

Nucleophilic Addition to Acetylenes in Superbasic Catalytic Systems: XIII.* Fluoride Cesium Containing Systems, Efficient Catalysts for Alkanols Vinylation

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Abstract—New catalytic systems CsF–MOH (M = Li, Na) were developed for the synthesis of alkyl vinyl ethers comparable in efficiency to cesium alcoholates. The addition of primary and secondary alcohols to acetylene occurs in the presence of these systems at the atmospheric (DMSO, 100°C) or at enhanced (without solvent, 135–140°C) acetylene pressure and affords alkyl vinyl ethers in up to 93% yield.

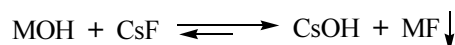
The systematic investigation of alcohols vinylation with acetylenes discovered by A.E. Faworsky [2] and further developed by W. Reppe [3] and M.F. Shostakovskii [4] provide deeper theoretical insight into the nucleophilic additions to the triple bond [5] and constant refining of the synthesis of vinyl ethers of versatile structures [3–12]. Here the main trend in stimulating vinylation reaction is the application of superbasic systems, like alkali metal hydroxide–polar solvent lacking hydroxy groups (DMSO, N-methylpyrrolidone, HMPA) [5, 7–12], or alkali metal alcoholate–Lewis base (Crown ether)–solvent lacking hydroxy groups (hydrocarbon) [13, 14].

We report here on the application of highly basic systems CsF–MOH and CsF–MOH–DMS (M = Li, Na) as efficient catalysts to alcohols vinylation.

In [15, 16] it was shown by an example of 1-heptanol vinylation under enhanced and atmospheric acetylene pressure in the presence of alkali metal hydroxides that the catalysts under investigation fit to the following series according to the decreasing efficiency: CsOH·H₂O ≥ RbOH·H₂O > 2KOH·H₂O > NaOH > KOH·H₂O > LiOH. The comparison of the catalytic activity of KOH hydrates (2KOH·H₂O and KOH·H₂O) confirmed the known [4, 7] negative effect of water on the vinylation process. Consequently, the use of anhydrous alkali metal hydroxides, first of all of CsOH would considerably accelerate the vinylation of the hydroxy compounds. However the preparation of anhydrous cesium and rubidium is a labo-

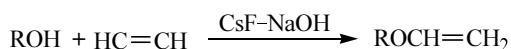
rious process. Usually azeotropic removal of water is used with an appropriate high-boiling solvent (octane, toluene). The present article contains findings evidencing the possibility of a successful application to the vinyl ethers synthesis of a catalytic system CsF–MOH (M = Li, Na) where the anhydrous CsOH is formed directly in the course of vinylation. This system possesses significant advantages compared to traditional vinylation catalysts like sodium and potassium hydroxides.

The high catalytic efficiency of the system developed is apparently due predominantly to the exchange between the lithium or sodium hydroxides and cesium fluoride resulting in cesium hydroxide and sparingly soluble lithium or sodium fluorides.



The nature of the alkali metal cation in the MOH (where M = Li, Na) used in the catalytic couple CsF–MOH did not virtually affect the rate of vinylation in keeping with the preliminary occurrence of the exchange reaction and with the actual catalysis of alcohol vinylation by the arising cesium hydroxide. The formation of sparingly soluble lithium and sodium fluorides shifts the exchange equilibrium to the right. Therewith the better solubility in alcohols of NaOH compared to LiOH ensures the faster and more complete preparation of an active catalyst in the system CsF–NaOH. Therefore the most results reported here were obtained with the use of just this catalytic couple.

* For communication XII see [1].



R = Pr, *i*-Pr, Bu, *i*-Bu, *s*-Bu, Et₂CHCH₂, *cyclo*-C₆H₁₁, *n*.-C₇H₁₅, *n*.-C₉H₁₉, *n*.-C₁₂H₂₅.

The reaction of acetylene with primary and secondary aliphatic alcohols in the presence of the catalytic system CsF–NaOH at 135–140°C (1–3 h) and enhanced acetylene pressure afforded alkyl vinyl ethers in a 73–89% yield (Table 1).

It was demonstrated by an example of 1-heptanol [16] that as large as this vinyl ether yield was obtained under similar conditions only in reaction in the presence of cesium heptylate.

The higher primary alcohols (R = Et₂CHCH₂, *n*.-C₇H₁₅, *n*.-C₉H₁₉, *n*.-C₁₂H₂₅) possess a similar reactivity and afford vinyl ethers in fairly equal yields and with a high selectivity (Table 1, runs nos. 7, 10–12, 14, 15, 17). The conversion of alcohol suggests that the reactivity tends to grow in the series C₄ < C₆ ≈ C₇ < C₉ ≈ C₁₂, whereas the selectivity of the reaction is virtually unchanged. The

Table 1. Vinylation of alcohols ROH with acetylene in the presence of CsF–NaOH at enhanced acetylene pressure^a

Run no.	R	CsF/NaOH, mol%	Time, h	Conversion of alcohol, %	Yield of vinyl ether, % ^b
1	Pr	10/10	3.0	73	80
2	<i>i</i> -Pr	10/10	3.0	56	73
3	Bu	5/5	3.0	76	82
4	Bu	10/10	3.0	98	78
5	<i>i</i> -Bu	5/5	2.0	96	82
6	<i>s</i> -Bu	10/10	3.0	69	78
7	Et ₂ CNCN ₂	5/5	2.0	86	86
8	<i>cyclo</i> -C ₆ H ₁₁	10/10	1.5	99	74
9	<i>cyclo</i> -C ₆ H ₁₁	0/10 ^c	2.5	85	80
10	<i>n</i> .-C ₇ H ₁₅	10/10	0.5	96	89
11	<i>n</i> .-C ₇ H ₁₅	5/5 ^d	1.5	85	92
12	<i>n</i> .-C ₇ H ₁₅	5/5	1.5	88	86
13	<i>n</i> .-C ₇ H ₁₅	0/5 ^c	1.5	61	85
14	<i>n</i> .-C ₇ H ₁₅	3/3	3.0	90	83
15	<i>n</i> .-C ₉ H ₁₉	5/5	1.0	98	88
16	<i>n</i> .-C ₉ H ₁₉	0/5 ^c	3.0	60	74
17	<i>n</i> .-C ₁₂ H ₂₅	5/5	1.0	90	89

^a 300 mmol of alcohol, 135–140°C, initial acetylene pressure 10–14 at, reactor of 1 liter capacity.

^b The yield is calculated with respect to the reacted alcohol.

^c Vinylation catalyst KOH.

^d Catalytic system CsF–LiOH.

high vinylation rate of the higher alcohols permitted the reduction of the catalyst concentration to 5 and even 3 mol% (Table 1, cf. runs nos. 10–12, 14), whereas with the lower (Table 1, runs nos. 3 and 4) and especially secondary (Table 1, runs nos. 2 and 6 cf. with runs nos. 1 and 4) alcohols the use of 10 mol% of the catalyst is more feasible.

The potassium hydroxide turned out to be less active than the new superbasic system: When instead of CsF–NaOH was used KOH (at catalyst concentration 5 mol%) the conversion of 1-heptanol into the vinyl heptyl ether decreased from 88 to 61% (Table 1, cf. runs nos. 12 and 13). The vinyl ethers (R = *cyclo*-C₆H₁₁, *n*.-C₉H₁₉) were obtained in lower yields even at the longer reaction period (Table 1, cf. runs nos. 8 and 9, 15 and 16).

It is known that the application of superbasic catalytic media of the type alkali metal hydroxide–polar solvent lacking hydroxy groups (DMSO, HMPA, N-methylpyrrolidone etc.) results in considerable acceleration of the nucleophilic addition to the acetylene [5, 7–12]. The higher vinylation rate permits performing the reaction under milder conditions, often under atmospheric pressure of the acetylene.

Table 2. Vinylation of alcohols ROH in superbasic catalytic systems at atmospheric pressure of acetylene^a

Run no.	R	CsF/NaOH, mol%	Time, h	Conversion of alcohol, %	Yield of vinyl ether, % ^b
1 ^c	Pr	10/10	4.5	97	77
2	<i>i</i> -Pr	10/10	5.5	65	86
3	Bu	10/10	3.5	99	79
4	<i>i</i> -Bu	10/10	5.0	98	76
5	<i>s</i> -Bu	10/10	6.0	70	77
6	Et ₂ CNCN ₂	10/10	3.0	100	83
7	<i>cyclo</i> -C ₆ H ₁₁	10/10	6.0	68	76
8	<i>cyclo</i> -C ₆ H ₁₁	20/20	4.0	96	80
9	<i>cyclo</i> -C ₆ H ₁₁	0/100 ^d	4.0	100	88
10	<i>n</i> .-C ₇ H ₁₅	10/10	2.5	100	89
11	<i>n</i> .-C ₇ H ₁₅	5/5	4.0	100	87
12	<i>n</i> .-C ₇ H ₁₅	0/20 ^c	5.0	78	88
13	<i>n</i> .-C ₉ H ₁₉	10/10	4.5	99	86
14	<i>n</i> .-C ₁₂ H ₂₅	10/10	4.5	100	93

^a 50 mmol of alcohol, 50 ml of DMSO, 100°C, acetylene flow rate ~2 l/h.

^b The yield is calculated with respect to the reacted alcohol.

^c 30 ml of DMSO

^d Vinylation catalyst KOH.

^e Vinylation catalyst NaOH.

These observations proved to be valid also for the newly developed systems CsF–MOH (M = Li, Na). The use of DMSO as a complexing solvent resulted in even more active superbasic catalytic systems CsF–MOH (M = Li, Na)–DMSO, considerably increased the vinylation efficiency in the presence of the system CsF–NaOH–DMSO. The latter system catalyzed the vinylation of alcohols at the atmospheric pressure and temperature 100°C in 76–93% yields (Table 2). The optimum catalyst concentration is 10 mol% of each catalyst component with respect to the alcohol brought into the vinylation

reaction, the alcohol concentration in DMSO should be ~1 mol l⁻¹, the rate of acetylene flow ~2 liter per hour. The catalytic couple CsF–NaOH functions efficiently even at concentration 5/5 mol%, but the complete conversion of the alcohol is reached in a longer period, approximately 1.5 times longer (Table 2, cf. runs nos. 10 and 11). Unlike this in the system NaOH–DMSO the complete conversion of n.-C₇H₁₅OH is not attained even at increasing the sodium hydroxide concentration to 20 mol% and at twice longer the process (Table 2, run no. 12, cf. with runs nos. 10, 11).

Table 3. Some physical constants and spectral characteristics of ethers ROCH=CH₂

R	bp., °C (<i>p</i> , mm Hg)	<i>n</i> _D ²⁰	¹ H NMR spectrum, δ, ppm (<i>J</i> , Hz)					
			OCH=, d.d	=CH _{trans} , d.d	=CH _{cis} , d.d	OCH, OCH ₂	CH, CH ₂	Me
Pr	64	1.3916	6.45	4.16 (<i>J</i> 14.3, 1.8)	3.95 (<i>J</i> 6.7, 1.8)	3.62 t (2H, <i>J</i> 6.6)	1.63 sextet (2H, <i>J</i> 7.3)	0.94 t (3H, <i>J</i> 7.3)
	65 [3, 4]	1.3922 [4]						
<i>i</i> -Pr	53	1.3840	6.28	4.24 (<i>J</i> 14.2, 1.4)	3.97 (<i>J</i> 6.6, 1.4)	4.05 septet (1H, <i>J</i> 6.1)		1.23 d (6H, <i>J</i> 6.1)
	55 [3, 4]	1.3862 [4]						
Bu	92	1.4026	6.44	4.15 (<i>J</i> 14.2, 1.8)	3.94 (<i>J</i> 6.8, 1.8)	3.66 t (2H, <i>J</i> 6.5)	1.63 t t (2H, <i>J</i> 6.5, 7.5), 1.41 sextet (2H, <i>J</i> 7.5)	0.92 t (3H, <i>J</i> 7.5)
	93 [3]	1.4017						
<i>i</i> -Bu	93.7 [4]	[21]						
	81	1.3944	6.45	4.14 (<i>J</i> 14.3, 1.8)	3.93 (<i>J</i> 6.7, 1.8)	3.42 d (2H, <i>J</i> 6.5)	1.93 septet (1H, <i>J</i> 6.6)	0.93 d (6H, <i>J</i> 6.7)
82 [3]	1.3990 [4]							
<i>s</i> -Bu	83 [4]	1.3965						
	80	1.3970	6.29	4.22 (<i>J</i> 14.2, 1.3)	3.93 (<i>J</i> 6.6, 1.3)	3.81 m (1H)	1.43 m (2H)	0.89 t (3H, <i>J</i> 7.5), 1.09 d (3H, <i>J</i> 6.1)
81 [22]								
Et ₂ CHCH ₂	30–33 (55) [3]							
	134	1.4182	6.46	4.15 (<i>J</i> 14.4, 1.8)	3.93 (<i>J</i> 6.8, 1.8)	3.56 d (2H, <i>J</i> 5.7)	1.51 sextet (1H, <i>J</i> 6.2), 1.63 m (4H)	0.87 t (6H, <i>J</i> 7.4)
40–42 (14) [3]								
<i>cyclo</i> -C ₆ H ₁₁	148	1.4540	6.31	4.26 (<i>J</i> 14.2, 1.4)	3.96 (<i>J</i> 6.6, 1.4)	3.72 (1H)	1.85 m (4H), 1.73 m (4H), 1.39 m (2H)	
		1.4546						
n.-C ₇ H ₁₅		[23]						
	60 (12)	1.4226	6.44	4.15 (<i>J</i> 14.4, 1.8)	3.92 (<i>J</i> 6.8, 1.8)	3.65 t (2H, <i>J</i> 6.6)	1.63 q (2H, <i>J</i> 6.6), 1.27–1.37 m (8H)	0.87 (3H, <i>J</i> 6.8)
166 [23]	1.4220							
n.-C ₉ H ₁₉		[23]						
	97 (13)	1.4323	6.44	4.15 (<i>J</i> 14.3, 1.8)	3.94 (<i>J</i> 6.8, 1.8)	3.65 t (2H, <i>J</i> 6.6)	1.64 q (2H, <i>J</i> 6.9), 1.32–1.37 m (2H), 1.21–1.32 m (10H)	0.87 t (3H, <i>J</i> 6.6)
206–207 [23]	1.4310							
n.-C ₁₂ H ₂₅		[23]						
	102 (2)	1.4412	6.43	4.14 (<i>J</i> 14.3, 1.8)	3.94 (<i>J</i> 6.7, 1.8)	3.64 t (2H, <i>J</i> 6.5)	1.63 q (2H, <i>J</i> 6.6), 1.26–1.45 m (18H)	0.86 t (3H, <i>J</i> 6.6)
126 (3) [21]								

Table 3. (Contd.)

R	IR spectrum, cm ⁻¹
Pr	467, 597, 700, 763, 813, 906, 927, 950, 965, 986, 1006, 1015, 1044, 1077, 1122, 1149, 1205, 1321, 1383, 1456, 1466, 1612, 1636, 1650 sh, 2869, 2938, 2976, 3047, 3079, 3119
<i>i</i> -Pr	467, 601, 697, 819, 898, 949, 968, 980, 1016, 1123, 1182, 1202, 1320, 1341, 1373, 1384, 1453, 1468, 1617, 1636, 1640 sh, 2882, 2935, 2977, 3018, 3043, 3076, 3118
Bu	433, 502, 602, 700, 740, 758, 811, 888, 947, 963, 979, 1009, 1024, 1036, 1065, 1078, 1124, 1204, 1320, 1378, 1466, 1611, 1638, 1650 sh, 2874, 2936, 2961, 3019, 3048, 3079, 3119
<i>i</i> -Bu	452, 594, 700, 736, 812, 865, 912, 945, 963, 1012, 1041, 1076, 1114, 1135, 1207, 1300, 1321, 1369, 1389, 1412, 1471, 1612, 1636, 1654, 2875, 2912, 2930, 2959, 3019, 3047, 3080, 3119
<i>s</i> -Bu	464, 696, 750, 822, 870, 913, 950, 965, 992, 1023, 1029, 1041, 1109, 1126, 1162, 1180, 1200, 1322, 1346, 1378, 1407, 1457, 1610, 1634, 2880, 2935, 2972, 3018, 3043, 3076, 3118
Et ₂ CHCH ₂	420, 605, 668, 700, 724, 811, 925, 945, 963, 978, 997, 1077, 1099, 1135, 1205, 1320, 1341, 1378, 1467, 1610, 1636, 1648, 2858, 2870, 2931, 2958, 3046, 3078, 3118
<i>cyclo</i> -C ₆ H ₁₁	474, 608, 697, 822, 863, 890, 907, 927, 947, 964, 986, 1024, 1039, 1054, 1077, 1095, 1129, 1143, 1174, 1200, 1249, 1260, 1327, 1341, 1367, 1450, 1612, 1633, 2858, 2834, 2982, 3015, 3039, 3073, 3116
<i>n</i> -C ₇ H ₁₅	605, 700, 724, 810, 945, 963, 980, 997, 1076, 1129, 1207, 1320, 1379, 1468, 1609, 1635, 1650, 2855, 2873, 2921, 2934, 2963, 3048, 3079, 3119
<i>n</i> -C ₉ H ₁₉	605, 699, 722, 810, 896, 945, 963, 978, 1078, 1132, 1204, 1320, 1379, 1413, 1467, 1610, 1635, 1649, 2855, 2926, 2955, 3015 sh, 3046, 3076, 3118
<i>n</i> -C ₁₂ H ₂₅	668, 721, 810, 945, 963, 998, 1060, 1076, 1131, 1204, 1320, 1378, 1466, 1609, 1635, 1648, 2854, 2925, 2960 sh, 3046, 3079, 3118

Likewise, good results were obtained with cyclohexanol as an example of secondary alcohols in reaction carried out in DMSO at moderate temperature (100°C, 4–6 h) using the new catalyst CsF–NaOH in a quantity of 10–20 mol% (Table 2, run no. 8), whereas a comparable preparative yield of vinyl cyclohexyl ether was attained in the system KOH–DMSO under similar conditions only at KOH concentration increased to 100 mol% (Table 2, run no. 9).

When *t*-BuOH was subjected to vinylation in the system CsF–NaOH–DMSO (atmospheric pressure, 10 mol% of catalyst with respect to the alcohol, 100°C, 5 h) even traces of *tert*-butyl vinyl ether were not detected. The initial alcohol was recovered from the reaction mixture to 80%. The potentiometric titration revealed that no active alkali remained in the reaction mixture, and the amount of acetates formed corresponded to 81% conversion of the initial sodium hydroxide. We believe that this pattern of the process is due both to the hindrances to the formation of *t*-BuOCs (the tertiary alcohols because of their low acidity difficultly react with alkali metals hydroxides [17]) and to the basicity of medium getting higher than the optimum value [18]. As a result other processes dominate, e.g., dehydration of the initial alcohol [19] and direct synthesis of acetates from acetylene, water, and alkali metal hydroxides [20].

The vinylation of *t*-BuOH in the system CsF–NaOH–DMSO under higher acetylene pressure (concentration

of CsF–NaOH 20/20 mol%, 100°C, 5 h, initial pressure 16 at) gave rise to *tert*-butyl vinyl ether in a 8% yield at 25% conversion of *t*-BuOH. Alongside the *tert*-butyl vinyl ether we found in the reaction mixture 2-vinyloxy-1,3-butadiene arising by hydration trimerization of acetylene [8, 12].

EXPERIMENTAL

IR spectra of compounds synthesized were recorded from thin films on a spectrometer Bruker JFS-25 in the region 400–4000 cm⁻¹. ¹H NMR spectra were registered at room temperature on spectrometer Bruker DPX-400 at operating frequency 400.13 MHz, solvent CDCl₃, internal reference HMDS. The reaction mixtures were analyzed by GLC on LKhM-80 instrument equipped with katharometer, column 3000×3 mm, stationary phase poly(ethylene glycol) 20000, 1% on NaCl, carrier gas helium.

The alcohols used in the study were distilled, NaOH was of “chemically pure” grade, CsF (Sigma-Aldrich) and DMSO (Merck) were commercial reagents.

General procedure for vinylation of alcohols at enhanced acetylene pressure. Into a rotating steel reactor of 1 liter capacity was charged 300 mmol of alcohol, NaOH and CsF in amounts indicated in Table 1, and acetylene was supplied to the initial pressure of 10–14 at. The reaction was carried out at stirring and heating to 135–140°C for 1–3 h. The reaction products were distilled at atmospheric or reduced pressure depending on

the boiling point of the vinyl ether and were analyzed by GLC. The yields of vinyl ethers ROCH=CH₂ are given in Table 1, their physicochemical and spectral characteristics are presented in Table 3.

General procedure for vinylation of alcohols at atmospheric pressure of acetylene. Into a reaction flask of 100 ml capacity, equipped with an efficient reflux condenser connected to a trap cooled to -60°C, thermometer, magnetic stirrer, and a bubbler for supplying acetylene was charged 50 ml of DMSO, 50 mmol of alcohol, NaOH and CsF in amounts indicated in Table 2, the content of the flask was heated to 100°C, and acetylene was flown through the mixture at a rate of 2 liter per hour. The process was monitored by GLC. On completion of the synthesis the reaction mixture was diluted with water (200 ml), the reaction product was extracted into the ethyl ether (4×50 ml), the extract was washed with water (3×20–30 ml), dried on K₂CO₃, combined with the substance condensed in the trap (in case of low boiling vinyl ethers), the solvent was removed on the rotary evaporator, and the residue was distilled. The details of experiments and the yields of vinyl ethers obtained are compiled in Table 2.

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