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Mendeleev Commun., 2006, **16(1)**, 13–14

Mendeleev
Communications

Superbase-catalysed addition of methanol to propyne and allene: an expedient synthesis of 2-methoxypropene

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DOI: 10.1070/MC2006v016n01ABEH002198

In the superbase catalytic systems Bu^{t}OK/NMP, Am^{t}OCs/NMP and KOH/DMSO, methanol readily adds to propyne and allene at 100–120 °C and atmospheric pressure to afford 2-methoxypropene in 80–97% yield with 75–94% methanol conversion.

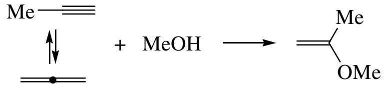
2-Methoxypropene (MP) is of interest as an important auxiliary in the synthesis of vitamins, carotinoids, flavour and fragrant compounds.[1–4] Among the known syntheses of MP,[5–13] direct nucleophilic addition of methanol to propyne or propyne–allene mixtures[5–9] represents the most straightforward and atom-economic route.

Despite the significant strides in direct isopropenylation of methanol with a propyne–allene mixture,[5–9] this reaction remains a synthetic challenge since it is conducted at 28–38 Torr and 140–190 °C (catalyst, NaOH; MP yield, 40%)[5] or in a gas phase at high temperatures (180–300 °C),[6–9] always accompanied by 2,2-dimethoxypropane as a by-product.

Meanwhile, the KOH/DMSO superbase catalytic system was shown to dramatically accelerate the vinylation of alcohols with acetylene.[14–18]

Here, we report that in the superbase catalytic systems Bu^{t}OK/*N*-methylpyrrolidone (NMP), Am^{t}OCs/NMP and KOH/DMSO methanol readily reacts with a propyne–allene mixture under atmospheric pressure at 100–120 °C to furnish MP chemo- and regioselectively in a practically quantitative yield and complete conversion.

Unlike the patent disclosure,[19] here for the first time we focus on the essential experimental details and basic peculiarities of the process, which help it to be reproducible.



Scheme 1

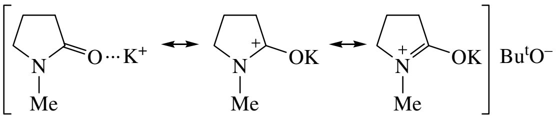
At a concentration of Bu^{t}OK in NMP equal to 1–0.5 mol dm^{-3}, the yield of MP is stable and equal to 93–97% (hereinafter, the yield of MP was calculated on the methanol consumed, methanol conversion being 88–93%),† while at a concentration of 0.25 mol dm^{-3}, methanol conversion drops to 40%, thus evidencing the importance of high basicity of the catalytic solution. Respectively, to maintain it, the methanol concentration in the reaction mixture is to be sustained on the lowest possible level, practically the methanol feeding rate should be 0.4–1.5 mol h^{-1} per 1 dm^3 of the catalytic solution. Volatile MP is continuously removed by the propyne–allene flow from the catalytic solution to be condensed in a cooled receiver.

The Am^{t}OCs/NMP system was equal in efficiency to Bu^{t}OK/NMP (MP yield, 93%; methanol conversion, 94%).[‡]

Under the same conditions,[‡] the Bu^{t}ONa-catalysed reaction gives 38% methanol conversion (MP yield of 86%), and CsF/NaOH gives 15% conversion (MP yield of 73%), whereas NaOH does not catalyse the addition (evidently, due to neutralization by NMP).

In the KOH/DMSO system, the yield of MP is about 80% at 75% methanol conversion.[§]

The higher activity of the Bu^{t}OK/NMP and Am^{t}OCs/NMP systems is likely due to the specific solvation (complexation) of the cations by the amide function, which results in an additional anion desolvation and a capture of propyne and allene as ligands by the complex cation with their relevant activation. The complex formation is evidenced by the charge-transfer bands in the UV spectrum of a solution of Bu^{t}OK in NMP (283, 543 and 580 nm, bright purple colour) and a high-frequency C=O stretching shift in the IR spectrum (1683 → 1693 cm^{-1}) apparently due to the C=N bond contribution.



Scheme 2

Note that no other products, except for MP, are detectable in the reaction mixture thus indicating that actual selectivity of the process for both methanol and propyne–allene is close to 100%.

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Received: 9th June 2005; Com. 05/2529

[†] GLC was performed on a Chrom-4 chromatograph; column, 2400× ×3.5 mm; liquid phase, polyethylene glycol 20000, 10%; solid phase, Inerton-AW-DMCS, 0.2–0.25 mm; thermal conductivity detector; helium as a carrier gas; column temperature, 65 °C. ^{1}H NMR spectra were run on a Bruker DPX-400 (400 MHz) spectrometer. Chemical shift values are in ppm relative to HMDS. IR spectra were recorded on a Bruker IFS-25 instrument in thin layers.

Commercial propyne (98%) and Bu^{t}OK (Aldrich) were employed. Am^{t}OCs was kindly presented by Professor L. Brandsma (Utrecht University, the Netherlands). The propyne–allene mixture (4:1) was prepared by dehydrochlorination of allyl chloride in the KOH/DMSO system.

Typical procedure. Bu^{t}OK (2.8 g, 25 mmol) was dissolved in NMP (50 ml) and placed in a four-neck flask (100 ml) equipped with a bubbler, a thermometer, a dropping funnel and a high performance reflux condenser connected with two coil traps. The solution was heated to 120 °C with stirring using a magnetic stirrer. Methanol (4.8 g, 150 mmol) was added dropwise at a feeding rate of 1 ml h^{-1} and the propyne–allene mixture (~1 dm^3 h^{-1}) was fed continuously into the catalytic solution. 2-Methoxypropene and methanol, partially removed with a flow of gases, were collected in a downstream cooled trap (–5 °C). Unused propyne and allene were collected in the second trap cooled to –60 °C and then returned to the reaction flask. After 12 h, the condensate consisting of MP (9.2 g, 128 mmol) and methanol (0.6 g, 18 mmol) was collected. The yield of MP based on methanol consumed was 97%. Distillation of the mixture gives the pure target product.

2-Methoxypropene: ^{1}H NMR (CDCl$_3$) δ: 3.76 (d, 2H, CH$_2$=, ^2J 2.0 Hz), 3.43 (s, 3H, OMe), 1.72 (s, 3H, Me). IR (CDCl$_3$, ν/cm^{-1}): 650, 734, 802, 822, 909, 935, 993, 1023, 1085, 1197, 1285, 1371, 1395, 1451, 1607, 1660, 2845, 2957, 3000, 3122.

[‡] Analogously, from methanol (4.8 g, 150 mmol) and propyne in the presence of Am^{t}OCs (11.0 g, 50 mmol) in NMP (50 ml) the condensate consisting of MP (9.4 g, 131 mmol, 87% yield) and methanol (0.3 g, 9 mmol) was collected. The total yield of MP based on methanol consumed was 93%.

[§] KOH (2.8 g, 50 mmol), methanol (1.6 g, 50 mmol) and DMSO (50 ml) were placed in a flask and saturated with the propyne–allene mixture at room temperature. The mixture was heated to 100 °C, and methanol (1.6 g, 50 mmol) in DMSO (2 ml) was added dropwise while propyne–allene mixture was bubbled for 3 h. The condensate contained 4.3 g (60 mmol) of MP and 0.8 g (25 mmol) of methanol. The yield of MP was 80%, the conversion of methanol was 75%.