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Reactions of Heterocumulenes with Organometallic Reagents: VII.* Reactions of Carbanions Derived from Alkoxy- and Alkylthioethenes with Isocyanates as a Simple Route to N-Substituted 2-Alkoxy- and 2-(Alkylthio)acrylamides

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Abstract—Metalated alkoxy- and alkylthioethenes readily add to isocyanates, and subsequent hydrolysis or alkylation of the adducts gives N-mono- and N,N-disubstituted 2-alkoxy- and 2-(alkylthio)acrylamides in up to 86% yield. The reactions with propyl and phenyl isocyanates do not stop at the stage of addition of one isocyanate molecule, and further addition leads to formation of linear and cyclic polyamide structures.

The amide moiety is very important in the chemistry of polypeptides, proteins [2, 3], and polyamides and construction, antifriction, and dielectric materials based thereon for both traditional (primarily for replacement of metals) and newest branches of technics (aviation, cosmics, electronics, heliotechnics, fiber optics), as well as for medicine [4–6]. The amide group also attracts considerable interest from the viewpoint of basic research in the field of theoretical and synthetic organic chemistry. Several ways lead to amide group formation [7–9]. In particular, reactions of isocyanates with a number of nucleophiles result in formation of amides [9, 10]. Isocyanates are known to react with carboxylic acids to give mixed anhydrides of the latter and carbamic acid. These anhydrides undergo spontaneous decomposition (with loss of carbon dioxide) to give the corresponding amide [9–11]. Another way to amides from isocyanates includes their reactions with carbanions, but examples of such transformations are relatively few in number [9, 10, 12, 13]. On the other hand, taking into account high reactivity of isocyanates toward nucleophiles [10], accessibility and diversity of CH acids, and easy generation of carbanions therefrom by the action of superbases [12–14], synthetic development of the above approach opens almost unlimited prospects for simple and efficient preparation of amides having various substituents.

The present work combines our persistent interest in the chemistry of vinyl ethers (which was the subject of our systematic studies for several decades [15–17]) and in reactions of unsaturated carbanions with heterocumulenes, systematic investigation of which has been started several years ago [18–21].

We were the first to examine reactions of a series of carbanions, which were generated *in situ* from substituted alkenes (methoxy-, ethoxy-, butoxy-, and ethylthioethenes **Ia**–**Id**) by the action of superbases, with aliphatic and aromatic isocyanates as a simple and convenient route to previously unknown or difficultly accessible *N*-mono- and *N*,*N*-disubstituted acrylamides **II** and **III**. Compounds **II** and **III** attract interest as promising monomers, intermediate products, biologically active substances, and models for physicochemical studies.

The reactions were carried out at –100 to –40°C in a tetrahydrofuran–hexane mixture in the presence of the superbasic reagent BuLi–*t*-BuOK (Lohmann–Schlosser base) [14] as deprotonating agent instead of expensive and pyrophoric *t*-BuLi in pentane (which is

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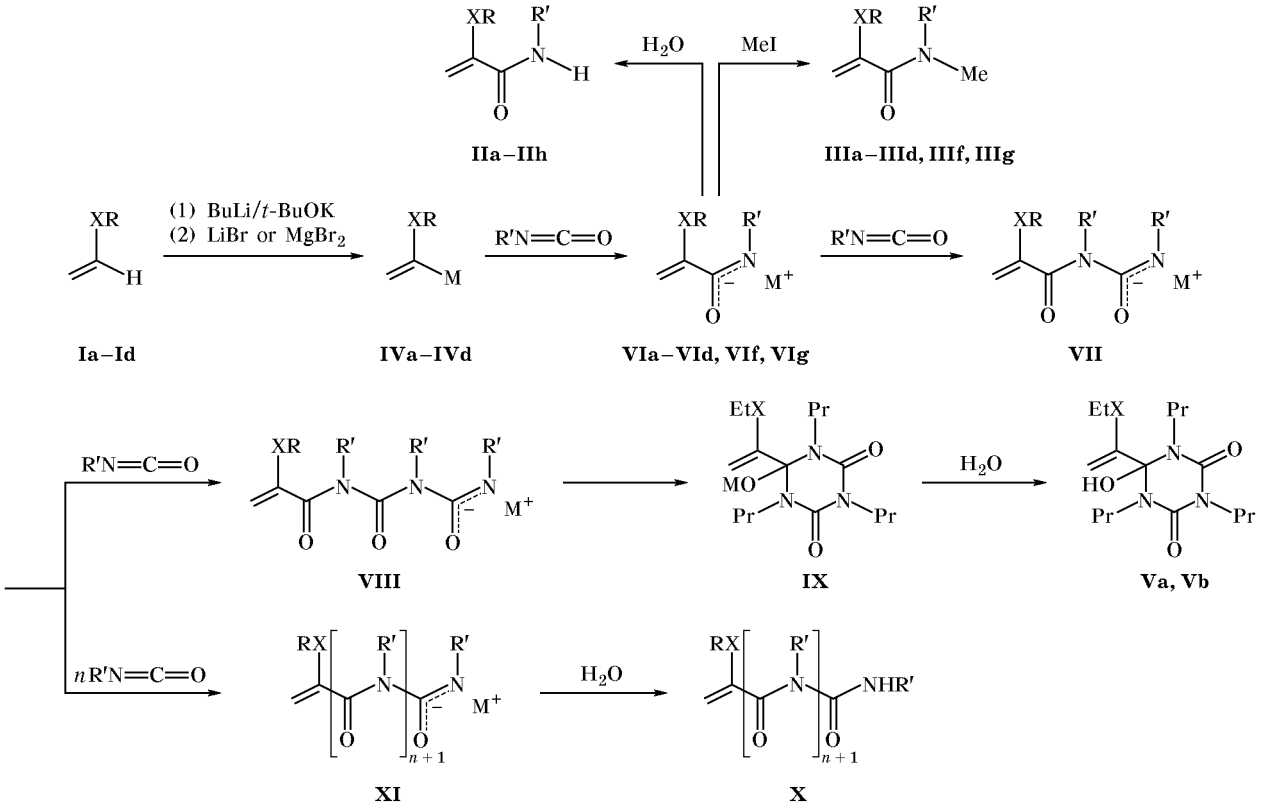
Scheme 1.



M = K, Li, MgBr; **I**, **IV**, X = O, R = Me (**a**), Et (**b**), Bu (**c**); X = S, R = Et (**d**); **II**, **III**, **VI**, X = O, R = Me, R′ = Pr (**a**); R = Et, R′ = Pr (**b**), *i*-Pr (**c**), Ph (**d**); R = Bu, R′ = Pr (**e**); X = S, R = Et, R′ = Pr (**f**), *i*-Pr (**g**), Ph (**h**); **X**, X = O, R = Me, R′ = Pr; R = Et, R′ = Pr, Ph; X = S, R = Et, R′ = Pr, Ph; **V**, X = O (**a**), S (**b**).

commonly used for lithiation of vinyl ethers [22–27]) or *s*-BuLi (which is used for generation of carbanions from vinyl sulfides [24–28]). It is known [13] that, depending on the reaction conditions and alkene structure, butyllithium promotes either formation of adducts at the double bond or cleavage of alkoxy- and alkylthioethenes.

According to our results [13, 29, 30] and published data [22–28], vinyl ethers and vinyl sulfides relatively readily react with appropriate bases to give α-metalated intermediates **IV**. In order to ensure complete consumption of the superbase, ~4–5.5 equiv of alkoxyethene and ~1–1.3 equiv of ethylthioethene were used [13]. The results are summarized in Table 1.

The reaction of propyl isocyanate with carbanion generated from ethylthioethene (**Id**) gave the expected acrylamide **IIf** and hitherto unknown 6-hydroxy-1,3,5-tripropyl-6-(1-ethylthiovinyl)hexahydro-1,3,5-triazine-2,4-dione (**Vb**) (Table 1, run no. 12). The latter is formed as a result of unexpectedly ready reaction of the ambident anion of potassium salt **VIf** with the second isocyanate molecule at –100 to –30°C, followed by addition of intermediate **VII** to the third isocyanate molecule, unusual intramolecular cyclization of **VIII**, and mild hydrolysis of **IX** (Scheme 1).

Unlike analogous reaction with isothiocyanates [29, 30], the process does not stop at the stage of formation of adduct **VI** even at an equimolar ratio of the reactants. In fact, there is a competition between the C- and N-centered nucleophiles **IV** and **VI** for electrophile, i.e., isocyanate molecule. Obviously, anion **VIf** with potassium cation as counterion is more active than the anion of **IVd** or at least their activities are comparable.

Michael addition to substituted olefins of highly nucleophilic anions generated from carboxamides by the action of metallic sodium or sodium amide or hydride is known as a covenient and reliable method for the selective synthesis of N-substituted amides [9]. Isocyanates also react with primary and secondary amides to afford *N*-acylureas or amidines [9, 31–33]. However, polyaddition of isocyanates occurring at such a low temperature, have not been reported so far; we were likely the first to discover this reaction.

Table 1. Reactions of intermediates CH_2=C(M)XR (**IV**) with isocyanates R′N=C=O (0.025–0.05 mol, –100 to –30°C, 10–15 min)

Run no.	XR	R′	M	Yield,[a] %					
				II[b]	**V**	**X**, n = 0[c]	**X**, n = 1[d]	**X**, n = 2[e]	**X**, n = 3[f]
1	OMe	Pr	K	**IIa**, 45[g]		9.6[g]	11[g]		22[g]
2	OMe	Pr	Li[h]	**IIa**, 90, 66[i]			10		
3	OEt	Pr	K	**IIb**, 48	~15	3		9	25
4	OEt	Pr[j]	K	**IIb**, 67, 14[i]	6	1		13	13
5	OEt	Pr	Li[h]	**IIb**, 30	50 (43)[i]			20	
6	OEt	Pr	MgBr[k]	**IIb**, 78, 18[i]	15			7	
7	OEt	Pr	MgBr[l]	**IIb**, 63	37				
8	OEt	*i*-Pr	K	**IIc**, 100,[g] 86[i]					
9	OEt	Ph	K	**IIg**, 43[e]					
10	OEt	Ph	Li[h]	**IId**, 91,[g] 83[i]					
11	OBu	Pr	Li[h]	**IIe**, 66			14	20	
12	SEt	Pr	K	**IIf**, 40[g]	51,[g] 44[i]				
13	SEt	Pr	Li[h]	**IIf**, 47[i]					
14	SEt	*i*-Pr	K	**IIg**, 100,[g] 72[i]					
15	SEt	Ph	K	**IIh**, 8[g]					
16	SEt	Ph	Li[h]	**IIh**, 45			55		
17	SEt	Ph	MgBr[k]	**IIh**, 85, 48[i]			15		

[a] Determined from the intensity of the vinyl proton signals in the ^{1}H NMR spectrum.
[b] δ, ppm: 4.38–4.40 d and 5.34–5.32 d.
[c] δ, ppm: 4.69 d and 5.09 d.
[d] δ, ppm: 4.73–4.76 d and 4.22–4.24 d.
[e] δ, ppm: 4.50 d and 4.34 d.
[f] δ, ppm: 4.43–4.44 d and 4.14–4.15 d.
[g] According to the GLC data.
[h] LiBr was added.
[i] Preparative yield.
[j] Added in a dropwise fashion.
[k] $MgBr_2$ was added.
[l] LiBr and $MgBr_2$ were added in succession.

The formation of cyclic trimers, specifically of 6-ethylidene-1,3,5-triphenylhexahydro-1,3,5-triazine-2,4-dione and 6,6-diethyl-1,3,5-triphenylhexahydro-1,3,5-triazine-2,4-diones (as a mixture with other products) was also observed in the reaction of triethylindium with a 3–6-fold excess of phenyl isocyanate (hexane, 0°C, 20 h) [34]. However, the structure of linear precursors of hexahydro-1,3,5-perhydrotriazine-2,4-diones described therein was essentially different from the structure of intermediates **VIII**; therefore, their cyclization followed a quite different mechanism. At an equimolar ratio of the reactants, the product was the corresponding monoadduct [34].

When the potassium cation in intermediate **IVd** was replaced by lithium (via addition of LiBr), the only product of the reaction with propyl isocyanate (after hydrolysis of adduct **VIf**) was acrylamide **IIf** (Table 1, run no. 13). Double, triple, and oligomeric adducts were also formed in the reaction of propyl isocyanate with intermediate **IVa** derived from methoxyethene (**Ia**) (Table 1, run no. 1). Potassium derivative of ether **Ia** gave rise to amide **IIa** (45%, according to the GLC data) and compounds **X**, most probably, di-, tri-, and tetramers (9.6, 10.9, and 21.9%, respectively; GLC). Insofar as inidividual polyadducts were not isolated, it remains unclear whether the tris-addition product has linear or cyclic structure. The ^{1}H NMR spectrum of the reaction mixture contained signals from amide **IIa** at δ 4.33 (d) and 5.16 ppm (d) (CH_2=), doublet signals from vinyl protons at δ 4.00 and 4.30, 4.22 and 4.78, and 4.60 and 4.95 ppm, and broadened singlets from NH

protons at δ 5.60, 6.65, and 8.00 ppm. These signals belong to three compounds of general formula **X** differing by the value of *n*. We succeeded in completely suppressing the oligomerization process by replacement of the potassium cation in **IVa** by lithium. According to the ^{1}H NMR data, the product contained ~90% of amide **IIa** and only ~10% of the corresponding trimer (Table 1, run no. 2).

The data in Table 1 show that the reactivity of adducts **VI** toward propyl isocyanate appreciably increases in going from metoxyethene (**Ia**) to ethoxy (**Ib**) and butoxy (**Ic**) analogs (Table 1, run nos. 3–7, 11). In these cases, polyaddition products are formed regardless of the counterion nature (K^+, Li^+, $MgBr^+$) in intermediates **IV** and **VI**. With potassium salt **IVb** we obtained a mixture of 5 products: amide **IIb** and 4 oligomeric adducts, presumably containing 2, 3, 4, and 5 isocyanate moieties (or a mixture of linear and cyclic bis- and tris-adducts); the product ratio was 48:3:15:9:25 (Table 1, run. no. 3). The addition of of propyl isocyanate to a solution of **IVb** (M = K) in a dropwise mode suppresses the polyaddition process, but only partially (Table 1, run no. 4). In this case, the fraction of amide **IIb** in the reaction mixture increases to ~67%, while the fraction of trimer **Va** decreases to ~6% (according to the ^{1}H NMR data); the fractions of the above noted oligoadducts with identical chemical shifts of the vinyl protons are, respectively, 13, 13, and 1%.

It should be emphasized that reactions of propyl isocyanate with lithium salts **IVa** and **IVd** derived from methoxy- and ethylthioethenes lead to almost exclusive formation of the corresponding monoamides **IIa** and **IIf** (Table 1, run nos. 2, 3). By contrast, replacement of the potassium cation in salt **IVb** by lithium not only does not increase the selectivity of the process with respect to amide **IIb** but leads to the opposite result (Table 1, run no. 5). The fraction of amide **IIb** in the product mixture is minimal (~30%) while the fraction of **Va** is maximal (~50%); therefore, we succeeded in isolating product **Va** in a preparative yield of 43% (Table 1, run no. 5). The polyaddition process could not be avoided even by replacement of K^+ or Li^+ ion in adduct **VI** by $MgBr^+$ (Table 1, run nos. 6, 7).

On the other hand, the only products of the reaction of potassium salts **IVb** and **IVd** with isopropyl isocyanate were the corresponding amides **IIc** and **IIg** which were formed in almost quantitative yield (Table 1, run. nos. 8, 14). Amides **IId** and **IIh** were obtained in high yield from phenyl isocyanate and salts **IVb** and **IVd**, respectively (Table 1, run nos. 10, 17). In the reaction with salt **IVb** (M = Li), no polyaddition products of phenyl isocyanate were detected in the mixture, whereas from salt **IVd** (M = Li) both mono- (**IIh**) and tris-adduct, the latter somewhat prevailing (~55%), were formed (Table 1, run no. 16). Even in the reaction of phenyl isocyanate with magnesium salt **IVd** (M = MgBr), the major product, amide **IIh**, was contaminated with ~15% of the tris-adduct.

Thus our results indicate that, unlike the reaction with isothiocyanates [30], the outcome of the reaction of metalated alkoxy- and alkylthioethenes with isocyanates depends on the velocity ratio of two concurrent processes which involve carbon- and nitrogen-centered anions **IV** and **VI**. This ratio is determined in turn by the nature of the initial reactants (heteroalkene and isocyanate) and the structure of the key intermediate (**IV** or **VI**). Here, especially important is the nature of the counterion M^+. However, a more rigorous interpretation of the obtained results with account taken of structural effects, which could reveal some general relations holding in the reaction under study, was difficult to draw. The lack of distinct pair correlations like structural parameter–yield of mono- or polyadduct suggests that the process is influenced by a number of factors, including electronic and steric parameters of substituents at both the nitrogen atom and at the C=C bond, nature and size of the cation M^+, and geometric parameters of intermediate **VI**. Obviously, different isomers of **VI** could exhibit different chemical reactivities. The ratio of such isomers depends *inter alia* on fine details of their structure.

The alkylation of carbon-centered nucleophiles obtained by addition of potassium derivatives of heteroethenes to isothiocyanates is known to be a fast process: the reaction takes 10–15 min and quantitatively gives the corresponding imidothioates even at low temperature (–70 to 0°C) [30]. Nitrogen-centered nucleophiles **VI** react with methyl iodide at a much lower rate: The process requires elevated temperature (40–60°C) and relatively long time (~1–3 h); the products are tertiary amides **III**. The alkylation of isopropyl isocyanate adducts **VIc** and **VIg** (Table 2) having potassium as counterion are alkylated appreciably more readily than analogous lithium derivatives of propyl isocyanate adducts **VIa** and **VIf**. This difference is likely to result from the effect of the cation nature rather than from the substituent on the nitrogen. Successful methylation of phenyl isocyanate adduct **VId** requires the use of DMSO as solvent.

The analytical data and parameters of the IR (Table 3) and ^{1}H, ^{13}C, and ^{15}N NMR spectra (Table 4) of compounds **II**, **III**, and **V** are consistent with the proposed structures.

Table 2. Synthesis of amides **III** by reaction of CH_2=C(XR)C(=O)NMR′ (**VI**) (~0.05 mol) with MeI (~1.8–4.7 mol)

Compound no.	XR	R′	M	Temperature, °C	Time, h	Yield,[a] %
VIa	OMe	Pr	Li	40–50	2.5	76 (**IIIa**)
VIb	OEt	Pr	Li	40–50	~2	70 (**IIIb**)
VIc	OEt	*i*-Pr	K	40–45	1	69 (**IIIc**)
VId	OEt	Ph	Li	~50	1[b]	66 (**IIId**)
VIf	SEt	Pr	Li	55–60	~1.3	62 (**IIIf**)
VIg	SEt	*i*-Pr	K	40–45	~0.8	65 (**IIIg**)

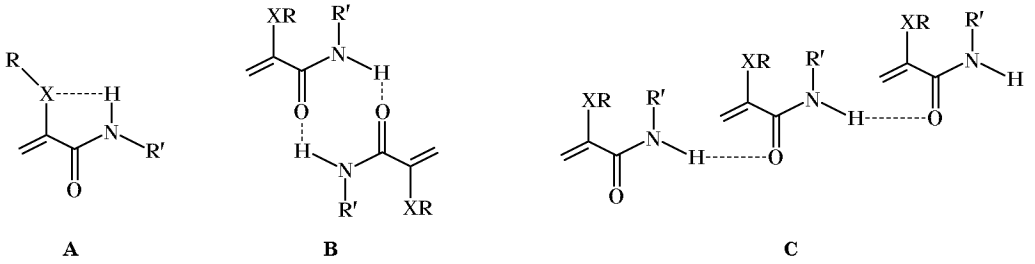
[a] Yield of the isolated product, calculated on the isocyanate taken.
[b] After 0.5 h, 30 ml of DMSO was added to the reaction mixture.

Table 3. IR spectra (KBr) of compounds **II**, **III**, and **V**

Compound no.	Vibration frequencies ν, cm^{-1}
IIa[a]	670, 740, 760, 790, 850, 900, 940, 1050, 1120, 1150, 1190, 1220, 1250, 1280, 1320, 1360, 1390, 1400, 1460, 1530, 1630, 1650–1670, 2850 sh, 2870, 2940, 2960, 3010 sh, 3050, 3300
IIb	970, 1060, 1110, 1150, 1200, 1250, 1300, 1380, 1440, 1450, 1520, 1620, 1660, 2870, 2930, 2970, 3420
IIc	670, 700, 750, 790 sh, 840 sh, 850, 920, 970, 1050, 1120, 1130, 1150, 1160, 1200, 1290, 1330, 1340, 1360, 1380, 1450, 1500, 1620, 1650, 2860, 2890, 2930, 2960, 3040, 3260
IId	690, 740, 750, 760, 780, 850, 900, 930, 970, 1050, 1120, 1170, 1240, 1280, 1330, 1360, 1370, 1440, 1520, 1590, 1630, 1660, 2870, 2940, 2970, 3050, 3300
IIf[a]	880, 890, 940, 970, 1050, 1150, 1260, 1290, 1380, 1440 sh, 1450, 1520, 1580, 1640, 2860, 2930, 2960, 3300
IIg	550, 660, 730, 780, 800, 860, 900, 920, 970, 1050, 1120, 1160, 1180, 1270, 1290, 1320, 1360, 1390, 1410, 1440, 1460, 1520 br, 1590, 1620 br, 2880, 2930, 2970, 3280
IIh[b]	480, 520, 580, 600, 700, 760, 790, 910, 930, 980, 1030, 1060, 1080, 1120, 1140, 1160, 1180, 1200, 1240, 1280, 1320, 1380, 1440, 1520, 1600, 1650 br, 2880, 2920, 2980, 3060, 1130, 3310
IIIa[a]	630, 660, 750, 770, 830, 890, 900, 960, 1045, 1080, 1135, 1190, 1220, 1250, 1280, 1310, 1350, 1380, 1400, 1440 sh, 1450, 1480, 1640, 2870, 2940, 2960, 3010 sh, 3120
IIIb	640, 660, 750, 780, 8120, 840 sh, 860, 890 sh, 950 sh, 970, 1045, 1080, 1130, 1200, 1245, 1270, 1300, 1340, 1370 sh, 1400, 1450 br, 1640 br, 1680 sh, 2860, 2920, 2950, 3110
IIIc[a]	630, 650, 720, 770, 820, 840 sh, 870, 880, 950, 970, 1050, 1100, 1160 sh, 1240–1260, 1340, 1360, 1380, 1400, 1450, 1480 sh, 1640, 2870, 2940, 2970
IIIf[a]	540, 600, 650, 700, 750, 860, 980, 1080, 1110, 1150, 1170, 1220, 1240, 1260, 1300, 1350, 1380, 1400, 1450 br, 1480, 1590, 1630 br, 2870, 2920, 2960
IIIg[a]	550, 620, 640, 760, 780, 800, 880, 950, 970, 1060, 1100, 1130, 1160, 1180, 1240, 1270, 1340, 1370, 1400, 1450 br, 1620 br, 2880, 2930, 2970
Va	530, 570, 600, 620, 710, 740, 770, 830, 870, 890, 930, 980, 1000, 1060, 1090, 1110, 1140, 1280, 1320, 1370, 1390, 1400, 1440, 1470, 1510 br, 1650, 1700, 2880, 2940, 2960, 3250
Vb	530 sh, 540, 560, 590, 610, 700, 740 sh, 750 sh, 760, 780, 810, 870, 890 sh, 930, 990, 1050, 1070, 1100, 1170, 1190 sh, 1250, 1270, 1290, 1300, 1310, 1350, 1360 sh, 1370, 1400, 1440, 1460 sh, 1500, 1510 sh, 1640, 1650 sh, 1690, 2870, 2940, 2960, 3300

[a] Film (neat).
[b] CCl_4 film.

Scheme 2.



A **B** **C**

The IR spectra of compounds **II** contain absorption bands typical of the amide fragment, 3300–3420 cm^{-1} (N–H) and 1620–1670 cm^{-1} (C=O), and C=C bond, 1580–1630 cm^{-1}. Displacement of the N–H absorption toward lower frequencies is likely to result from strong hydrogen bonding (see structures **A**–**C** in Scheme 2). Bending vibrations of the amide N–H bonds appear in the region 1500–1530 cm^{-1}. In the IR spectra of **Va** and **Vb** we observed an additional strong broadened absorption band at 1700 and 1690 cm^{-1}, respectively, which corresponds to stretching vibrations of the amide carbonyl group.

We did not identified geometric isomers of amides **II** and **III**, but their existence is clearly seen from the NMR spectra, especially from the ^{13}C NMR spectra. *E*,*Z*-Isomerism in the series of amides **II** and **III** may arise not only from restricted rotation about partially double C(O)–N bond [8, 9] but also from different orientations of the key molecular fragments with respect to each other, e.g., of the vinyl and amide groups [35], or of substituent R in the XR group relative to the C=C bond [36]. In the ^{1}H and ^{13}C NMR spectra of unsymmetrical amides **III** we observed splitting and displacement of signals from the NMe and NCH_2 protons (**IIIa**) or $=CH_2$ protons (**IIIf**, **IIIg**) and from almost all carbon atoms. By contrast, the spectra of secondary amides **II** (except for **IIa**) indicate the presence of only one isomer. Judging by the ^{1}H NMR spectrum, amide **IIa** also exists as a single isomer; however, its ^{13}C NMR spectrum contains several groups of signals for each carbon atom (except for C=O and =C). Probably, the time necessary to record the ^{1}H NMR spectrum is insufficient for the isomer equilibrium to establish.

The ^{1}H NMR spectra of hexahydro-1,3,5-triazine-2,4-diones **Va** and **Vb**, apart from signals belonging to the $EtXC=CH_2$ fragment (X = O, S), contain multiplet signals from protons of three $NCH_2CH_2CH_3$ groups with an overall intensity corresponding to 21 protons. The difference in the chemical shifts of the propyl protons in the spectra of **IIb**, **IIIb**, **Va** and **IIf**, **IIIf**, **Vb** is insignificant both within each series and between alkoxy and alkylthio derivatives. On the other hand, signals from the vinyl protons turned out to be very sensitive to the nature of the substituent at the C=C bond, whether it is OEt or SEt, (O=C)NHR′ or (O=C)N(Me)R′, and (O=C)NHR or perhydro-1,3,5-triazine-2,4-dione moiety (Table 5).

Signals from the vinyl protons in the spectrum of **Va** are displaced appreciably upfield relative to those of monoadduct **IIb**, $\Delta\delta_{cis}$ = 0.17, $\Delta\delta_{trans}$ = 0.63 ppm; they appear as two doublets at δ 4.23 and 4.72 ppm with a geminal coupling constant of 2.4 Hz. A similar pattern is observed in the spectra of **IIf** and **Vb**. The vinyl proton signals of **Vb** are located in a stronger field as two doublets at δ 5.14 and 5.89 ppm ($\Delta\delta_{cis}$ = 0.45, $\Delta\delta_{trans}$ = 0.52 ppm; ^{2}J = 0.8 Hz). The data in Table 5 show that the largest downfield shifts (by ~0.9–1.2 ppm) for both *cis*- and *trans*-proton signals are observed in going from ethoxy (**IIb**, **IIIb**, **Va**) to ethylthio derivatives (**IIf**, **IIIf**, **Vb**).

The ^{13}C NMR spectra of **IIb** and **Va** and/or **IIe** and **Vb** also display considerable differences both in the chemical shifts of carbon nuclei belonging to similar molecular fragments and in the number of signals. For example, the spectra of **Va** and **Vb** contain additional signals at δ_C 92.10 and 94.26 ppm (C^6), respectively. The propyl groups in positions *1* and *5* of the 1,3,5-triazine ring are characterized by similar chemical shifts, so that the corresponding signals have a double intensity.

The tris-addition product of potassium salt **IVd** and propyl isocyanate (compound **Vb**) was initially assigned linear structure **X** (*n* = 1) [37]. In order to prove the structure of compounds **Va** and **Vb** more reliably and to assign their NMR signals more rigorously, we applied 2D homo- (^{1}H–^{1}H-NOESY) and heteronuclear correlation techniques (^{1}H–^{13}C-HSQS, ^{1}H–^{13}C-HMBC, and ^{1}H–^{15}N-HMBC) with the use of pulse field gradient (PFG) sequence. According to the HMBC spectrum of compound **IIb**, the signal at δ_C 162.51 ppm, which correlates with the NCH_2 protons, belongs to the carbonyl carbon atom, and the signal at δ_C 153.32 ppm, which correlates with

Table 4. ^{1}H, ^{13}C, and ^{15}N NMR spectra of compounds **II**, **III**, and **V**

Comp. no.	^{1}H chemical shifts δ, ppm (*J*, Hz), $CDCl_3$
IIa	0.93 t (3H, Me, *J* = 7.4), 1.55 m (2H, β-CH_2), 3.26 m (2H, NCH_2), 3.64 s (3H, OMe), 4.40 d (1H, CH_2=, *J* = 2.3), 5.36 d (1H, CH_2=, *J* = 2.3), 6.65 br.s (1H, NH)
IIb	0.93 t (3H, $NCH_2CH_2C\mathbf{H}_3$, *J* = 7.5), 1.36 t (3H, $OCH_2C\mathbf{H}_3$, *J* = 7.1), 1.56 sex (2H, β-CH_2, *J* = 7.2), 3.27 t.d (2H, NCH_2, *J* = 7.2, *J* = 6.3), 3.83 q (2H, OCH_2, *J* = 7.1), 4.40 d (1H, CH_2=, *cis*, *J* = 2.2), 5.35 d (1H, CH_2=, *trans*, *J* = 2.2), 6.63 br.s (1H, NH)
IIc	1.19 d (6H, $CH\mathbf{Me}_2$, *J* = 6.5), 1.37 t (3H, $OCH_2C\mathbf{H}_3$, *J* = 7.0), 3.83 q (2H, OCH_2, *J* = 7.0), 4.13 m (1H, NCH), 4.37 d (1H, CH_2=, *J* = 2.0), 5.35 d (1H, CH_2=, *J* = 2.0)
IId	1.43 t (3H, Me, *J* = 7.0), 3.92 q (2H, OCH_2, *J* = 7.0), 4.51 d (1H, CH_2=, *J* = 2.4), 5.49 d (1H, CH_2=, *J* = 2.4), 7.11 t.m (1H, Ph), 7.32 t.t (2H, Ph), 7.58 d.m (1H, Ph), 8.37 br.s (NH)
IIf	0.93 t [3H, $N(CH_2)_2C\mathbf{H}_3$, *J* = 7.3], 1.26 t (3H, $SCH_2C\mathbf{H}_3$, *J* = 7.3), 1.55 t (2H, β-CH_2, *J* = 7.1), 2.71 q (2H, SCH_2, *J* = 7.5), 3.27 t.d (2H, NCH_2, 3*J* = 6.0), 5.59 d and 6.41 d (2H, CH_2=, *J* 0.4), 6.85 br.s (NH)
IIg	1.19 d (6H, $CH\mathbf{Me}_2$, *J* = 6.4), 1.27 t (3H, $SCH_2C\mathbf{H}_3$, *J* = 7.3), 2.70 q (2H, SCH_2, *J* = 7.3), 4.11 m (1H, NCH), 5.61 s (1H, CH_2=, *cis*, *J* = 0.4), 6.44 s (1H, CH_2=, *trans*, *J* 0.4), 6.57 br.s (1H, NH)
IIh	1.30 t (3H, Me, *J* = 7.4), 2.78 q (2H, SCH_2, *J* = 7.4), 5.81 d (1H, CH_2=, *cis*, *J* = 0.6), 6.63 d (1H, CH_2=, *trans*, *J* = 0.6), 7.10–7.59 m (5H, Ph), 8.69 br.s (1H, NH)
IIIa	0.92 m (3H, Me), 1.58 m (2H, β-CH_2), 2.92 s and 2.96 s (3H, NMe), 3.24 m and 3.33 m (2H, NCH_2), 3.62 s (3H, OMe), 4.30 d (1H, CH_2=, *J* = 3.1), 4.46 d (1H, CH_2=, *J* = 3.0)
IIIb	0.88 m (3H, $NCH_2CH_2C\mathbf{H}_3$), 1.34 t (3H, $OCH_2C\mathbf{H}_3$), 1.61 m (2H, β-CH_2), 2.92 s and 2.98 s (3H, NMe), 3.24 t and 3.34 t (2H, NCH_2), 3.81 q (2H, OCH_2), 4.28 d (1H, CH_2=, *cis*), 4.44 d (1H, CH_2=, *trans*)
IIIc	1.13 m (6H, $CH\mathbf{Me}_2$), 1.29 t (3H, $OCH_2C\mathbf{H}_3$, *J* = 7.0), 2.75 s and 2.79 s (3H, NMe), 3.77 q (2H, OCH_2, *J* = 7.0), 4.05 m (1H, NCH), 4.21 d (1H, CH_2=, *J* = 2.0), 4.36 d (1H, CH_2=, *J* = 2.0)
IIId	0.82 t (3H, Me), 3.35 m (2H, OCH_2), 3.34 s (3H, NMe), 4.18 d (1H, CH_2=, *cis*, *J* = 2.6), 4.68 d (1H, CH_2=, *trans*, *J* = 2.6), 7.16–7.28 m (5H, Ph)
IIIf	0.89 m (3H, $N(CH_2)_2C\mathbf{H}_3$), 1.31 t (3H, $SCH_2C\mathbf{H}_3$, *J* = 7.4), 1.61 m (2H, β-CH_2), 2.76 q (2H, SCH_2, *J* = 7.4), 2.93 s and 3.03 s (3H, NMe), 3.34 m (2H, NCH_2), 5.17 s, 5.20 s, and 5.30 s (2H, CH_2=)
IIIg	1.09 m (6H, $CH\mathbf{Me}_2$), 1.23 t (3H, $SCH_2C\mathbf{H}_3$, *J* = 7.4), 2.66 q (2H, SCH_2, *J* = 7.4), 2.72 s and 2.80 s (3H, NMe), 4.11 m (1H, NCH), 5.05 s, 5.09 s, and 5.20 s (2H, CH_2=)
Va	0.83 t (6H, $2NCH_2CH_2C\mathbf{H}_3$, *J* = 7.4), 0.87 t (3H, $NCH_2CH_2C\mathbf{H}_3$, *J* = 7.0), 1.19 t (3H, $OCH_2C\mathbf{H}_3$, *J* = 6.7), 1.57 br.m (6H, 3β-CH_2), 3.08 m (2H, NCH_2), 3.30 m (2H, NCH_2), 3.67 m (2H, NCH_2), 3.68 q (2H, OCH_2, *J* = 6.7), 4.23 d (1H, CH_2=, *cis*, *J* = 2.4), 4.72 d (1H, CH_2=, *trans*, *J* = 2.4), 4.33 br.s (1H, OH)
Vb	0.86 t [6H, $2(CH_2)_2C\mathbf{H}_3$, *J* = 7.4], 0.90 t [3H, $N(CH_2)_2C\mathbf{H}_3$, *J* = 7.3], 1.27 t (3H, $SCH_2C\mathbf{H}_3$, *J* = 7.4), 1.65 br.m (6H, 3β-CH_2), 2.70 q (2H, SCH_2, *J* = 7.4), 3.00 m (2H, NCH_2), 3.37 m (2H, NCH_2), 3.71 m (2H, NCH_2), 4.28 br.s (OH), 5.14 d and 5.89 d (2H, CH_2=, *J* = 0.8)
Comp. no.	^{13}C chemical shifts δ_C, ppm ($CDCl_3$)
IIa	11.22, 11.38, 11.42 (Me); 22.68, 22.77, 23.18 (β-CH_2); 40.97, 42.25, 47.94 (NCH_2); 55.14, 55.51 (OMe); 87.34, 89.44 (CH_2=); 154.25 (C=); 162.28 (C=O)
IIb[a]	11.46 ($NCH_2CH_2\mathbf{C}H_3$), 14.45 ($OCH_2\mathbf{C}H_3$), 22.89 (β-CH_2), 41.03 (NCH_2), 64.06 (OCH_2), 89.87 (CH_2=), 153.32 (C=), 162.51 (C=O)
IIc	14.42 ($OCH_2\mathbf{C}H_3$), 22.73 ($CH\mathbf{Me}_2$), 41.25 (NCH), 64.06 (OCH_2), 89.80 (CH_2=), 153.36 (C=), 161.62 (C=O)
IId	14.35 (Me), 64.38 (OCH_2), 91.00 (CH_2=), 119.97 (C^m), 124.43 (C^p), 128.96 (C^o), 137.43 (C^i), 152.58 (C=), 159.86 (C=O)

Table 4. (Contd.)

Comp. no.	^{13}C chemical shifts δ_C, ppm ($CDCl_3$)
IIf[b]	10.97 ($N(CH_2)_2\mathbf{C}H_3$), 13.48 ($SCH_2\mathbf{C}H_3$), 22.34 (β-CH_2), 27.49 (SCH_2), 41.35 (NCH_2), 123.61 (CH_2=), 137.72 (C=), 164.08 (C=O)
IIg	13.98 ($SCH_2\mathbf{C}H_3$), 22.68 (CH**Me**$_2$), 28.00 (SCH_2), 42.06 (NCH), 124.37 (CH_2=), 138.09 (C=), 163.60 (C=O)
IIh	13.99 (Me), 28.54 (SCH_2), 119.89 (C^m), 124.66 (CH_2=), 128.38 (C^p), 129.16 (C^o), 137.47 (C=), 129.27 (C^i), 162.37 (C=O)
IIIa	11.05, 11.18 (Me); 20.11, 21.00, 21.61 (β-CH_2); 28.31, 28.52, 32.60, 36.23 (NMe); 44.50, 45.10, 48.94 (NCH_2); 52.45, 54.88 (OMe); 86.46 (CH_2=); 157.54 (C=); 166.41, 166.78 (C=O)
IIIb	11.04, 11.16, 11.22 ($NCH_2CH_2\mathbf{C}H_3$); 14.27 ($OCH_2\mathbf{C}H_3$); 20.15, 20.94, 21.62 (β-CH_2); 28.54, 32.66, 36.24 (NMe); 44.52, 48.96, 52.49 (NCH_2); 63.32 (OCH_2); 86.78 (CH_2=); 156.97 (C=); 166.65 (C=O)
IIIc	14.30, 14.42 ($OCH_2\mathbf{C}H_3$); 19.22, 20.41, 22.71 (CH**Me**$_2$); 25.72, 28.24, 28.60, 29.52 (NMe); 41.25, 44.39, 49.50 (NCH); 63.31, 64.08 (OCH_2); 86.05, 86.61, 89.71 (CH_2=); 157.13 (C=); 166.50, 166.67 (C=O)
IIIf	11.00, 11.16 ($N(CH_2)_2\mathbf{C}H_3$); 13.62, 13.69 ($SCH_2\mathbf{C}H_3$); 20.24, 21.70 (β-CH_2); 25.85, 25.95 (SCH_2); 28.49, 30.35, 32.31 (NMe); 48.70, 52.56 (NCH_2); 111.65, 111.89 (CH_2=); 140.57, 140.74 (C=); 168.13, 168.50 (C=O)
IIIg	13.42 ($SCH_2\mathbf{C}H_3$); 19.02, 20.08 (CH**Me**$_2$); 25.66, 28.17, 30.06 (NMe); 25.26, 28.25 (SCH_2); 43.91, 49.30 (NCH); 110.52, 111.20 (CH_2=); 140.66 (C=); 167.78 (C=O)
Va[c]	10.87 ($NCH_2CH_2\mathbf{C}H_3$), 11.22 ($2NCH_2CH_2\mathbf{C}H_3$), 13.99 ($OCH_2\mathbf{C}H_3$), 21.57 (β-CH_2), 21.62 (2β-CH_2), 42.64 (NCH_2), 44.67 ($2NCH_2$), 63.16 (OCH_2), 85.37 (CH_2=), 92.10 (C^6), 151.04 (2C=O), 156.81 (C=)
Vb[d]	11.26 [$N(CH_2)_2\mathbf{C}H_3$], 11.63 [$2N(CH_2)_2\mathbf{C}H_3$], 13.22 ($SCH_2\mathbf{C}H_3$), 21.85 (β-CH_2), 22.51 (2β-CH_2), 26.33 (SCH_2), 43.18 (NCH_2), 45.56 ($2NCH_2$), 94.26 (C^6), 112.34 (CH_2=), 145.74 (C=), 150.49 (2C=O)

^{15}N NMR spectra, δ_N, ppm: [a] –275; [b] –263; [c] –269, –255; [d] –263, –249.

Table 5. Displacements of the vinyl proton signals in the ^1H NMR spectra of compounds **IIb**, **IIf**, **IIIb**, **IIIf**, **Va**, and **Vb**

$\Delta\delta$[a, b]	**IIb→IIIb**	**IIb→Va**	**IIIb→Va**	**IIf→IIIf**	**IIf→Vb**	**IIIf→Vb**	**IIb→IIf**	**IIIb→IIIf**	**Va→Vb**
$\Delta\delta_{cis}$	0.12	0.17	0.05	0.42	0.45	0.03	–1.19	–0.89	–0.91
$\Delta\delta_{trans}$	0.91	0.63	–0.28	1.11	0.52	–0.59	–1.06	–0.86	–1.17

[a] Negative values correspond to downfield shift.

[b] $\Delta\delta_{cis,trans}$ values for compounds **IIb**, **IIf**, **IIIb**, **IIIf**, **Va**, and **Vb** are, respectively, 0.95, 0.82, 0.16, 0.13, 0.49, and 0.75 ppm.

protons of the OCH_2 group, belongs to the carbon atom at the double bond.

Using the two-dimensional ^1H–^{15}N-HMBC technique, we detected two nonequivalent ^{15}N resonances for compounds **Va** and **Vb** and determined the corresponding chemical shifts. The α-protons of the propyl groups on N^1 and N^5 give cross peaks at δ_N –269 (**Va**) and –263 ppm (**Vb**) (relative to $MeNO_2$), and the α-protons of the N^3-propyl group give a cross peak at δ_N –255 (**Va**) and –249 ppm (**Vb**).

Signals from the PrN groups and carbonyl carbon atoms (δ_C 151.04 ppm) in the ^{13}C NMR spectrum of **Va** have a double intensity, indicating magnetic equivalence of these groups due to symmetry of the cyclic fragment. As follows from the proton-coupled ^{13}C NMR spectrum, the signal at δ_C 92.10 ppm belongs to a quaternary carbon atom. The chemical shift is typical of an sp^3-hybridized carbon atom attached to a heteroatom. Further assignment was performed using the 2D HMBC technique optimized for a long-range coupling constant of about 7 Hz. Protons of the vinyl group showed a correlation with ^{13}C carbon nuclei with δ_C 92.10 and 156.81 ppm. Cross peaks were observed between the NCH_2 protons (which appeared as multiplets at δ 3.08 and 3.30 ppm with a double intensity) and carbon nuclei with

δ_C 151.04 and 92.10 ppm. Protons of the NCH_2 group with δ 3.67 ppm showed a long-range coupling constant $^3J_{CH}$ with the carbon nuclei resonating at δ_C 151.04 ppm. A correlation was also found between the OCH_2 protons and carbon nuclei resonating at δ_C 156.81 ppm.

Analogous correlations were observed in the HMBC spectrum of **Vb**. The CH_2= carbon signal shifts downfield ($\Delta\delta_C$ = 26.97 ppm) and appears at δ_C 112.34 ppm. Two equivalent carbonyl carbon atoms give a signal at δ_C 150.49 ppm with a double intensity. Characteristic signals from the quaternary C^6 carbon atom and C^1 atom of the vinyl group are located at δ_C 94.26 and 145.74 ppm, respectively. The proton signals of **Vb** were assigned on the basis of the NOESY spectrum. The *cis* configuration of the EtSC=CH_2 fragment is confirmed by observation of NOE for the SCH_2 protons and *cis*-proton of the =CH_2 group.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75IR spectrometer from samples prepared as thin films (neat), KBr pellets, or CCl_4 films. The NMR spectra were recorded on a Bruker DPX-400 instrument (400, 100, and 40 MHz for ^1H, ^{13}C, and ^{15}N, respectively) from ~1–5% (^1H), ~5–15% (^{13}C), and ~30–50% solutions (^{15}N) in $CDCl_3$ at room temperature. Hexamethyldisiloxane was used as internal reference for ^1H and ^{13}C, and $MeNO_2$, for ^{15}N. The ^{13}C NMR spectra were also obtained on a Varian EM-390 spectrometer at 90 MHz from ~20% solutions in CCl_4 with tetramethylsilane as internal reference. The ^{13}C signals were assigned by analysis of unidimensional *J* spectra optimized for a direct coupling constant $^1J_{CH}$ of 145 Hz. GLC analysis was performed using a Varian 3400 chromatograph equipped with a flame-ionization detector; 15-m × 0.53-mm DB-5 capillary column (film thickness 1.5 μm); carrier gas nitrogen.

All operations were carried out under nitrogen or argon. Tetrahydrofuran was purified by treatment with KOH (~50 g/l, mechanically dispersed) and subsequent distillation over $LiAlH_4$ in the presence of benzophenone under nitrogen. Magnesium dibromide was prepared by the procedure described in [38]. Butyllithium (as a 1.6 M solution in hexane) was prepared from butyl chloride and lithium, or was a commercial reagent (Chemetall, Germany). The other reagents and solvents used in this work were commercial products. Liquid nitrogen was used as cooling agent.

2-Methoxy-*N*-propylacrylamide (IIa). A solution of 6 g of potassium *tert*-butoxide in 50 ml of THF and a cold solution of 14.6 g of ether **Ia** in 15 ml of THF were added in succession to a solution of 0.057 mol of BuLi in 36 ml of hexane under stirring at –100°C. The mixture was allowed to warm up to –40°C, and a solution of 7 g of LiBr in 20 ml of THF was added (the temperature rose to –30°C). The mixture (a grey suspension) was cooled again to –100°C, 5.12 g of propyl isocyanate was added (the suspension turned yellow), the cooling bath was removed, and the mixture was treated at –30°C with a saturated aqueous solution of ammonium chloride. The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 50 ml), and the extracts were combined with the organic phase and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was distilled in a vacuum. Yield 4.69 g (66%), light yellow liquid, bp 88–92°C (0.5 mm), n_D^{20} = 1.4670. ^1H NMR spectrum (CCl_4), δ, ppm: 0.93 t (3H, Me), 1.53 m (2H, β-CH_2), 3.20 q (2H, NCH_2), 3.63 s (3H, OMe), 4.30 d (1H, CH_2=, *cis*), 5.22 d (1H, CH_2=, *trans*), 6.87 br.s (1H, NH). Found, %: N 9.74. $C_7H_{13}NO_2$. Calculated, %: N 9.78.

2-Ethoxy-*N*-propylacrylamide (IIb). A solution of 3 g of potassium *tert*-butoxide in 40 ml of THF and 7.6 g of ether **Ib** were added in succession to a solution of 0.032 mol of BuLi in 20 ml of hexane under stirring at –100°C. The mixture was allowed to warm up to –40°C, and a solution of 0.035 mol of $MgBr_2$ in diethyl ether was added (the temperature rose to –20°C). The mixture (a white suspension) was cooled to –40°C, a solution of 2.4 g of propyl isocyanate in 15 ml of THF was added, and the mixture was treated as described above at 0°C. Yield 0.75 g (18%), mp 45–48°C (from hexane). Found, %: N 8.95. $C_8H_{15}NO_2$. Calculated, %: N 8.91.

2-Ethoxy-*N*-isopropylacrylamide (IIc). A solution of 6 g of potassium *tert*-butoxide in 50 ml of THF and 20 g of ether **Ib** were added in succession to a solution of 0.06 mol of BuLi in 38 ml of hexane under stirring at –100°C. The mixture warmed up to –40°C. It was cooled to –100°C, 5 g of isopropyl isocyanate was added (the mixture changed from orange to yellow), the cooling bath was removed, and the mixture was treated as described above at –30°C. Yield 7.24 g (86%), purity ~100% (GLC), bp ~70°C (0.5 mm). After distillation, the product crystallized. mp 44–47°C. ^1H NMR spectrum (CCl_4), δ, ppm: 1.20 d (6H, CH**Me**$_2$), 1.37 t (3H, OCH_2**Me**), 3.78 q (2H, OCH_2), 3.97 m (1H, NCH), 4.25 d (1H, CH_2=, *cis*), 5.17 d (1H, CH_2=, *trans*), 6.60 br.s (1H, NH). Found, %: N 8.34. $C_8H_{15}NO_2$. Calculated, %: N 8.91.

2-Ethoxy-*N*-phenylacrylamide (IId). A solution of 6 g of *t*-BuOK in 50 ml of THF and 20 g of ether **Ib** were added in succession to a solution of 0.06 mol of BuLi in 38 ml of hexane under stirring at –100°C. The mixture was allowed to warm up to –40°C, and a solution of 7 g of LiBr in 20 ml of THF was added. The mixture was cooled to –100°C, a solution of 6 g of phenyl isocyanate in 20 ml of THF was added, and the mixture was allowed to warm up to –30°C and was treated as described above. Yield 9.6 g (~100%), light yellow substance with a purity of 91% (GLC). Recrystallization gave 7.65 g (83%) of compound **IId** containing ~100% of the main substance (GLC). mp 69–70°C (from ethanol–pentane, ~3:1). ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.35 t (3H, Me), 3.77 q (2H, OCH_2), 4.33 d (1H, CH_2=, *cis*), 5.33 d (1H, CH_2=, *trans*), 6.86–7.28 m and 7.55 m (5H, Ph), 8.30 br.s (1H, NH). Found, %: N 7.11. $C_{11}H_{13}NO_2$. Calculated, %: N 7.32.

2-Butoxy-*N*-propylacrylamide (IIe). A solution of 3 g of *t*-BuOK in 40 ml of THF and 7.14 g of ether **Ic** were added in succession to a solution of 0.03 mol of BuLi in 20 ml of hexane under stirring at –90°C. The mixture was allowed to warm up to –40°C, and a solution of 3.5 g of LiBr in 10 ml of THF was added. The mixture was cooled to –100°C, 2.6 g of propyl isocyanate in 15 ml of THF was added, and the mixture was allowed to warm up to –40°C and was treated as described above. The solvent was removed on a rotary evaporator to obtain 3.9 g (70%) of a product which, according to the ^{1}H NMR data, was a mixture of amide **IIe** and oligoadducts **X** (*n* = 1, 2) at a ratio of 66:14:20 (Table 1, run no. 11). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: amide **IIe**: 5.33 d (1H, CH_2=, *cis*), 4.38 d (1H, CH_2=, *trans*), 6.65 br.s (1H, NH); **X** (*n* = 1): 4.74 d (1H, CH_2=, *cis*), 4.23 d (1H, CH_2=, *trans*), 8.83 br.s (1H, NH); **X** (*n* = 2): 4.48 d (1H, CH_2=, *cis*), 4.34 d (1H, CH_2=, *trans*); protons of the NPr and OBu groups appeared as unresolved multiplets.

2-Ethylthio-*N*-propylacrylamide (IIf). A solution of 6 g of *t*-BuOK in 50 ml of THF and 5 g of sulfide **Id** were added in succession to a solution of 0.06 mol of BuLi in 37 ml of hexane under stirring at –100°C. The mixture was allowed to warm up to –40°C, and a solution of 7 g of LiBr in 20 ml of THF was added. The mixture was cooled to –100°C, 4.3 g of propyl isocyanate was added, and the mixture was allowed to warm up to –30°C and was treated as described above. Yield 4.1 g (47%), bp 90–92°C (0.7 mm), n_D^{20} = 1.5110. ^{1}H NMR spectrum (CCl_4), δ, ppm: 0.95 t [3H, $N(CH_2)_2$**Me**], 1.30 t (3H, SCH_2**Me**), 1.45 br.m (2H, β-CH_2), 2.70 q (2H, SCH_2), 3.23 q (2H, NCH_2), 5.43 s (1H, CH_2=, *cis*), 6.20 s (1H, CH_2=, *trans*), 7.40 br.s (NH). Found, %: N 8.03; S 17.63. $C_8H_{15}NOS$. Calculated, %: N 8.08; S 18.51.

2-Ethylthio-*N*-isopropylacrylamide (IIg) was synthesized as described above using solutions of 0.06 mol of BuLi in 38 ml of hexane and of 6 g of *t*-BuOK in 50 ml of THF, 6 g of sulfide **Id**, and 5 g of isopropyl isocyanate. After appropriate treatment and removal of the solvent, the residue was recrystallized to obtain 6.7 g (72%) of compound **IIg** with a purity of ~100% (GLC), mp 45–47°C (from EtOH–pentane, ~3:1). Found, %: N 7.70. $C_8H_{15}NOS$. Calculated, %: N 8.08.

2-Ethylthio-*N*-phenylacrylamide (IIh). A solution of 6 g of *t*-BuOK in 50 ml of THF and 6 g of sulfide **Id** were added in succession to a solution of 0.06 mol of BuLi in 38 ml of hexane under stirring at –100°C. The mixture was allowed to warm up to –40°C, and a solution of 0.07 mol of $MgBr_2$ in diethyl ether was added. The mixture (a white suspension) was cooled to –90°C, a solution of 6 g of phenyl isocyanate in 20 ml of THF was added, and the mixture was allowed to warm up to –30°C and was treated as described above to isolate 5 g (48%) of compound **IIh** as a paraffin-like substance. Found, %: N 6.82. $C_{11}H_{13}NOS$. Calculated, %: N 6.76.

2-Methoxy-*N*-methyl-*N*-propylacrylamide (IIIa). Methyl iodide, 36 g, was added with stirring at –20°C to a solution of 0.053 mol of compound **VIa** in 85 ml of THF and 38 ml of hexane, which was prepared as described above from 15 g of ether **Ia**, 0.06 mol of BuLi, 6 g of *t*-BuOK, 7 g of LiBr, and 5 g of propyl isocyanate. The orange suspension was heated for 2.5 h at 40–50°C, cooled to room temperature, and treated as described above. The solvent was removed under reduced pressure, and the residue was distilled in vacuo. Yield 6.42 g (76%), bp 105–110°C (6.8 mm), n_D^{20} = 1.4640. ^{1}H NMR spectrum (CCl_4), δ, ppm: 0.88 t (3H, Me), 1.50 m (2H, β-CH_2), 2.83 s (3H, NMe), 3.15 q (2H, NCH_2), 3.57 s (3H, OMe), 4.20 d (1H, CH_2=, *cis*), 4.33 d (1H, CH_2=, *trans*). Found, %: N 9.74. $C_8H_{15}NO_2$. Calculated, %: N 8.91.

2-Ethoxy-*N*-methyl-*N*-propylacrylamide (IIIb). Methyl iodide, 15 g, was added with stirring at –30°C to a solution of 0.027 mol of compound **VIb** in 40 ml of THF and 20 ml of hexane, which was prepared from 7.6 g of ether **Ib**, 0.032 mol of BuLi, 3 g of *t*-BuOK, 3.5 g of LiBr, and 2.4 g of propyl isocyanate. The mixture was heated for ~2 h at 40–50°C, cooled to room temperature, and treated as described above. Removal of the solvent gave 4.29 g (94%) of compound **IIIb** which was purified by vacuum

distillation. Yield 3.23 g (70%), bp 80–85°C (1.5–2 mm), n_D^{20} = 1.4600. Found, %: N 8.55. $C_9H_{17}NO_2$. Calculated, %: N 8.18.

2-Ethoxy-*N*-isopropyl-*N*-methylacrylamide (IIIc). Methyl iodide, 20 g, was added at –30°C under stirring to a solution of 0.053 mol of compound **VIc** in 85 ml of THF and 38 ml of hexane, which was prepared by the above procedure from 20 g of ether **Ib**, 0.06 mol of BuLi, 6 g of *t*-BuOK, and 5 g of isopropyl isocyanate. The mixture was stirred for 1 h at 40–45°C, cooled, and treated as described above. Yield 6.36 g (69%), purity ~95% (GLC), bp 110–115°C (8 mm), n_D^{20} = 1.4590. ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.15 d (6H, CH**Me**$_2$), 1.32 t (3H, OCH$_2$**Me**), 2.74 s (3H, NMe), 3.77 q (2H, OCH$_2$), 4.15 d (1H, CH$_2$=, *cis*), 4.25 d (1H, CH$_2$=, *trans*). Found, %: N 9.74. $C_9H_{17}NO_2$. Calculated, %: N 8.18.

2-Ethoxy-*N*-methyl-*N*-phenylacrylamide (IIId). Methyl iodide, 30 g, was added at –10°C under stirring to a solution of 0.053 mol of compound **VId** in 85 ml of THF and 38 ml of hexane, which was prepared by the above procedure from 20 g of ether **Ib**, 0.06 mol of BuLi, 6 g of *t*-BuOK, 7 g of LiBr, and 6 g of phenyl isocyanate. The mixture was heated for 0.5 h at 50°C. According to the GLC data, the mixture contained ~50% of amide **IId**. Dimethyl sulfoxide, ~30 ml, was added, and the mixture was stirred for 0.5 h and treated as described above to obtain 6.5 g (66%) of compound **IIId** containing ~72% of the main substance (GLC), bp 90–100°C (0.2 mm), n_D^{20} = 1.5230. ^{1}H NMR spectrum (CCl_4), δ, ppm: 0.75 t (3H, Me), 3.25 s (3H, NMe), 3.25 q (2H, OCH$_2$), 4.08 d (1H, CH$_2$=, *cis*), 4.60 d (1H, CH$_2$=, *trans*), 7.18 m (5H, Ph). Found, %: N 6.63. $C_{12}H_{15}NO_2$. Calculated, %: N 6.82.

2-Ethylthio-*N*-methyl-*N*-propylacrylamide (IIIf). Methyl iodide, 14 g, was added at 0°C under stirring to a solution of 0.053 mol of compound **VIf** in 85 ml of THF and 37 ml of hexane, which was prepared as described above from 5 g of sulfide **Id**, 0.06 mol of BuLi, 6 g of *t*-BuOK, 7 g of LiBr, and 5.03 g of propyl isocyanate. The mixture was stirred for 80 min at 55–60°C. After appropriate treatment and removal of the solvent, the residue was distilled under reduced pressure to obtain 6.2 g (62%) of compound **IIIf** containing 94% of the main substance (GLC), bp 125–127°C (8 mm), n_D^{20} = 1.4970. Found, %: N 7.13. $C_9H_{17}NOS$. Calculated, %: N 7.48.

2-Ethylthio-*N*-isopropyl-*N*-methylacrylamide (IIIg). A solution of 6 g of *t*-BuOK in 50 ml of THF and 6 g of sulfide **Id** were added in succession to a solution of 0.06 mol of BuLi in 38 ml of hexane under stirring at –100°C. The temperature rose to –40°C. The mixture was cooled again to –100°C, 5 g of isopropyl isocyanate was added, the mixture was allowed to warm up to –30°C, 20 g of methyl iodide was added, and the mixture was stirred for 50 min at 40–45°C, cooled to room temperature, and treated as described above. Yield of **IIIg** 6.5 g (65%), purity 85% (GLC), bp 100–115°C (7.3 mm), n_D^{20} = 1.4940. Found, %: N 7.72. $C_9H_{17}NOS$. Calculated, %: N 7.48.

6-(1-Ethoxyvinyl)-6-hydroxy-1,3,5-tripropylhexahydro-1,3,5-triazine-2,4-dione (Va). A solution of 3 g of *t*-BuOK in 40 ml of THF and 7.6 g of ether **Ib** were added in succession to a solution of 0.032 mol of BuLi in 20 ml of hexane under stirring at –100°C. The mixture was allowed to warm up to –40°C, and a solution of 3.5 g of LiBr in 10 ml of THF was added. The mixture was cooled to –100°C, 2.4 g of propyl isocyanate was added, and the mixture was allowed to warm up to –30°C and was treated as described above. Yield 1.24 g (43%), mp 120–122°C (from hexane). Found, %: N 12.95. $C_{16}H_{29}N_3O_4$. Calculated, %: N 12.83.

6-(1-Ethylthiovinyl)-6-hydroxy-1,3,5-tripropylhexahydro-1,3,5-triazine-2,4-dione (Vb). A solution of 5.6 g of *t*-BuOK in 50 ml of THF and 4.4 g of sulfide **Id** were added in succession to a solution of 0.06 mol of BuLi in 37 ml of hexane under stirring at –100°C. The mixture quickly warmed up to –40°C. It was cooled to –100°C, 4.3 g of propyl isocyanate was added, and the mixture was allowed to warm up to –30°C and was treated as described above. Yield 2.5 g (44%), mp 145–150°C (from ether). ^{1}H NMR spectrum (CCl_4), δ, ppm: 0.90 t [9H, 3N(CH$_2$)$_2$**Me**], 1.30 t (3H, SCH$_2$**Me**), 1.60 br.m (6H, 3β-CH$_2$), 2.70 q (2H, SCH$_2$), 2.90–3.50 m (4H, 2NCH$_2$), 3.70 m (2H, NCH$_2$), 4.90 br.s (OH), 5.13 d and 5.90 d (2H, CH$_2$=). Found, %: N 11.46; S 8.80. $C_{16}H_{29}N_3O_3S$. Calculated, %: N 12.23; S 9.34.

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