (ppm) 2.03 (s, 3H), 5.37 (s, 1H), 5.46 (s, 1H), 7.33 (d, 2H, *J*=8.3 Hz), 7.47 (d, 2H, *J*=8.3 Hz); ^{13}CNMR ($CDCl_3$, 125 MHz), δ (ppm) 23.82, 87.83, 92.16, 121.51, 122.83, 127.07, 131.98, 133.43, 133.55; MS *m/e* 222 ($C_{11}H_9{}^{81}Br$), 221, 220 ($C_{11}H_9{}^{79}Br$), 219, 207, 205, 141, 126, 115; Anal. calcd for $C_{11}H_9Br$: C, 59.73; H, 4.07, found: C, 59.58; H, 4.27.

2-Methyl-4-(4′-nitrophenyl)but-1-en-3-yne (**5B**): Yield 80%, pale yellow solid; m.p. 95.5–96.5°C; IR(KBr, cm^{-1}), 3075, 2923, 2207, 1592, 1515, 1345, 1108, 915, 854, 754, 692; ^{1}HNMR ($CDCl_3$, 80 MHz), δ (ppm) 1.91 (s, 3H), 5.31 (d, 1H, *J*= 1.4 Hz), 5.36 (d, 1H, *J*=1.4 Hz), 7.47 (d, 2H, *J*=8.8 Hz), 8.09 (d, 2H, *J*=8.8 Hz); ^{13}CNMR ($CDCl_3$, 20.15 MHz), δ (ppm) 22.85, 85.90, 95.34, 123.51, 123.90, 126.37, 130.15, 132.10, 146.92; MS *m/e* 187, 157, 139, 128, 115; Exact M^+ calcd for $C_{11}H_9NO_2$: 187.0634, found: 187.0628.

2-Methyl-4-(4′-acetylphenyl)but-1-en-3-yne (**6B**): Yield 70%, yellow solid; m.p. 42.5–43.5°C; IR(KBr, cm^{-1}), 3075, 2915, 2202, 1677, 1608, 1354, 1269, 908, 831, 600; ^{1}HNMR ($CDCl_3$, 500 MHz), δ (ppm) 2.09 (s, 3H), 2.67 (s, 3H), 5.50 (d, 1H, *J*=2.5 Hz) 5.54 (d, 1H, *J*=2.5 Hz), 7.60 (d, 2H, *J*=8.6 Hz), 8.00 (d, 2H, *J*=8.6 Hz); ^{13}CNMR ($CDCl_3$, 125 MHz), δ (ppm) 23.80, 27.21, 87.85, 94.60, 123.82, 126.92, 128.68, 128.70, 132.35, 136.30, 197.71; MS *m/e* 184, 169, 139, 115; Exact M^+ calcd for $C_{13}H_{12}O$: 184.0889, found: 184.0888.

2-Methyl-4-(4′-bromo-2′-nitrophenyl)but-1-en-3-yne (**7B**): Yield 65%, yellow solid; m.p. 50–51°C; IR(KBr, cm^{-1}), 3080, 2923, 2200, 1598, 1523, 1338, 1276, 1092, 900, 838; ^{1}HNMR ($CDCl_3$, 80 MHz), δ (ppm) 2.03 (s, 3H), 5.33 (s, 1H), 5.41 (s, 1H), 7.34 (d, 1H, *J*= 8.4 Hz), 7.59 (d, 1H, *J*=8.4 Hz), 8.06 (s, 1H); ^{13}CNMR ($CDCl_3$, 20.15 MHz), δ (ppm) 22.92, 83.05, 99.75, 117.75, 122.15, 124.82, 126.32, 127.75, 135.91, 136.05, 149.53; MS *m/e* 267 ($C_{11}H_8NO_2{}^{81}Br$), 265 ($C_{11}H_8NO_2{}^{79}Br$), 250, 248, 226, 224, 210, 208, 184, 182, 156, 154, 139, 128, 114, 113, 75; Exact M^+ calcd for $C_{11}H_8NO_2Br$: 264. 9738, found: 264.9831.

1′,4′-Bis-[4-(2-methylbut-1-en-3-yne)]benzene (**8B**): Yield 80%, pale yellow solid; m.p. 97.5–98.5°C; IR(KBr, cm^{-1}), 3060, 2938, 2200, 1608, 1500, 1315, 908, 846; ^{1}HNMR ($CDCl_3$, 500 MHz), δ (ppm) 1.92 (s, 6H), 5.26 (d, 2H, *J*=2.2 Hz), 5.34 (d, 2H, *J*=2.2 Hz), 7.32 (s, 4H); ^{13}CNMR ($CDCl_3$, 125 MHz), δ (ppm) 23.10, 82.25, 92.20, 122.34, 122.60, 126.76, 131.40; MS *m/e* 206, 191, 189, 176, 165, 141; Anal. calcd for $C_{16}H_{14}$: C, 93.20; H, 6.80, found: C, 93.05; H, 6.87.

1′,3′,5′-Tris-[4-(2-methylbut-1-en-3-yne)]benzene (**9B**): Yield 65%, white solid; m.p. 71.5–72.5°C; IR(KBr, cm^{-1}), 3060, 2962, 2300, 1610, 1576, 1415, 1260, 1100, 877, 807, 685; ^{1}HNMR ($CDCl_3$, 500 MHz), δ (ppm) 2.00 (s, 9H), 5.35 (s, 3H), 5.42 (s, 3H), 7.47 (s, 3H); ^{13}CNMR ($CDCl_3$, 125 MHz), δ (ppm) 23.81, 87.15, 92.05, 123.12, 124.43, 127.08, 134.60; MS *m/e* 270, 255, 253, 239, 226, 213, 202, 189, 135, 113; Exact M^+ calcd for $C_{21}H_{18}$: 270.1409, found: 270.1391.

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