

Vinyl Ethers Containing an Isothiocyanato Group: XVII.* Bis-Acetals Containing Isothiocyanato Groups on the Basis of Aromatic Diols

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Abstract—2-Vinyloxyethyl isothiocyanate reacts with aromatic diols: catechol, resorcinol, hydroquinone, 2,3-dihydroxynaphthalene, and 2,2-bis(*p*-hydroxyphenyl)propane, in the presence of 0.25–0.5 wt % of trifluoroacetic acid (55–80°C, 0.5–2 h) to give bis-acetals containing isothiocyanato groups in quantitative yield.

Prior to our studies [2–9] there were no published data on reactions of hydroxy compounds with vinyl-oxyalkyl isothiocyanates, for such vinyl ethers were previously unknown. The first compound of this series, 2-(vinyloxy)ethyl isothiocyanate (**I**) was described by us in [10]. It combines typical properties of both vinyl ethers and isothiocyanates, which opens the way to functionalization of various compounds, including alcohols, thiols, carboxylic acids, and amines, via selective addition to one of the two reaction center, vinyloxy or isothiocyanato group [11, 12]. As a result, new families of not only vinyl ethers and isothiocyanates, but also heterocyclic structures (such as pyrroles and dihydropyridines) became available through a simple and effective procedure [13–15].

We showed previously [2, 3], that 2-(vinyloxy)-ethyl isothiocyanate takes up alcohols and phenols under fairly mild conditions: in the presence of 0.2–0.5 wt % of trifluoroacetic acid, heptafluorobutyric acid, or *p*-toluenesulfonic acid as catalyst at 40–70°C (1–2 h). The reaction occurs regioselectively at the vinyloxy group and yields 35 to 100% of hitherto unknown acetaldehyde 2-isothiocyanatoethyl acetals. As a rule, the acetals derived from lower alkanols (such as metanol, 1-propanol, 1-butanol, etc.), undergo alcoholysis during the process to give undesirable dialkyl acetals and 1,3-oxazolidine-2-thione (which is formed by intramolecular cyclization of 2-hydroxyethyl isothiocyanate [16] released in the alcoholysis

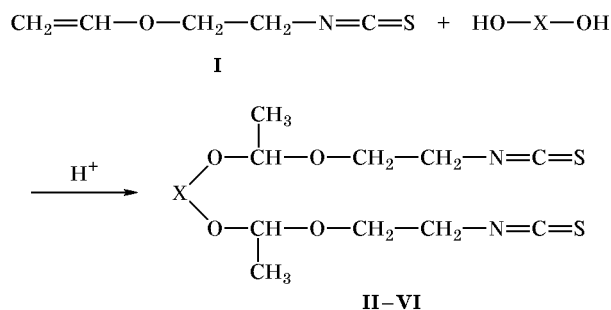
of the acetals). As a result, the yield of the target mixed acetals is reduced. To suppress the alcoholysis, it is advisable to use excess of ether **I** or to slowly add (dropwise) the alcohol to ether **I** containing an acid catalyst. In this case, mixed acetaldehyde 2-isothiocyanatoethyl acetals are preferentially formed. An analogous effect is observed in the presence of *p*-toluenesulfonic acid [3] which is stronger than perfluorocarboxylic acids.

Unlike alkanols, addition to ether **I** of more acidic polyfluorinated alcohols ($pK_a \sim 12\text{--}13$) [4], as well as of 2-propyn-1-ol and phenol (pK_a 13.6 and 9.95, respectively) [2, 3] is not accompanied by undesirable side reactions, and the corresponding mixed acetals are formed in almost quantitative yield. These data led us to expect that reactions of 2-vinyloxyethyl isothiocyanate with aromatic di- and polyols will provide a simple route to new promising di- and polyisothiocyanates containing acetal moieties. Such products possess wide and diverse potentialities for practical application [17, 18].

In the present work we studied the addition to 2-vinyloxyethyl isothiocyanate (**I**) of aromatic diols: catechol, resorcinol, hydroquinone, 2,3-dihydroxynaphthalene, and 2,2-bis(*p*-hydroxyphenyl)propane with the goal of obtaining a new series of polyfunctional acetals containing isothiocyanato groups. These compounds are promising as cross-linking agents, modifiers for polymeric materials, and starting compounds for organic synthesis and preparation of non-trivial products.

* For communication XVI, see [1].

Scheme 1.



II, X = *o*-C₆H₄; **III**, X = *m*-C₆H₄; **IV**, X = *p*-C₆H₄; **V**, X = 2,3-C₁₀H₆; **VI**, X = *p*-C₆H₄C(CH₃)₂C₆H₄-*p*.

The progress of reactions was monitored by IR and ¹H NMR spectroscopy. The reaction was assumed to be complete when absorption bands of the hydroxy (3250–3500 cm⁻¹) and vinyloxy groups (810, 1200, 1320, 1600–1620, and 3100 cm⁻¹) disappeared from the IR spectrum of the mixture and bands typical of acetal (1000–1190 cm⁻¹, broad, O–C–O) and CH₃ groups (2960–2990 cm⁻¹) appeared. Bands belonging to functional groups which were not involved in the reaction were retained: 2100–2200 cm⁻¹ (N=C=S); 1460–1500, 1570–1580, 1600, 3040–3050 cm⁻¹ (C₆H₄, C₁₀H₆). When the reaction was complete, the ¹H NMR spectrum of the mixture contained no signals from the vinyloxy group, δ, ppm: 6.45 q (OCH=),

Table 1. Reactions of 2-vinyloxyethyl isothiocyanate (**I**) with aromatic diols HOXOH; molar ratio **I**:HOXOH 2:1, amounts of the reactants 0.01–0.015 mol

Product no.	Amount of CF ₃ CO ₂ H, ^a wt %	Reaction time, h	Temperature, °C
II	0.25	2	55–60
	0.5	1.5	55–60
	0.5	2	70–75
III	0.25	1.5	60–65
	0.5	1	60–65
	0.5	1.5	60–65
IV	0.25	1.5	70–80
	0.5	0.5	70–80
V	0.5 ^b	1	75–80
VI	0.25	1	70–75
	0.5 ^b	0.12	70–75
	0.5 ^b	0.5	60–65
	0.5 ^b	1	70–75

^a The catalyst was added to the reaction mixture stirred at 40°C.

^b The catalyst was added at room temperature.

4.19 d.d (*trans*-CH₂=), 4.00 d.d (*cis*-CH₂=). Instead, signals from the OCH(CH₃)O acetal moiety appeared in the region δ 5.33–5.51 ppm, q (OCHO), and 1.45–1.55 ppm, d (CH₃).

The reaction conditions are summarized in Table 1. In all experiments the yield of the bis-acetal was quantitative (calculated on the initial diol). It is seen that ether **I** quantitatively takes up aromatic diols under the same conditions as those reported for poly-fluoroalkanols [4] and phenol [3]: without a solvent at a stoichiometric reactant ratio in the presence of 0.25–0.5 wt % of trifluoroacetic acid at 55–80°C in 0.5–2 h. The products are previously unknown bis-acetals **II–VI** containing isothiocyanato groups (Scheme 1).

As expected, the addition to ether **I** of aromatic diols, unlike aliphatic alcohols and diols (ethylene glycol) [3], was not accompanied by symmetrization of the resulting mixed acetals via disproportionation or alcoholysis process. No easily identifiable 1,3-oxazolidine-2-thione was detected among the products (it would inevitably be formed as a result of alcoholysis).

Mixed acetals **II–VI** are stable colorless or slightly colored, moderately viscous liquids which are readily soluble in most organic solvents. If the reactants were purified just before use (by distillation or recrystallization) and were taken in strictly stoichiometric amounts, products **II–VI** did not require additional purification, and they can be used immediately in further syntheses as starting compounds, intermediate products, and key building blocks. Their structure is confirmed by the elemental analyses (Table 2) and IR and ¹H NMR spectra (Table 3).

EXPERIMENTAL

The IR spectra were recorded on Specord 75-IR and IFS-25 spectrometers (films). The ¹H NMR spectra were recorded on a Jeol FX90Q instrument (90 MHz) at room temperature using CDCl₃ as solvent and HMDS as internal reference.

2-Vinyloxyethyl isothiocyanate (**I**) was synthesized by the procedure reported in [19]. Aromatic diols were commercial products which were additionally purified by recrystallization.

1,2-Bis[1-(2-isothiocyanatoethoxy)ethoxy]benzene (II). 2-Vinyloxyethyl isothiocyanate (**I**), 0.02 mol, was added to 0.01 mol of catechol, the mixture was heated to ~40°C while stirring, and specified amount of trifluoroacetic acid (Table 1) was added. The mixture was stirred for 1.5–2 h (depending on the amount

Table 2. Refractive indices and elemental analyses of bis-acetals **II–VI**

Compound no.	n_D^{20}	Found, %				Formula	Calculated, %			
		C	H	N	S		C	H	N	S
II	1.5626	52.33	5.42	7.62	17.29	$C_{16}H_{20}N_2O_4S_2$	52.15	5.47	7.60	17.40
III	1.5700	52.38	5.39	7.67	17.42	$C_{16}H_{20}N_2O_4S_2$	52.15	5.47	7.60	17.40
IV	1.5640	52.24	5.37	7.61	16.41	$C_{16}H_{20}N_2O_4S_2$	52.15	5.47	7.60	17.40
V	1.6020	57.62	5.45	6.37	15.15	$C_{20}H_{22}N_2O_4S_2$	57.39	5.30	6.69	15.32
VI	1.5780	61.67	6.73	5.64	13.42	$C_{25}H_{30}N_2O_4S_2$	61.70	6.21	5.76	13.18

Table 3. Spectral parameters of acetals **II–VI**

Compound no.	IR spectrum, ν , cm^{-1}	1H NMR spectrum ($CDCl_3$), δ , ppm			
		OCHO	CH_3	NCH_2 , OCH_2	R
II	730, 800, 860 sh, 900, 1010–1045–1075–1100–1135 sh, 1170, 1230, 1310, 1360, 1410, 1430, 1470, 1570, 2100–2180, 2860, 2925, 2970, 3050	5.37 q	1.49 d	3.80 m, 3.63 m	7.01 m
III	655, 740, 800, 900, 960, 1000–1010–1050–1100–1120–1150, 1235, 1250, 1310, 1350, 1410, 1460, 1570, 2100–2180, 2860, 2930, 2970, 3050	5.44 q	1.50 d	3.85 m, 3.67 m	7.12 m, 6.66 m
IV	620, 810, 900, 980, 1030–1070–1140, 1180, 1260, 1330, 1360, 1420, 1475, 2100–2180, 2865, 2935, 2980, 3040	5.33 q	1.45 d	3.80 m, 3.65 m	6.93 m
V	479, 620, 646, 694, 750, 868, 890, 933, 1046, 1077, 1098, 1135, 1170, 1254, 1345, 1382, 1440, 1476, 1507, 1599, 1628, 2116–2206, 2881, 2937, 2990, 3056	5.50 q	1.56 d	3.59 m	7.40 m, 7.33 m
VI	840, 940, 1000, 1050, 1070, 1130, 1170, 1240, 1290, 1345, 1380, 1445, 1500, 1570, 1600, 2100–2210, 2890, 2945, 2970, 3000, 3050	5.39 q	1.48 d	3.80 m, 3.65 m	1.60 s, 6.99 d.d

of the catalyst) at 55–60°C, the progress of the reaction being monitored by the IR and 1H NMR spectra.

Compounds **III–VI** were synthesized by a similar procedure (for specific conditions, see Table 1).

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