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Dedicated to Academician M.G.Voronkov on occasion of his 80th birthday

Functional Methacryloyoxy Acetals: II. Electophilic Addition of Alcohols to Vinyloxyalkyl Methacrylates

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Abstract—Alcohols of various structures, in particular, ethylene, acetylene, fluorocontaining alcohols, add regio- and chemoselectively to the vinyloxy group of vinyloxyalkyl methacrylates at 20–40°C in the presence of catalytic quantities of trifluoroacetic acid affording functional acetalmethacrylates in high yield.

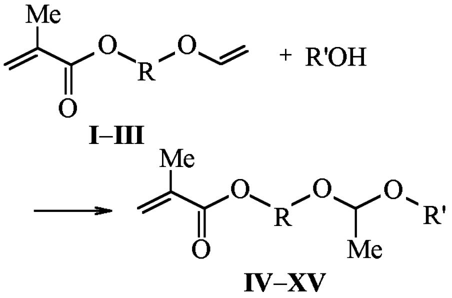
Vinyloxyalkyl methacrylates are highly active bifunctional monomers containing a reactive (“anchor”) vinyloxy group that can easily undergo addition to various hydroxy, thiol, and carboxy functions. Yet this approach to methacrylates synthesis is not developed up till now although the electrophilic addition of alcohols to the other vinyl ethers is studied intensively [2–13]. As a rule the vinyl ethers in the presence of acidic catalysts readily take up alcohols to furnish the corresponding acetals in high yield [5–10]. It should be noted that acids can also catalyze the nucleophilic addition of alcohols to the double bond of methacrylates (due to electrophilic assistance through the carboxy group) [14]. Therefore the possible result of the reaction between vinyloxyalkyl methacrylates with alcohols is not unambiguous.

We report here for the first time on results of research on the reaction between vinyloxyalkyl methacrylates with alcohols aimed at the synthesis of new polyfunctional methacrylates, promising synthons and monomers for preparation of new types of methacrylate polymers.

We found conditions of the reaction providing regio- and chemoselective addition of alcohols with different structures (alkanols, 2,2,3,3,-tetrafluoropropan-1-ol, 2-propen-1-ol, 3-butyn-1-ol, 2-methoxyethanol) to vinyloxyalkyl methacrylates only across the vinyloxy group furnishing the products **IV–XV** in high yield (Scheme 1).

The reaction occurs under mild conditions (20–40°C, 0.5–2 h, under argon) at stirring equivalent amounts of reagents under catalysis with trifluoroacetic acid (1–2 wt%).

Scheme 1.



R = $(CH_2)_2$ (**I, IV**–**XII**), $(CH_2)_2O(CH_2)_2$ (**II, XIII**), $CH(Me)(CH_2)_2$ (**III, XIV, XV**); R' = Me (**IV, XIII**), Et (**V, XIV**), *i*-Pr (**VII**), *t*-Bu (**VIII, XV**), $CHF_2CF_2CH_2$ (**IX**), $CH_2{=}CHCH_2$ (**X**), $CH{\equiv}C(CH_2)_2$ (**XI**), $MeO(CH_2)_2$ (**XII**).

The addition is accompanied with slight heat evolution (2–7°C with vinyl ethers **I** and **III** and 15–20°C with ether **II**). The reaction progress was monitored by IR and ^{1}H NMR spectroscopy. In the course of reaction gradually disappear the characteristic absorption bands of the vinyloxy group (830–850, 963–965, 1205, 1367, 1620, 3060 cm^{-1}) and the hydroxy group (3375 cm^{-1}) and changes the set of bands in the absorption region of C–O–C–moiety (1050–1205 cm^{-1}). At the same time the absorption bands corresponding to stretching vibrations of the fragments in the methacrylate moiety C=C–C=O (1640, 1720 cm^{-1}) and CH_2= (3100 cm^{-1}) remain unchanged. In the ^{1}H NMR

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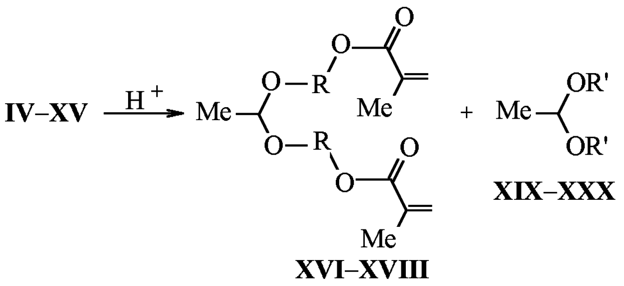
[*] For communication I see [1].

Scheme 2.



spectra (δ, ppm) of the reaction mixtures was observed only one signal from methine proton (4.6–4.9 q) and one signal of a methyl group (~1.3 d) belonging to the acetal fragment evidencing that (1-organylethoxy)alkyl methacrylates **IV**–**XV** were the only reaction products and that they formed in virtually quantitative yield.

The complete conversion of 2-vinyloxyethyl methacrylate (**I**) in reactions with ethanol, 2-propanol, and *tert*-butanol into the corresponding acetals **V, VI, VIII** is attained within 2 h at 20°C whereas with stronger OH-acids (2,2,3,3-tetrafluoropropan-1-ol, 3-butyn-1-ol, 2-propen-1-ol, methanol, 2-methoxyethanol) [15] the reaction completes already in 1–1.5 h. The rate of the reaction studied was also affected by the structure of the initial methacrylates **I**–**III**; the most active among them turned out to be 2-[(2-vinyloxy)ethoxy]ethyl methacrylate (**II**).

It was confirmed that the trifluoroacetic acid is a specific, highly selective and mild catalyst of alcohols addition to the vinyloxy group [6, 7]. The replacement of this acid by a dioxane solution of dry HCl in reaction of vinyl ether **I** with methanol resulted in nearly twice faster process (1 wt% of catalyst, 20°C, 0.5 h) but the target actalmethacrylate **IV** suffered disproportionation into acetaldehyde bis(2-methacryloylethyl) acetal (**XVI**) and acetaldehyde dimethylacetal (**XIX**): in the ^{1}H NMR spectrum appeared three quartets of methine protons at 4.85, 4.68, and 4.58 ppm.

The regio and chemoselectivity of the reactions are not hampered even by the use of excess alcohol with respect to vinyloxyalkyl methacrylate: In the latter case still do not form adducts at the double bond of the methacrylate group. Yet the mixing of 2-vinyloxyethyl methacrylate (**I**) with a double excess of methanol afforded alongside the expected acetalmethacrylate **IV** also the corresponding symmetrical acetaldehyde bis(2-methacryloylethyl) acetal (**XVI**) and acetaldehyde dimethylacetal (**XIX**). The overall yield of acetals **IV, XVI**, and **XIX** is virtually quantitative, and their ratio is respectively 2.9 : 1.4 : 1.0.

The acetals **IV**–**XV** obtained also undergo disproportionation on storage in the presence of acid providing the corresponding symmetrical acetals **XVI**–**XVIII** and **XIX**–**XXX** (Scheme 2).

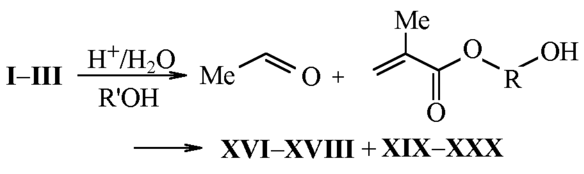
To avoid this process the acid catalyst should be neutralized just after the completion of the reaction between the alcohol and the vinyloxyalkyl methacrylate.

The disproportionation of acetalmethacrylates **IV**–**XV** occurs not only under the action of acids but also at heating (100–160°C) during the fractional distillation in a vacuum. Therefore the GLC analysis of the reaction mixtures is not reliable since in the vaporizer (250–300°C) the acetals synthesized suffer deep transformation, not only disproportionation, but also pyrolysis to the initial compounds as show the GLC and ^{1}H NMR data.

Yet such probable side processes as polymerization of the initial vinyl ethers **I**–**III** or their reaction with the forming acetals **IV**–**XV** usually catalyzed by acids [2–4] were not observed in the study of the reaction in question.

The reaction of vinyloxyalkyl methacrylates with alcohols (Scheme 1) is sensitive to moisture that hydrolyses the original vinyl ethers **I**–**III**. The following reaction of the acetaldehyde formed both with the initial and arising from the hydrolysis alcohol furnishes symmetrical acetals **XVI**–**XXX** (Scheme 3) appearing in the ^{1}H NMR spectrum as a triple set of the proton signals from the acetal fragments. Thus the hydrolysis is another reason (besides the symmetrization) of formation of acetals mixture in the course of the reaction under study.

Scheme 3.



The stability of the acetals obtained to the disproportionation depends also on the structure of the alcohol radical R'. Thus in the presence of acids and at heating the acetals with electronegative groups R'O **IX**–**XI** are less prone to disproportionation and pyrolysis than alkoxyacetals **IV**–**VIII, XII**–**XV**; therefore the former are prepared in better preparative

Table 1. Yields and characteristics of methacrylates **IV**–**XV**

Compd. no.	Yield,[a] %	bp, °C (*p*, mm Hg)	n_D^{20}	Found, %		Formula	Calculated, %	
				C	H		C	H
IV	78	50 (2)	1.4342	57.55	8.62	$C_9H_{16}O_4$	57.43	8.57
V	83	53 (2)	1.4308	59.62	9.12	$C_{10}H_{18}O_4$	59.39	8.97
VI	68	65 (3)	1.4328	61.16	9.60	$C_{11}H_{20}O_4$	61.09	9.32
VII	88	67 (2)	1.4398	62.76	9.80	$C_{12}H_{22}O_4$	62.58	9.63
VIII	78	76 (3)	1.4350	62.71	9.67	$C_{12}H_{22}O_4$	62.58	9.63
IX[b]	85	81 (2)	1.4058	45.92	5.24	$C_{11}H_{16}F_4O_4$	45.83	5.59
X	88	87 (2)	1.4444	61.48	8.50	$C_{11}H_{18}O_4$	61.66	8.46
XI	87	76 (2)	1.4566	63.72	8.11	$C_{12}H_{18}O_4$	63.69	8.02
XII	65	97 (2)	1.4398	56.69	8.43	$C_{11}H_{20}O_5$	56.88	8.67
XIII	70	85 (2)	1.4424	56.94	8.55	$C_{11}H_{20}O_5$	56.88	8.67
XIV	70	85 (2)	1.4360	62.78	9.76	$C_{12}H_{22}O_4$	62.58	9.63
XV	66	88 (2)	1.4358	65.06	10.18	$C_{14}H_{26}O_4$	65.08	10.14

[a] Preparative yields are given. [b] Found, %: F 26.32. Calculated, %: F 26.36.

Table 2. Spectral characteristics of methacrylates **IV**–**XV**

Compd. no.	IR spectrum (cm^{-1})
IV	517, 537, 604, 654, 816, 866, 940, 994, 1041, 1059, 1089, 1120, 1136, 1170, 1244, 1297, 1320, 1388, 1454, 1638, 1721, 2830, 2930, 2955, 2989, 3106
V	530, 603, 654, 816, 858, 948, 960, 1007, 1061, 1084, 1101, 1137, 1170, 1244, 1297, 1320, 1340, 1382, 1402, 1453, 1638, 1721, 2882, 2931, 2978, 3106
VI	534, 603, 654, 816, 848, 886, 937, 985, 1007, 1054, 1085, 1135, 1168, 1244, 1297, 1321, 1381, 1454, 1638, 1721, 2876, 2932, 2974, 3106
VII	519, 603, 655, 739, 760, 815, 853, 878, 937, 1007, 1044, 1078, 1096, 1112, 1138,1169, 1248. 1297, 1320, 1341, 1382, 1404, 1455, 1638, 1721, 2874, 2934, 2959, 2987, 3105
VIII	517, 556, 602, 654, 749, 816, 859, 875, 940, 975, 1009, 1056, 1091, 1126, 1170, 1196, 1239, 1260, 1297, 1320, 1366, 1382, 1455, 1638, 1721, 2876, 2934, 2978, 3105
IX	546, 578, 655, 692, 816, 835, 880, 941, 1010, 1044, 1106, 1145, 1169, 1233, 1298, 1321, 1387, 1455, 1638, 1721, 2891, 2955, 2992, 3115
X	518, 602, 655, 815, 881, 938, 990, 1039, 1099, 1137, 1169, 1247, 1297, 1320, 1339, 1388, 1454, 1638, 1721, 2881, 2929, 2957, 2989, 3082, 3102
XI	651, 815, 878, 943, 1003, 1042, 1078, 1101, 1138, 1170, 1246, 1298, 1320, 1384, 1402, 1454, 1637, 1719, 2121, 2884, 2928, 2989, 3107, 3292
XII	655, 815, 856, 944, 991, 1043, 1076, 1103, 1140, 1170, 1249, 1297, 1320, 1340, 1387, 1454, 1638, 1720, 2820, 2882, 2932, 2988, 3107
XIII	536, 595, 656, 816, 860, 891, 943, 994, 1046, 1095, 1135, 1170, 1249, 1297, 1320, 1342, 1387, 1402, 1453, 1638, 1720, 2830, 2882, 2933, 2988, 3107
XIV	657, 815, 845, 862, 891, 938, 989, 1010, 1060, 1084, 1135, 1172, 1296, 1321, 1365, 1380, 1452, 1638, 1718, 2889, 2930, 2979, 3107
XV	655, 815, 848, 939, 976, 1009, 1089, 1118, 1172, 1235, 1260, 1296, 1321 1365, 1380, 1452, 1638, 1718, 2879, 2933, 2978, 3107

Table 2. (Contd.)

Compd. no.	^{1}H NMR spectrum (CDCl$_3$), δ, ppm (*J*, Hz)					
	OCHO q (^3J)	Me, d (^3J)	= CH$_2$ (^2J, ^4J)	Me–C= , d.d (^4J)	R (^3J)	R'
IV	4.69 (5.2)	1.30 (5.2)	5.56 d.q (*trans*, 1.5, 1.6), 6.12 m (*cis*)	1.94 (0.8, 1.6)	3.70 m, 3.77 m (each 1H, OCH$_2$), 4.30 t (2H, OCH$_2$, 5.5)	3.30 s (3H, Me)
V	4.75 (5.4)	1.30 (5.4)	5.56 d.q (*trans*, 1.6, 1.6), 6.12 m (*cis*)	1.94 (0.8, 1.6)	3.71 m, 3.78 m (each 1H, OCH$_2$), 4.28 t (2H, OCH$_2$, 5.7)	1.18 t (3H, Me, ^3J 7.1), 3.42 d.q, 3.57 d.q (each 1H, OCH$_2$, ^3J 7.1, ^2J 11.8)
VI	4.81 (5.2)	1.29 (5.2)	5.55 d.q (*trans*, 1.6, 1.6), 6.11 m (*cis*)	1.94 (1.0, 1.6)	3.70 m, 3.75 m (each 1H, OCH$_2$), 4.28 t (2H, OCH$_2$, 5.7)	1.15 two d (each 3H, Me, ^3J 6.2), 3.89 d.q (1H, CH, ^3J 6.2)
VII	4.69 (5.4)	1.28 (5.4)	5.54 d.q (*trans*, 1.5, 1.6), 6.09 m (*cis*)	1.93 (0.9, 1.6)	3.66 m, 3.75 m (each 1H, OCH$_2$), 4.25 t (2H, OCH$_2$, 5.4)	0.91 t (3H, Me, ^3J 7.3), 1.36 m, 1.52 m (each 2H, CH$_2$), 3.38 d.t, 3.55 d.t (each 1H, OCH$_2$, ^3J 6.6, ^2J 9.3)
VIII	4.98 (5.3)	1.28 (5.3)	5.55 d.q (*trans*, 1.6, 1.6), 6.11 m (*cis*)	1.94 (1.0, 1.6)	3.69 t (2H, OCH$_2$, 5.1), 4.27 t (2H, OCH$_2$, 5.8)	1.23 s (9H, Me)
IX	4.86 (5.4)	1.32 (5.4)	5.58 d.q (*trans*, 1.5, 1.6), 6.11 m (*cis*)	1.93 (1.0, 1.6)	3.68 m, 3.80 m (each 1H, OCH$_2$), 4.29 t (2H, OCH$_2$, 5.8)	3.86 m (2H, OCH$_2$), 5.90 t.t (1H, CHF, ^3J 5.1, ^2J 53.2)
X	4.80 (5.2)	1.32 (5.2)	5.55 d.q (*trans*, 1.6, 1.6), 6.11 m (*cis*)	1.94 (0.9, 1.6)	3.71 m, 3.77 m (each 1H, OCH$_2$), 4.28 t (2H, OCH$_2$, 5.6)	4.00 d.d (^3J 5.3, ^2J 12.8), 4.12 d.d (^3J 5.7, ^2J 12.8), (each 1H, OCH$_2$), 3.15 d.d, 3.25 d.d (each 1H, CH$_2$= , ^3J 10.4, ^3J 17.2, ^4J 1.5), 5.88 q.t (1H, CH= , ^3J 10.4, ^3J 17.2)
XI	4.80 (5.4)	1.31 (5.4)	5.56 d.q (*trans*, 1.6, 1.6), 6.12 m (*cis*)	1.94 (0.8, 1.6)	3.59 m, 3.69 m (each 1H, OCH$_2$), 4.28 t (2H, OCH$_2$, 5.6)	1.97 s (1H, CH≡), 2.44 t (2H, CH$_2$, ^3J 6.8), 3.60 t (2H, OCH$_2$, ^3J 6.8)
XII	4.78 (5.2)	1.30 (5.2)	5.54 d.q (*trans*, 1.5, 1.6), 6.09 m (*cis*)	1.93 (1.2, 1.6)	3.67 m, 3.76 m (each 1H, OCH$_2$), 4.26 t (2H, OCH$_2$, 5.8)	3.34 s (3H, Me), 3.46 t (2H, OCH$_2$, ^3J 4.8), 3.55 m, 3.67 m (each 1H, OCH$_2$)
XIII	4.67 (5.2)	1.28 (5.2)	5.55 d.q (*trans*, 1.6, 1.6), 6.11 m (*cis*)	1.93 (1.2, 1.6)	3.58 m, 3.67 m (each 1H, OCH$_2$), 3.65 t, 3.74 t (4H, OCH$_2$, 5.2), 4.29 t (2H, OCH$_2$, 5.1)	3.30 s (3H, Me)
XIV	4.65 (5.4)	1.26 (5.4)	5.52 d.q (*trans*, 1.5, 1.5), 6.07 m (*cis*)	1.92 br.s	1.28 (3H, Me, 6.2), 1.83–1.89 m (2H, CH$_2$), 3.46 m, 3.59 m (each 1H, OCH$_2$), 5.09 m (1H, OCH)	1.17 t (3H, Me, ^3J 7.0), 3.46 m, 3.59 m (each 1H, OCH$_2$)
XV	4.84 (5.3)	1.24 (5.3)	5.48 br.s (*trans*), 6.03 m (*cis*)	1.89 br.s	1.19 (3H, Me, 6.0), 1.76–1.84 m (2H, CH$_2$), 3.44 m, 3.52 m (each 1H, OCH$_2$), 5.04 m (1H, OCH)	1.18 s (9H, Me)

yield (Table 1). Such effect of substituents on the reactivity of acetals was already described before [8].

The synthesized acetalmethacrylates **IV–XV** were isolated from the reaction mixtures after the catalyst neutralization by vacuum distillation in the presence of inhibitors of the radical polymerization (hydroquinone, ionol, argon). At it in the case of acetals **IV–VIII, XII–XV** was observed partial disproportionation resulting in a mixture of the initial asymmetrical and two symmetrical acetals. The expected elimination of alcohols from acetals **IV–XV** to give vinyl ethers **I–III** in no case was observed during the distillation. Acetalmethacrylates **IV–XV** are colorless liquids soluble in most organic solvents, easily polymerizable by radical mechanism. Their constants are given in Table 1, and spectral characteristics in Table 2.

EXPERIMENTAL

IR spectra were recorded on spectrometer Bruker JFS-25 from samples as microfilms. ^{1}H NMR spectra were registered on spectrometer Bruker DPX-400 (400 MHz) in $CDCl_3$, internal reference HMDS.

The alcohols prior to the synthesis were thoroughly dried and distilled, their physical constants were consistent with the published data. Vinyloxyalkyl methacrylates were prepared and purified along procedure [1].

1-Vinyloxy-3-methylpropyl methacrylate (III). From 55 g (0.55 mol) of methyl methacrylate, 12.8 g (0.11 mol) of vinyl monoether of 1,3-butanediole, 0.4 g of sodium, and 0.6 g of hydroquinone was obtained 12.1 g of vinyl ether **III**, yield 60%, bp 57°C (2 mm Hg), n_D^{20} 1.4389. IR spectrum (microfilm, cm^{-1}): 654, 815, 895, 945, 963, 993, 1010, 1059, 1108, 1144, 1175, 1202, 1296, 1322, 1355, 1380, 1452, 1617, 1637, 1719, 2881, 2930, 2979, 3050, 3080, 3118. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 6.39 d.d (1 H, CH=), 4.11 d.d, 3.95 d.d (each 1 H, CH_2=, $^3J_{trans}$ 14.4, $^3J_{cis}$ 6.8, ^2J 2.0 Hz), 6.06 d.q, 5.51 d.q (each 1H, CH_2=, ^2J 1.6, ^4J 0.9, ^4J 1.6 Hz), 1.93 d.d (3 H, Me, ^4J 0.9, ^4J 1.6 Hz), 5.08 m (1 H, OCH), 3.69 t (2H, OCH_2, ^3J 6.4 Hz), 1.96–1.89 m (2H, CH_2), 1.29 d (3H, Me, ^3J ‘6.4 Hz).

2-(1-Methoxyethoxy)ethyl methacrylate (IV). To a mixture of 1.56 g (0.01 mol) of vinyl ether **I** and 0.32 g (0.01 mol) of methanol was added 0,02 g of trifluoroacetic acid (1 wt%). The mixture was stirred for 1 h at 20°C till complete disappearance of vinyl ether **I** (IR spectroscopy). The reaction mixture was neutralized with 5% water solution of $NaHCO_3$, the organic layer was separated, and the water layer was extracted with ethyl ether (5 × 3 ml). The extracts and organic layer were combined, washed with water, dried with Na_2SO_4, the solvent was distilled off, and the residue was subjected to fractional distillation in a vacuum in the presence of hydroquinone (1 wt%). Yield 1.46 g (78%). Methacrylates **V–XV** were obtained in a similar way. The symmetrical acetals **XVI–XVIII** and **XX–XXX** arising in the course of the reaction and during distillation were identified with the help of ^{1}H NMR spectroscopy or by GLC using the comparison with the authentic compounds.

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