Nucleophilic Addition to Acetylenes in Superbasic Catalytic Systems: XIV*. Vinilation of Diols in a System CsF−NaOH

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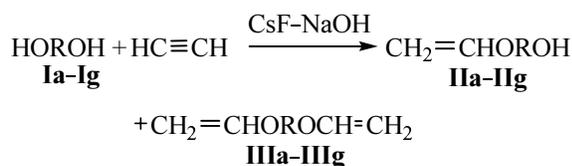*e-mail: oparina@irioch.irk.ru*
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Abstract—A new catalytic system CsF–NaOH was developed for the synthesis of mono- and divinyl ethers of alkanediols exceeding in efficiency KOH. The nucleophilic addition of diols to acetylene in the presence of this system occurs both at enhance pressure (without solvent, 140–160°C) and atmospheric pressure (in DMSO medium, 100°C) of acetylene. Conditions were established of a selective preparation in a high yield of divinyl ethers from diols.

Nucleophilic mono- and diaddition of diols to acetylene occurs under effect of strong bases (alkali metal hydroxides and alcoholates, superbasic system KOH–DMSO etc.) at enhanced or atmospheric pressure of acetylene [2–10] and is accompanied as a rule by further transformations of the target mono- and divinyl ethers (acetalization, the rupture of C–O bonds, elimination of a vinyl alcohol etc.) [2–13]. Therefore the search for new catalysts for the efficient and selective synthesis of mono- and divinyl ethers from diols remains an urgent problem. With this goal we have for the first time studied a reaction of acetylene with diols in the presence of a new catalytic system CsF–NaOH [1, 14] whose efficiency is due apparently mainly to the formation *in situ* of anhydrous cesium hydroxide nanoparticles. The an-hydrous cesium hydroxide is known to be more active [15] but less available than KOH vinylation catalyst.

By an example of a series of primary and secondary diols **Ia–Ig** containing from 2 to 7 carbon atoms between the hydroxy groups we demonstrated that the main products of these diols vinylation under acetylene pressure in the presence of the catalytic system CsF–NaOH were mono- **IIa–IIg** and divinyl **IIIa–IIIg** ethers formed in an overall yield 60–85% (Tables 1 and 2).

The effect of the vinylation conditions [reaction temperature (136–158°C), heating time (1.5–3.0 h), concentration of the catalytic system CsF–NaOH (5/5–10/10 mol% of each component)] on the yield and relative amount of final products **II** and **III** was investigated by an example of 1,4-butanediol (**Ie**) (Table 1) that was known to add to acetylene in the presence of potassium hydroxide [2, 16] in a highly selective fashion with a minimal formation of side products.

As seen from Table 1 under comparable conditions the optimum amount of the catalytic system CsF–NaOH is apparently 7 mol% of each component with respect to butanediol **Ie** (Table 1, runs nos. *2–4*): Using this concentration of the catalyst it is easy by varying the reaction conditions and the ratio diol:acetylene to direct the process to predominant formation of mono- (Table 1, runs nos. *2* and *3*) or divinyl ether (run no. *4*). At lower catalyst concentration (Table 1, run no. *1*) the conversion of the initial diol within the same period decreases from 100 to 85% (Table 1, cf. runs nos. *1* and *3*). Correspondingly, the increase in the catalyst concentration to 10 mol% of each component (Table 1, run no. *5*) results in the predominant formation of divinyl ether **IIIe,** however in an insufficient yield (52%) apparently due to side processes. Therewith the reaction mixture often suffers self-heating (for instance, from 137 to 150°C, run no. *5*,

$$\text{HOROH} + \text{HC}\equiv\text{CH} \xrightarrow{\text{CsF–NaOH}} \text{CH}_2\text{=CHOROH}$$
$$\mathbf{Ia\text{-}Ig} \qquad\qquad\qquad\qquad \mathbf{IIa\text{-}IIg}$$
$$+ \text{CH}_2\text{=CHOROCH=CH}_2$$
$$\mathbf{IIIa\text{-}IIIg}$$

R = (CH$_2$)$_2$ (**a**), CH(CH$_3$)CH(CH$_3$) (**b**), (CH$_2$)$_3$ (**c**), CH(CH$_3$)(CH$_2$)$_2$ (**d**), (CH$_2$)$_4$ (**e**), CH(CH$_3$)(CH$_2$)$_2$CH(CH$_3$) (**f**), (CH$_2$)$_7$ (**g**).

* For communication XII see [1].

Table 1. Vinylation of diols **Id–Ig** in the presence of CsF–NaOH at enhanced acetylene pressure[a]

Run no.	Diol, mol	CsF/NaOH, mol%	Temperature, °C	Time, h	Diol conversion, %	Yield of products, %	
						II	**III**
1	**Ie**, 0.2	5/5	136–138	3.0	85	32	30
2	**Ie**, 0.4	7/7	138–140	2.0	70	48	10
3	**Ie**, 0.2	7/7	138–140	3.0	100	47	33
4	**Ie**, 0.2	7/7	155–158	2.0	100	3	76
5	**Ie**, 0.2	10/10	137–150	1.5	98	12	52
6	**Ie**, 0.2	7[b]	150–158	3.0	98	16	58
7	**If**, 0.2	7/7	150–158	2.0	100	22	47
8	**If**, 0.2	10/10	140–142	3.0	99	13	55
9	**If**, 0.3	7/7	135–140	3.0	100	56	19
10	**Ig**, 0.2	7/7	150–158	1.0	100	0	85

[a] Initial pressure of acetylene 10–12 at, reactor of 1 liter capacity. [b] KOH was used as catalyst.

Table 2. Vinylation of 1,2- and 1,3-diols **Ia–Id** in the presence of CsF–NaOH at enhanced acetylene pressure[a]

Run no.	Diol, mol	CsF/NaOH, mol%	Temperature, °C	Time, h	Diol conversion, %	Yield of products, %		
						II	**III**	**IV**
1	**Ia**, 0.4	5/5	138–142	3.5	52	26	11	4
2	**Ia**, 0.4	10/10	138–142	5.0	60	24	15	8
3	**Ia**, 0.6	5/5	138–142	5.0	44	25	5	5
4	**Ib**, 0.2	7/7	138–142	3.0	90	8	6	49
5	**Ic**, 0.2	7/7	150–160	3.0	95	12	55	1
6	**Ic**, 0.4	7/7	140–150	3.0	60	35	10	4
7	**Id**, 0.2	7/7	150–160	3.0	100	38	25	5
8	**Id**, 0.2	10/10	140–150	2.0	100	31	34	6
9	**Id**, 0.3	5/5	138–142	3.0	100	59	15	3
10	**Id**, 0.2	3/3	139–141	3.0	74	52	4	1
11	**Id**, 0.2	5[b]	138–143	3.0	82	52	7	6

[a] Initial pressure of acetylene 14 at, reactor of 1 liter capacity. [b] KOH was used as catalyst.

Table 1), i.e. at the reaction acceleration the possibility of its control decreases.

In vinylation of 1,4-butanediol (**Ie**) the potassium hydroxide proved to be under comparable conditions a weaker catalyst than the system CsF–NaOH: With the latter catalyst the complete conversion of diol **Ie** was reached 1.5 times faster, and the yield of 1,4-butandiol divinyl ether **IIIe** was 76% against 58% (Table 1, cf. runs nos. *4* and *6*). The lower catalytic activity of the potassium hydroxide than that of the system CsF–NaOH is also obvious from comparison of the rates of acetylene consumption in the course of 1,4-butanediol vinylation in the presence of these catalysts (Fig. 1).

For diols with a linear structure (**Ic, Ie,** and **Ig**) a certain trend was observed in increase of the rate and efficiency of the reaction under study with growing length of the carbon chain between the hydroxy groups. For instance, in going from 1,3-propanediol (**Ic**) to 1,4-butane-diol (**Ie**) and further to 1,7-heptanediol (**Ig**) the period of reaction sufficient for complete vinylation (150–160°C, CsF–NaOH concentration of 7 mol% of each component, molar excess of acetylene with respect to diol) decreased respectively 2 and 3-fold (Table 2, run no. *5*; Table 1, run no. *4*, *10*); therewith the yield of divinyl ethers **IIIc**, **IIIe**, and **IIIg** was equal to 55, 76, and 85% respectively.

The vinylation of the secondary hydroxy group is known [2, 8] to occur more difficultly than the primary one. Actually under optimum conditions for the synthesis of 1,4-butanediol divinyl ether **IIIe** (150–158°C, 2 h, 7/7 mol% CsF–NaOH) the yield of 2,5-divinyloxy-hexane (**IIIf**) was lower and attained 47% at the overall yield of ethers **IIf** and **IIIf** 69% (Table 1, cf. runs nos. *4* and *7*)

but the conversion of 2,5-hexanediol (**If**) was complete. Diol **If** and its monovinyl ether **IIf** were presumably consumed in side reactions of Dumas–Stass type [17]. The increased to 10 mol% catalyst concentration favored divinyl ether **IIIf** formation (Table 1, run no. *8*), and the use of excess 2,5-hexanediol (**If**) with respect to acetylene and carrying out the vinylation reaction at a moderate temperature (below 140°C) facilitated prevailing preparation of monovinyl ether **IIf** (Table 1, run no. *9*).

A well known feature of the base-catalyzed vinylation of 1,2- and 1,3-diols is a side process consisting in cyclization of their vinyl monoethers into the corresponding cyclic acetals (1,3-dioxacyclanes) [2, 8, 9, 13]. The use of the catalytic system CsF–NaOH instead of potassium hydroxide does not prevent this cyclization (Table 2). Moreover, cyclic acetal **IVb** is the main product from 2,3-butanediol **IIb** (Table 2, run no. *4*).

$$CH_2=CHOCHR(CH_2)_nCHR'OH \longrightarrow$$

IIa–IId   **IVa–IVd**
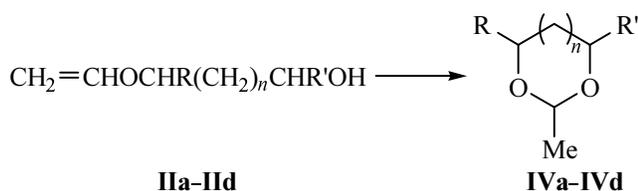
$n = 0$, $R = R' = H$ (**a**), $R = R' = CH_3$ (**b**); $n = 1$, $R = R' = H$ (**c**), $R = H$, $R' = CH_3$ (**d**).

The relative amount of arising cyclic acetals, mono-, and divinyl ethers depends on the ratio diol:acetylene: catalyst, on the temperatire and time of reaction. For instance, acetylene deficit (Table 2, runs nos. *1–3*, *6*) results in incomplete diol conversion and to predominant formation of the monovinyl ethers, the raising of the temperature and increased catalyst concentration, as we have shown previously [13], accelerates both the vinylation and acetalization of monovinyl ethers and favors the formation of divinyl ethers and cyclic acetals even at the acetylene deficit (Table 2, runs nos. *2, 5, 7, 8*).

The comparison with KOH (Table 2, runs nos. *9* and *11*) demonstrated the higher activity of the catalytic couple CsF–NaOH in vinylation of 1,2- and 1,3-diols, but the selectivity of the process still remained insufficient. The prevalence of one among the ethers like was attained at vinylation, for instance, of 1,4-butanediol (**Ie**) (Table 1, run no. *4*) or 1,7-heptanediol (**Ig**) (Table 1, run no. *10*) we failed to achieve.

Attention should also be drawn to the fact, that ethanediol vinylation stopped with retention of some excessive pressure in the reactor even when the initial acetylene amount was insufficient for the exhaustive
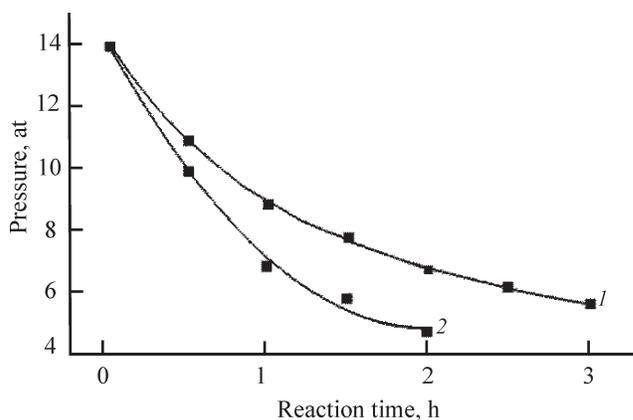
Fig. 1. Change of acetylene pressure in the course of 1,4-butanediol (**Ie**) vinylation: *1,* in the presence of KOH, 7 mol%, *2,* in the presence of CsF–NaOH, 7/7 mol% (reaction temperature 150–158°C).

vinylation of the diol (Table 2, runs nos. *1–3*). The assumption that the catalytic system totally deactivated was not confirmed since the adding of acetylene into the reaction mixture cooled to room temperature resulted in reanimation of the reaction with a faire rate at the repeated heating of the reactor. Presumably, in the strongly basic medium generated by CsOH where crown-like complexes besides may form with the ethylene-oxide diol **Ia** moieties elimination of vinyl alcohol occurs from ethanediol divinyl ether **IIIa** [6, 7, 12]. The arising volatile divinyl ether conserves the pressure in the reactor. Apart from the divinyl ether a hydrogen liberation may occur along the Dumas–Stass reaction [17] and by the known process of acetylene consumption affording acetates [18–20]. However it should be mentioned that inasmuch as both latter processes require alkali consumption, the repeated start of diol **Ia** vinylation at the supply of the fresh acetylene portion and insignificant decrease in the vinylation rate indicate that the alkali consumption was small in this case, and consequently, these processes do not notably affect ethanediol (**Ia**) vinylation.

Hence all the features of ethanediol (**Ia**) vinylation under acetylene pressure in the presence of potassium hydroxide described in the literature [2, 6–9] and previously observed in our studies [11–13] were also revealed at catalysis of the reaction by the system CsF–NaOH; the use of the system did not permit us any significant refinement of the process characteristics.

We showed formerly that vinylation of diols in a superbasic catalytic system KOH–DMSO occurred under atmospheric pressure of acetylene and at relatively mild temperature conditions, and therewith the system KOH–DMSO selectively catalyzed the synthesis of divinyl ethers
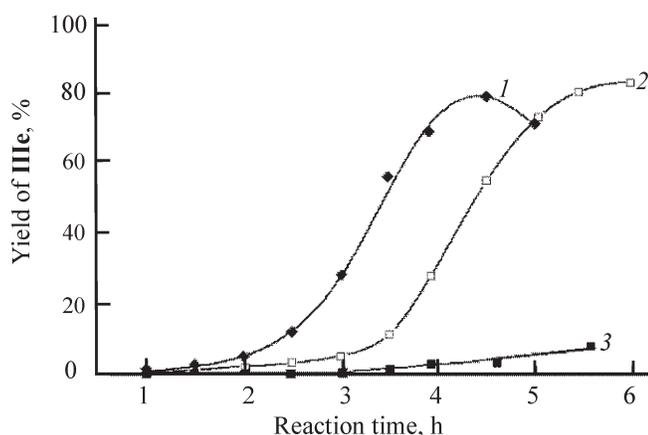
Fig. 2. Vinylation of 1,4-butanediol (**Ie**) at atmospheric pressure of acetylene in the presence of a superbasic system CsF–NaOH–DMSO. (*1*) CsF–NaOH 30/30 mol%; (*2*) CsF–NaOH 20/20 mol%; (*3*), CsF–NaOH 10/10 mol%.

[16]. On the other hand, the vinylation of 1-heptanol effected by CsOH·H$_2$O also was considerably faster in DMSO than in the absence of solvent [21]. It was of interest to study the effect on diol vinylation of a new catalytic system CsF–NaOH–DMSO. This was especially important for 1,2- and 1,3-diols whose vinylation as was shown above did not afford satisfactory yields of divinyl ethers in the absence of DMSO.

The optimization of the reaction conditions was performed as before by an example of 1,4-butanediol (**Ie**) whose vinylation in the presence of basic catalysts occurred more smoothly than with 1,2- and 1,3-diols.

It turned out that the vinylation of diols in the superbasic system CsF–NaOH–DMSO occurred less efficiently than the vinylation of monohydric alcohols [1]. Thus, in the presence of catalyst CsF–NaOH (10 mol% each, corresponding to the concentration of 5/5 mol% to every hydroxy group) in the reaction mixture after heating to 100°C for 5–6 h was identified alongside initial 1,4-butanediol (**Ie**) predominantly monovinyl ether (yield 30%), and the yield of divinyl ether **IIIe** was no more than 10% (Table 3, run no. *8*; Fig. 2, curve *3*). Under comparable conditions [1] the yield of vinyl heptyl ether obtained by vinylation of 1-heptanol was 87%.

On increasing the concentration of the catalyst CsF–NaOH to 20/20 mol% the rate of 1,4-butanediol (**Ie**) reaction with acetylene in DMSO (100°C) sharply increased, and in 5.5 h the yield of divinyl ether **IIIe** reached 86% (Table 3, run no. *9*; Fig. 2, curve *2*). However further concentration increase is not feasible under these conditions for the vinylation of 1,4-butanediol (**Ie**) in the presence of 30/30 mol% of catalytic couple CsF–NaOH resulted already within 4.5 h not only in complete conversion of the initial diol and its monovinyl ether **IIe**, but also in decrease in the yield of the corresponding divinyl ether **IIIe** to 70% (Table 3, run no. *10*; Fig. 2, curve *1*). Apparently in the presence of large amounts of the basic catalyst the side processes occurring alongside the diol vinylation are also accelerated, for instance, the formation of carboxylic acids salts [11, 15, 21] or vinyl alcohol cleavage from the arising vinyl ethers **IIe** and **IIIe** [12] etc.

Table 3. Vinylation of diols **Ia, Ic–Ie,** and **Ig** in the presence of CsF–NaOH–DMSO at atmospheric acetylene pressure[a]

Run no.	Diol	CsF/NaOH, mol%	Time, h	Diol conversion, %	Yield of products, %	
					II	**III**
1	**Ia**	10/10	6.0	84	12	15
2	**Ia**	10/10[b]	5.5	74	11	1
3	**Ia**	20/20	6.0	80	16	20
4	**Ia**	30/30	6.0	100	12	37
5	**Ia**	40/40	4.5	100	0	31
6	**Ic**	20/20	5.5	100	0	44
7	**Id**	20/20	5.0	100	57	21
8	**Ie**	10/10	5.5	72	30	8
9	**Ie**	20/20	5.5	100	0	86
10	**Ie**	30/30	4.5	100	0	70
11	**Ie**	20[c]	6.0	78	26	10
12	**Ig**	20/20	2.5	100	0	87

[a] 0.05 mol of diol, 50 ml of DMSO, 100°C, rate of acetylene flow ~2 l/h.

[b] Alcoholate obtained by distilling off water was used as catalyst. .

[c] KOH was used as catalyst.

The vinylation of 1,4-butanediol (**Ie**) with acetylene under comparable conditions in the presence of the traditional superbasic system KOH (20 mol%)–DMSO or of the new catalytic system CsF–NaOH (20/20 mol%)–DMSO (Table 3, runs nos. *11* and *9* respectively) demonstrate the advantages of the latter: the yield of divinyl ether **IIIe** was in the first case 10%, in the second 86%. We succeeded to prepare divinyl ether **IIIe** in a 86% yield in the system KOH–DMSO only at the use at equimolar amount of KOH [i.e., in the presence of 100 mol% KOH with respect to 1,4-butanediol (**Ie**)] [16].

The conditions we found for selective and efficient synthesis of divinyl ether **IIIe** from 1,4-butanediol (**Ie**) and acetylene in the system CsF–NaOH–DMSO (Table 3, run no. *9*) proved to be plausible also for the exhaustive vinylation of 1,7-heptane-diol (**Ig**) (Table 3, run no. *12*) confirming the general character of the reaction, at least for diols with a normal backbone and no less than four CH$_2$ groups in the molecule. At heating (100°C, 2.5 h) 1,7-heptanediol (**Ig**) in the system CsF (20 mol%)–NaOH (20 mol%)–DMSO in an acetylene flow 1,7-divinyloxyheptane (**IIIg**) was obtained in a 87% yield at the complete conversion of the initial diol.

In the system KOH–DMSO a similar result was obtained applying 100 mol% of KOH with respect to initial 1,7-heptanediol (**Ig**) [16].

Inasmuch as the secondary alcohols add to acetylene slower than primary [2, 8] it was presumable that under comparable conditions the yield of the divinyl ether from 1,3-butanediol **IIId** would be lower than the yield of the divinyl ether from 1,4-butanediol **IIIe**. The vinylation at 100°C within 5 h of 1,3-butanediol (**Id**) in the system CsF (20 mol%)–NaOH (20 mol%)–DMSO actually afforded divinyl ether **IIId** in a low yield (21%), and in the reaction mixture was present a significant amount of monovinyl ether **IId** (yield 57%) (Table 3, run no. *7*). But 2,4-dimethyl-1,3-dioxane (**IVd**) was virtually lacking in the product, meaning that no cyclization of the monovinyl ether occurred that commonly accompanied the vinylation of 1,2- and 1,3-diols. Taking into account that the yield of divinyl ether from 1,3-butanediol **IIId** in vinylation effected by the system KOH–DMSO at the use of equimolar amount of KOH attained 60% [16] and that according to our data [13] the cyclization of monovinyl ethers was also catalyzed by alkali, apparently, the applied amount of the alkaline catalyst, namely, 20/20 mol% of the system CsF–NaOH, was insufficient for an efficient catalysis of competing reactions of vinylation

and cyclization of 1,3-butanediol monovinyl ether **IId**.

The reaction of ethanediol (**Ia**) with acetylene under atmospheric pressure in the system CsF–NaOH–DMSO with the use of the catalytic reagents in amounts from 10/10 to 40/40 mol% gave rise to formation of mono-**IIa** and divinyl **IIIa** ethers in an overall yield not exceeding 49% (Table 3, runs nos. *1–5*), although the initial diol **Ia** conversion was 74–100%.

The most probable side processes in vinylation of ethanediol (**Ia**) are apparently the Dumas–Stass reaction and the base-catalyzed elimination of the vinyl alcohol from the arising vinyl ethers **IIa** and **IIIa** [12], since we have not observed formation in a significant amount of dioxolane **IVa** (may be due to a stringent mode of the GLC analysis of the reaction mixtures caused by the presence of DMSO and hampering a reliable identification of volatile impurities).

It should be especially mentioned that although the ethanediol (**Ia**) vinylation took a long time (4.5–6 h) monovinyl ether **IIa** remained in the reaction mixture, and the complete conversion of initial diol **Ia** reached 100% only at the use of large amount of the catalyst (30/30 and more mol% of CsF–NaOH). Obviously the catalyst is consumed in the side processes, first of all, in the formation of carboxylic acids salts by Dumas–Stass reaction. Surprisingly this process of a general character [15, 21] was the most apparent in the vinylation of 1,2- and 1,3-diols presumably due to the formation of crown-like complexes of alkali metal cations both with the initial diols and their vinylation products.

Thus the new catalytic systems CsF–NaOH and CsF–NaOH–DMSO are more efficient than the traditional catalysts KOH and KOH–DMSO in the vinylation of alkanediols with a long chain, but are second to the latter in vinylation of 1,2- and 1,3-diols due to the high activity in catalyzing side processes.

EXPERIMENTAL

IR spectra of compounds synthesized were recorded from thin films on a spectrometer Bruker JFS-25 in the region 400–4000 cm^{-1}. ^{1}H NMR spectra were registered at room temperature on spectrometer Bruker DPX-400 at operating frequency 400.13 MHz, solvent CDCl$_3$, internal reference HMDS. The reaction mixtures were analyzed by GLC on LKhM-80 instrument equipped with a katharometer, column 3000×3 mm, stationary phase poly(ethylene glycol) 20000, 1% on NaCl, carrier gas helium.

The diols 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 diols at enhanced acetylene pressure. Into a rotating steel reactor of 1 liter capacity was charged 0.2–0.6 mols of diol **Ia–Ig**, NaOH and CsF in amounts indicated in Tables 1 and 2 (0.006–0.04 mol of each component), 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 1–5 h as indicated in Tables 1 and 2. The reaction products were distilled at atmospheric or reduced pressure depending on the boiling point of the monovinyl and divinyl ethers and were analyzed by GLC. Diol conversions and vinyl ethers yields are given in Tables 1 and 2, the physical constants and spectral characteristics of compounds obtained are consistent with those published in [2, 8, 9, 16].

General procedure for vinylation of diols at atmospheric pressure of acetylene. Into a reaction flask of 100 ml capacity, equipped with an efficient reflux condenser, thermometer, magnetic stirrer, and a bubbler for supplying acetylene was charged 0.05 mol of diol **I**, NaOH and CsF in amounts indicated in Table 3 (0.005–0.02 mol of each component), and 50 ml of DMSO, the content of the flask was heated to 100°C, and acetylene was passed through the mixture at a rate of 2 liter per hour. The process was monitored by GLC. The vinilation reaction time is given in Table 3. From the mixture obtained the reaction products were extracted with petroleum ether (4×50 ml), the extract was washed with water (3×20–30 ml), and dried with calcined potassium carbonate. On removing the petroleum ether the residue was distilled. Diol conversions and vinyl ethers yields are given in Table 3.

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