Alkyl Shifts in 1,4-Dipoles from Tosyl Iso(thio)cyanate and Imido(thio)carbonates or Isoureas

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O→*N* alkyl shifts are observed in the dipoles **3**, **13** from tosyl isocyanate (**2a**) and imido(thio)carbonates **1** (**12**) to give (thio)allophanates **5** (**14**). Similarly, addition of tosyl isothiocyanate (**2b**) to isourea **24a** leads to the product **28** of an *O*→*S* methyl shift. A cross-over experiment involving **2a** and imidothiocarbonates **12b,c** gives the four products **14a–d** proving the intermolecular nature of the rearrangement. However, on mixing **2a** and isoureas **24a,b** or **2b** and imido(thio)carbonates **1** (**12**), the reaction stops at the stage of dipoles **8**, **19**, **25a,b**.

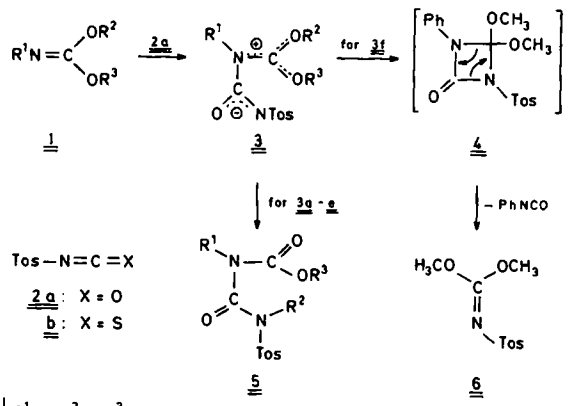
Alkyl-Verschiebungen in 1,4-Dipolen aus Tosyliso(thio)cyanat und Imido(thio)kohlensäureestern oder Isoharnstoffen

Die Dipole **3**, **13** aus Tosylisocyanat (**2a**) und Imido(thio)kohlensäureestern **1** (**12**) geben *O*→*N*-Alkyl-Verschiebungen zu (Thio)Allophansäureestern **5** (**14**). Ähnlich führt die Addition von Tosylisothiocyanat (**2b**) an den Isoharnstoff **24a** zum Produkt **28** einer *O*→*S*-Methyl-Verschiebung. Ausgehend von **2a** und den Imidothiokohlensäureestern **12b,c** ergab ein Kreuzungsversuch die vier Produkte **14a–d** und bewies so den intermolekularen Verlauf der Umlagerung. Beim Zusammengeben des Isothiocyanats **2b** und der Imido(thio)kohlensäureester **1** (**12**) oder von **2a** und der Isoharnstoffe **24a,b** bleibt die Reaktion jedoch auf der Stufe der Dipole **8**, **19**, **25a,b** stehen.

Usually, only indirect evidence can be obtained for an intermediate in a cycloaddition reaction[1,2]. Mechanistic tools that are frequently employed include kinetic measurements as well as evaluation of the stereochemical outcome of the reaction or of secondary isotope effects[2]. However, in the [2 + 2] cycloaddition between iso(thio)cyanates and electron-rich double-bond systems, efficient charge stabilization may allow a 1,4-dipolar intermediate to be identified spectroscopically or even be isolated[1,3]. Another line of evidence for 1,4-dipoles comes from the formation of products other than [2 + 2] cycloadducts, e.g. 1,4-dipolar cycloadducts[4] or products resulting from hydrogen shifts[5]. In the reaction between iso(thio)cyanates and ketene *O,O*- or *-O,N*-acetals, even methyl shifts from the cation to the anion part of the zwitterion were observed[6,7]. In addition reactions involving the related imidocarbonates or isoureas, the same type of rearrangement seems possible and encouraged a study of their reaction with the particularly reactive heterocumulenes tosyl isocyanate (**2a**) and isothiocyanate (**2b**).

Reactions of Imidocarbonates 1

On heating, *N*-alkylimidocarbonates **1a–d** react with tosyl isocyanate (**2a**) to give a series of 1:1 adducts **5**, whereas the addition of **1e** to **2a** yields also an isomer **7**. For both types of products, the reluctance to undergo hydrolysis allows to exclude the 1,4-dipolar constitution **3**, and *two* absorptions in the double-bond range of the IR and the ^{13}C-NMR spectra are not compatible with a β-lactam-type cycloadduct **4**. However, the spectroscopic data substantiate formation of **5** in a rearrangement consisting of an *O*→*N* shift as the prevailing process. This assignment is based on an IR band at 1690 cm^{-1} which is characteristic of the *N*-tosylurea moiety and on a large shift difference between the *O*-methyl(ene) signal of the urethane function and that of the shifted *N*-alkyl group in the ^{1}H NMR and, for **5c**, also of the ^{13}C-NMR spectrum (Table 2). On the other hand, constitution **7** is substantiated by an IR absorption for the tosylimino moiety at lower wavenumber and only a minor shift difference between the *O*-methylene signals (Table 2).



		R^1	R^2	R^3
1,3,5,8a		Me	Me	Me
	b	Me	Me	Et
	c	Me	Et	Et
1,3,5	d	c-C_6H_{11}	Me	Me
	e	c-C_6H_{11}	Et	Et
1,3	f	Ph	Me	Me
	g	Me	Ph	Ph

Starting from **1f**, ring-closure of **3f** rather than rearrangement is observed. The resulting diazetidinone **4** then gives a [2 + 2] cycloreversion[8] to provide *N*-tosylimidocarbonate **6**. A more complex pattern is observed in the reaction of diphenyl imidocarbonate **1g** with isocyanate **2a**. Three products were isolated by chromatography and the constitutions **9**, **10**, and **11b**, respectively, were assigned based on the spectroscopic data. Support for the suggested constitutions comes from the spectroscopic data of the related com-

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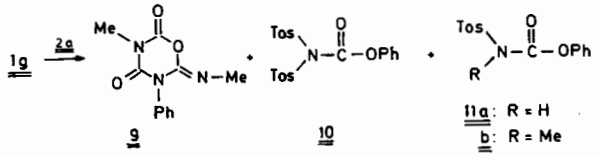
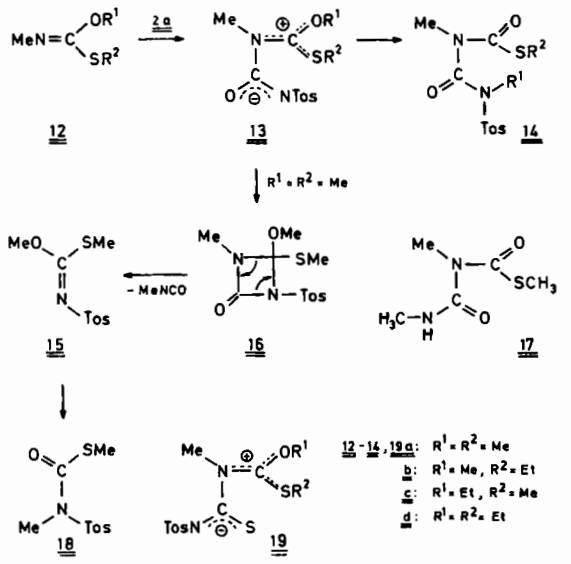
pound **11a** (cf. Experimental Part and Table 2). Aside from the reaction products, there is no experimental evidence as to the reaction mechanism, but the *N*-phenyl group of **9** shows that an $O \rightarrow N$ phenyl shift is involved. Furthermore, formation of **10** indicates that an intermediate is present which is an efficient tosylating agent.



Contrary to tosyl isocyanate (**2a**), isothiocyanate **2b** does not lead to rearrangement in the reaction with imidocarbonates **1a–c**. Only labile 1:1 adducts are formed which in solution are in equilibrium with the starting materials. The products are sensitive to moisture which is explained in terms of the zwitterionic constitution **8** or of the orthocarbonate moiety in a [2 + 2] cycloadduct. Similar to the zwitterions from **2b** and guanidines[3b] or isothioureas[3c], the products show IR absorptions between 1610 and 1630 cm^{-1} suggesting the 1,4-dipolar constitution **8**. On the contrary, for the alternative constitution of 2-(tosylimino)-1,3-thiazetidines (cf. **29**) a C=N absorption at lower wavenumbers seems probably as in the case for **6**, **7**, **15** (Table 2), *N*-tosylisothioureas[3a] or *N*-tosyliminothietanes[2b]. However, only weak support in favor of the zwitterionic constitution **8** comes from the ^{1}H-NMR spectra of the cation portions of the products, where, compared to **1**, a downfield shift of not more than $\Delta\delta = 0.20$ is observed, whereas a stronger deshielding effect of the positive charge might have been expected.

Reactions of *O,S*-Dialkyl Imidothiocarbonates 12

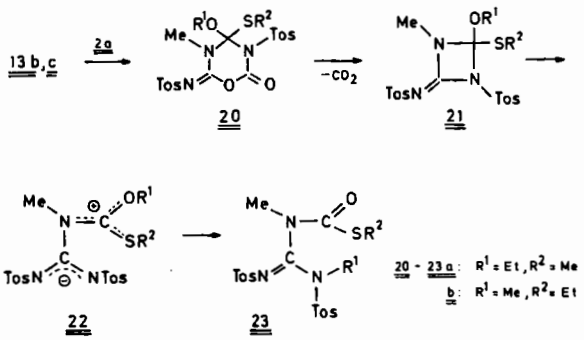
Imidothiocarbonates **12** are slightly more reactive toward isocyanate **2a** than imidocarbonates **1**. The main reaction pathway leads to rearranged products **14** obviously via dipoles **13**. In addition to the spectroscopic evidence (Table 2),



the constitution **14** resulting from an $O \rightarrow N$ alkyl shift is proven by acid-catalyzed hydrolysis of **14a** which gave thioallophanate **17**, whereas a *N*-tosylimino moiety should lead to tosylamide.

A side product of the reaction between **2a** and **12a** is thiocarbamate **18**. A probable precursor seems to be imidothiocarbonate **15** as formed from cycloadduct **16** in a [2 + 2] cycloreversion[8], which implies a Chapman-type rearrangement[9] of **15** to **18** under the reaction conditions. In fact, an independent synthesis of **15** and heating led to product **18**.

In the reaction of **2a** with **12b,c**, 3-(tosylimino)thioallophanates **23** are formed as additional products. A plausible mechanism is based on a 1,4-dipolar cycloaddition[4] of zwitterions **13b,c** to isocyanate **2a** to give **20** and subsequent loss of carbon dioxide – probably in a two-step process[1]. The resulting diazetidine **21** may be in equilibrium with zwitterion **22** which allows another $O \rightarrow N$ alkyl shift to yield the isolated products **23**.



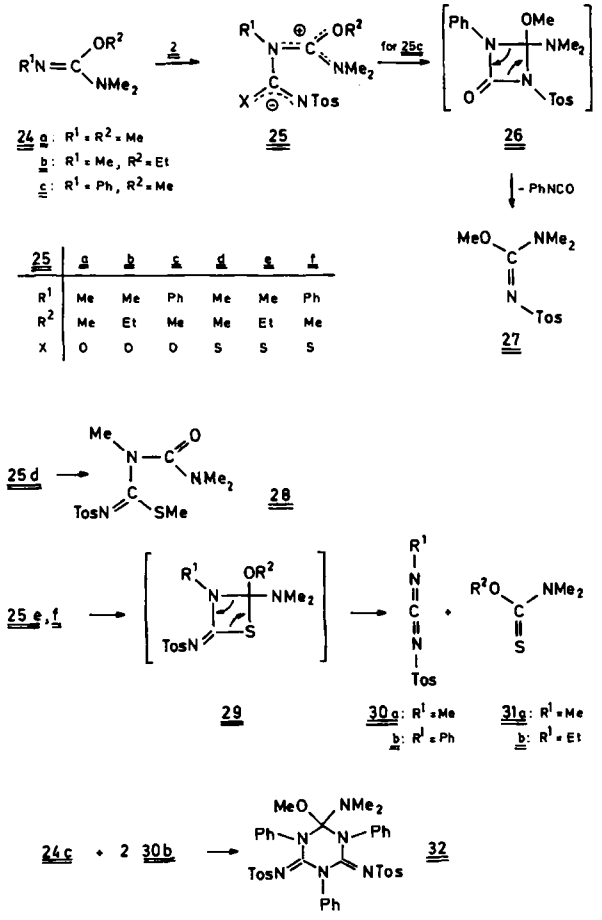
The reaction of isothiocyanate **2b** with imidothiocarbonates **12** leads to products which closely resemble those formed from **2b** and **1**. Again, we prefer the dipolar constitution **19** rather than that of the alternative 2-(tosylimino)-1,3-thiazetidines. As shown for **19a**, heating of a sample does not give the rearrangement, but favors cleavage to the starting materials **2b** and **12**.

Reactions of Isoureas 24

Earlier work has shown that dimethylamino groups are particularly effective in stabilizing the cation part of 1,4-dipoles[3]. In accord with these reports, addition of isocyanate **2a** to isoureas **24a,b** in ether immediately leads to 1:1 adducts, for which two IR absorptions at 1640 and 1670 cm^{-1} support the constitution **25a,b** with partial double-bonds in the cation as well as the anion moiety. Compared to **24**, the ^{1}H-NMR spectra reveal a downfield shift by $\Delta\delta = 0.16–0.17$ ppm only for the signal of the dimethylamino group, which apparently takes up most of the positive charge. As *o*-dichlorobenzene had to be used as solvent, an upfield shift is observed for most of the other signals. Attempts to induce a rearrangement of **25a,b** by heating only resulted in complex decomposition.

From the reaction of isocyanate **2a** and *N*-phenyl derivative **24c**, zwitterion **25c** cannot be isolated, but, in subsequent ring-closure/cycloreversion steps[8], *N*-tosylisourea **27**

is formed. This results parallels the behavior of *N*-phenylimidocarbonte **1f** in the reaction with **2a**.



As with **2a**, reaction of **24a,b** with isothiocyanate **2b** in ether also leads to precipitates which, by analogy, should be dipoles **25d,e**. Intermediate **25d** slowly dissolves and, contrary to **8** or **19**, forms the rearranged product **28**. The $O \rightarrow S$ alkyl shift is supported by the spectroscopic data (Table 2) and is in line with sulfur being the most nucleophilic atom of the ambident anion part in **25d**.

Also **25e** is not stable in the reaction mixture, chromatography yields *O*-ethyl thiocarbamate **31b** which obviously results from [2 + 2] cycloreversion[8] of cycloadduct **29**. The product **30a** is known to be unstable[3c] and was not isolated. Similarly, carbodiimide **30b** appears to be an intermediate in the reaction of isothiocyanate **2b** with **24c**. However, by analogy with the chemistry of the corresponding isothiourea[3c], two molecules of **30b** add to untransformed **24c** to give heterocycle **32** in a [2 + 2 + 2] cycloaddition[4].

Consequently, the presence of the dimethylamino group largely changes the behavior of the 1,4-dipoles under study: whereas the products from **1a–c** or **12** with isothiocyanate **2b** do not rearrange or give the [2 + 2] cycloreversion, these reactions occur in the zwitterions from **2b** and **24b,c** and, as to the rearrangement, the reverse is true for the corresponding reactions of isocyanate **2a**. This may reflect complex electronic, steric, and conformational influences. However, a consistent tendency to undergo the cycloreversion reaction[8] is seen in the reactions of the *N*-phenyl derivatives **1f**, **24c**.

Cross-over Experiment

A cross-over experiment should tell whether the rearrangement of 1,4-dipoles proceedes intra- or intermolecularly. The experiment requires transfer of the methyl and the ethyl group in the same reaction mixture at comparable rates to give a clear-cut information. However, the reaction of imidocarbonate **1b** with isocyanate **2a** gives only **5b**, the product of methyl transfer indicating that the ethyl shift in **3b** occurs much slower. The more pronounced migratory aptitude of the methyl group is also reflected in the successful rearrangement of **25d** as compared to its absence in the *O*-ethyl derivative **25e**.

A better chance for a cross-over experiment was seen in the reactions of **2a** with imidothiocarbonates **12b,c**. Here, the intramolecular process would provide **14b,c** only, whereas an intermolecular mechanism would lead to the four products **14a–d**. The latter is the actual experimental result. The yields of 4-ethyl products are lower than those of 4-methyl-thioallophanates indicating again a faster methyl transfer. Overall, the yields are not good which may reflect that, after the bimolecular alkyl shift, the resulting cation and anion may undergo secondary reactions rather than another alkyl transfer. In any case, the intermolecular nature of the alkyl shifts is in accord with predictions based on the feasability of an endocyclic S_N reaction[10] or of a 6-*endo*-tet process[11] and was also proven for the rearrangement of dipoles from **2a** and ketene acetals[7].

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Experimental

Melting points: uncorrected, Leitz hot-stage microscope. – IR spectra: Perkin-Elmer 297. – ^{1}H-NMR spectra: Varian T 60, EM 360, and NV 14. – ^{13}C-NMR spectra: Bruker WP 60. – Mass spectra (MS): Varian MAT CH 7. – Preparative TLC: silica gel plates (20 × 90 cm), fluorescent indicator.

Starting Materials **1**, **2**, **12**, **24**: *Dimethyl N-methylimidocarbonate* (**1a**, b.p. 110°C) was obtained by the reaction of *N*-methylimidocarbonyl dichloride[12,13] with sodium methoxide[14] (48%) or, with less problems in the distillative purification, via the alkylation of methyl methylcarbamate with trimethyloxonium tetrafluoroborate following the general procedure[15] (21%). The latter approach also gave *ethyl methyl N-methylimidocarbonate* (**1b**, 33%, b.p. 121°C) and *diethyl N-methylimidocarbonate* (**1c**, 53%, b.p. 139°C). Reaction of *N*-cyclohexylimidocarbonyl dichloride[16] with the corresponding alkoxides[14] provided *dimethyl N-cyclohexylimidocarbonate* (**1d**; 62%, b.p. 206°C, n_D^{20} = 1.4607) and *diethyl N-cyclohexylimidocarbonate* (**1e**; 59%, b.p. 110°C/21 Torr), respectively. The syntheses of imidocarbonates **1f**[14] and **g**[13] had been reported previously. – Tosyl isocyanate (**2a**) is commercially available, whereas for isothiocyanate **2b** Hartke's method was employed[17]. – Imidothiocarbonates **12** were accessible by the reaction of methyl isothiocyanate with sodium methoxide or ethoxide and subsequent alkylation with methyl or ethyl iodide[18] to give **12a** (56%, b.p. 144°C; ref.[17] b.p. 142–144°C), *S-ethyl O-methyl N-methylimido-*

thiocarbonate (**12b**, 48%, b.p. 158°C), **12c** (58%, b.p. 159°C; ref.[18] 159°C), and **12d** (45%, b.p. 184°C; cf. ref.[19]). – *O*-Alkylation of the corresponding ureas with Meerweins's reagent led to *1,1,2,3-tetramethylisourea* (**24a**, 10%, b.p. 150°C) and *2-ethyl-1,1,3-trimethylisourea* (**24b**, 32%, b.p. 153°C)[15,20]. For the synthesis of **24c**, a patent procedure[21] was employed (yield 67%, b.p. 134°C/20 Torr; ref.[21] b.p. 126–128°C/14 Torr). – For selected spectroscopic data of **1**, **12**, **24** see Table 2.

Reaction of Imidocarbonates **1a–e** *with Isocyanate* **2a**: 2–3 mmol of **1** was stirred at 80°C with the equivalent amount of **2a** for 10 h. After cooling, products **5**, **7** were isolated by preparative TLC with ethyl acetate/petroleum ether (1:3 or 2:3). *Methyl methyl[(methyltosylamino)carbonyl]carbamate* (**5a**, yield 25%) was obtained as an oil and gave no satisfactory elementary analysis. For other data of products **5**, **7** see Tables 1, 2. Additional data for **5c**: ^{13}C NMR ($CDCl_3$): δ = 13.9 (NCH_2CH_3), 14.2 (OCH_2CH_3), 21.5

Table 1. Physical properties and elemental analyses of the reaction products

Name	% Yield	M.p. [°C]	Molecular formula (mass)		Analytical data C	H	N	S
Ethyl methyl [(methyltosylamino)carbonyl]carbamate (**5b**)	32	oil	$C_{13}H_{18}N_2O_5S$ (314.4)	Calcd.	49.67	5.77	8.91	10.20
				Found	49.39	5.36	8.64	9.88
Ethyl [(ethyltosylamino)carbonyl](methyl)carbamate (**5c**)	23	oil	$C_{14}H_{20}N_2O_5S$ (328.4)	Calcd.	51.21	6.14	8.53	9.76
				Found	51.44	6.34	8.08	9.52
Methyl cyclohexyl[(methyltosylamino)carbonyl]carbamate (**5d**)	71	115	$C_{17}H_{24}N_2O_5S$ (368.4)	Calcd.	55.42	6.57	7.60	8.70
				Found	55.52	6.69	7.56	8.84
Ethyl cyclohexyl[(ethyltosylamino)carbonyl]carbamate (**5e**)	10	94	$C_{19}H_{28}N_2O_5S$ (396.5)	Calcd.	57.55	7.12	7.06	8.09
				Found	57.22	7.19	7.02	8.32
Dimethyl *N*-tosylimidocarbonate (**6**)	91	154	$C_{10}H_{13}NO_4S$ (243.3)	Calcd.	49.37	5.39	5.76	13.18
				Found	49.15	5.37	5.53	13.10
Ethyl cyclohexyl[ethoxy(tosylimino)methyl]carbamate (**7**)	11	96	$C_{19}H_{28}N_2O_5S$ (396.5)	Calcd.	57.55	7.12	7.06	8.09
				Found	57.73	7.32	7.02	8.22
C-[(Dimethoxymethylene)methylammonio]-*N*-(tosyl)thioformamidate (**8a**)	89	98 (dec.)	$C_{12}H_{16}N_2O_4S_2$ (316.2)	Calcd.	45.55	5.10	8.85	20.27
				Found	45.59	5.09	8.47	20.00
C-[(Ethoxymethoxymethylene)methylammonio]-*N*-(tosyl)thioformamidate (**8b**)	67	53–56	$C_{13}H_{18}N_2O_4S_2$ (330.5)	Calcd.	47.26	5.49	8.48	19.40
				Found	46.35	5.23	8.16	20.34
C-[(Diethoxymethylene)methylammonio]-*N*-(tosyl)thioformamidate (**8c**)	36	oil	$C_{14}H_{20}N_2O_4S_2$ (344.5)	Calcd.	48.82	5.85	8.13	18.61
				Found	47.64	5.76	7.76	–[a]
5,6-Dihydro-3-methyl-6-(methylimino)-5-phenyl-2*H*-1,3,5-oxadiazine-2,4(3*H*)-dione (**9**)	31	163–166	$C_{11}H_{11}N_3O_3$ (233.2)	Calcd.	56.65	4.75	18.01	–
				Found	56.68	4.94	17.35	–
Phenyl ditosylcarbamate (**10**)	40	150–151	$C_{21}H_{19}NO_6S_2$ (445.5)	Calcd.	56.62	4.30	3.14	14.39
				Found	56.60	4.30	3.13	14.32
Phenyl methyltosylcarbamate (**11b**)	10	101–102	$C_{15}H_{15}NO_4S$ (305.4)	Calcd.	59.00	4.95	4.59	10.49
				Found	59.22	4.95	4.57	10.55
S-Methyl methyl[(methyltosylamino)carbonyl]thiocarbamate (**14a**)	63	130	$C_{12}H_{16}N_2O_4S_2$ (316.4)	Calcd.	45.55	5.10	8.85	20.27
				Found	45.76	5.33	8.87	20.03
S-Ethyl methyl[(methyltosylamino)carbonyl]thiocarbamate (**14b**)	20	59	$C_{13}H_{18}N_2O_4S_2$ (330.4)	Calcd.	47.26	5.49	8.48	19.40
				Found	47.07	5.32	8.35	19.41
S-Methyl [(ethyltosylamino)carbonyl](methyl)thiocarbamate (**14c**)	12	70–72	$C_{13}H_{18}N_2O_4S_2$ (330.4)	Calcd.	47.26	5.49	8.48	19.40
				Found	46.94	5.44	8.06	18.77
S-Ethyl [(ethyltosylamino)carbonyl](methyl)thiocarbamate (**14d**)	7	oil	$C_{14}H_{20}N_2O_4S_2$ (344.4)	Calcd.	48.83	5.85	8.13	18.62
				Found	48.73	5.70	8.11	18.30
S-Methyl methyl(tosyl)thiocarbamate (**18**)	6	82	$C_{10}H_{13}NO_3S_2$ (259.3)	Calcd.	46.31	5.05	5.40	24.72
				Found	46.28	5.04	5.31	24.72
C-{[Methoxy(methylthio)methylene]methylammonio}-*N*-(tosyl)thioformamidate (**19a**)	56	94	$C_{12}H_{16}N_2O_3S_3$ (332.5)	Calcd.	43.35	4.35	8.43	28.93
				Found	43.50	4.92	8.43	28.45
C-{[Ethoxy(methylthio)methylene]methylammonio}-*N*-(tosyl)thioformamidate (**19c**)	45	oil	$C_{13}H_{18}N_2O_3S_3$ (346.5)	Calcd.	45.06	5.24	8.08	27.76
				Found	44.02	5.01	7.73	27.47
S-Methyl [(ethyltosylamino)(tosylimino)methyl](methyl)thiocarbamate (**23a**)	25	134–136	$C_{20}H_{25}N_3O_5S_3$ (483.6)	Calcd.	49.67	5.21	8.68	19.89
				Found	49.39	5.23	8.64	20.21
S-Ethyl methyl[(methyltosylamino)(tosylimino)methyl]thiocarbamate (**23b**)	36	74	$C_{20}H_{25}N_3O_5S_3$ (483.6)	Calcd.	49.67	5.21	8.68	19.89
				Found	49.65	5.22	8.61	19.65
2-Ethyl-1,3,3-trimethylisouronium-1-(*N*-tosylcarboxamidate) (**25b**)	87	–[b]	$C_{14}H_{21}N_3O_4S$ (327.4)	Calcd.	51.36	6.46	12.83	9.79
				Found	51.45	6.74	12.64	9.92
1,1,3-Trimethyl-3-[(methylthio)(tosylimino)methyl]urea (**28**)	57	86	$C_{13}H_{19}N_3O_3S_2$ (329.4)	Calcd.	47.40	5.81	12.75	19.46
				Found	47.46	5.83	12.61	19.54
Hexahydro-2-methoxy-*N*,*N*-dimethyl-1,3,5-triphenyl-4,6-bis(tosylimino)-1,3,5-triazine-2-amine (**32**)	42	78 (dec.)	$C_{38}H_{38}N_6O_5S_2$ (722.9)	Calcd.	63.14	5.30	11.36	8.87
				Found	62.81	5.30	11.18	9.17

[a] Not determined. – [b] Crystals which liquify in air.

Table 2. Significant IR (film spectra for oils, otherwise KBr pellets) and ^{1}H-NMR spectroscopic data (in $CDCl_3$, unless otherwise noted; singlets or quartets with the expected intensities) of novel starting materials and products

	IR $\tilde{\nu}$ [cm^{-1}]	^{1}H NMR [ppm] δ_{NCH_3}	δ_{NCH_2}	δ_{OCH_3}	δ_{SCH_3}	δ_{OCH_2}	δ_{SCH_2}
1a	1700	2.83	-	3.72	-	-	-
1b	1695	2.80	-	3.70	-	4.09	-
1c	1690	2.84	-	-	-	4.13	-
1d	1680	-	-	3.69	-	-	-
1e	1685	-	-	-	-	4.10	-
5a	1690,1715	3.00,3.14	-	3.73	-	-	-
5b	1690,1730	3.12,3.22	-	-	-	4.27	-
5c	1690,1730	3.09	3.75	-	-	4.23	-
5d	1685,1730	3.29	-	3.75	-	-	-
5e	1690,1725	-	3.80	-	-	4.20	-
6	1585	-	-	3.90	-	-	-
7	1615,1735	-	-	-	-	4.25,4.29	-
8a	1640	2.75	-	3.55	-	-	-
8b	1630	2.83	-	3.61	-	4.12	-
8c	1610	2.83	-	-	-	4.13	-
9	1620,1680, 1735	3.34,3.56	-	-	-	-	-
10	1780	-	-	-	-	-	-
11a	1770	-	-	-	-	-	-
11b	1760	3.54	-	-	-	-	-
12a	1646	2.95	-	3.73	2.34	-	-
12b	1648	2.91	-	3.68	-	-	2.88
12c	1643	2.96	-	-	2.35	4.18	-
12d	1642	2.91	-	-	-	4.13	2.90
14a	1680,1700	3.12,3.25	-	-	2.29	-	-
14b	1660,1710	3.11,3.20	-	-	-	-	2.93
14c	1655,1720	3.28	3.55	-	2.28	-	-
14d	1660,1700	3.24	3.60	-	-	-	2.91
15	1530	-	-	3.93	2.42	-	-
17	1650,1710, 3340	2.89 (d), 3.34	-	-	2.35	-	-
18	1665	3.34 3.44 [a]	-	-	2.23 2.28 [a]	-	-
19a	1615	2.87	-	3.64	2.19	-	-
19b	1620	2.80	-	3.52	-	-	2.80
19c	1615	2.86	-	-	2.16	4.19	-
19d	1615	2.87	-	-	-	4.13	2.90
23a	1570,1670	3.19	3.81	-	2.10	-	-
23b	1585,1670	3.28,3.32	-	-	-	-	2.83
24a	1660	2.80,3.00	-	3.74	-	-	-
24b	1660	2.79,2.98	-	-	-	4.01	-
25a	1640,1670	2.75,2.97 [a]	-	3.66 [a]	-	-	-
25b	1640,1670	3.10,3.24	-	-	-	4.43	-
		2.74,2.95 [a]	-	-	-	4.13	-
28	1490,1680	2.97,3.30	-	-	2.48	-	-
31b	1520	3.12, 3.36	-	-	-	4.48	-
32	1565,1605, 1640	2.75	-	3.65	-	-	-

[a] In *o*-dichlorobenzene.

(aryl-Me), 33.8 (NMe), 43.0 (NCH_2), 63.2 (OCH_2), 127.6–144.5 (aryl-C), 154.0, 154.6 (C=O).

Reaction of Imidocarbonate **1f** *with Isocyanate* **2a**: Without solvent, 1.65 g (10.0 mmol) of **1f** and 1.97 g (10.0 mmol) of **2a** were kept at 120°C for 2 h. The cooled reaction mixture was treated with ether. Product **6** spontaneously separated as colorless crystals (see Tables 1, 2).

Reaction of Imidocarbonate **1g** *with Isocyanate* **2a**: A solution of 0.68 g (3.0 mmol) of **1g**[13] and 0.59 g (3.0 mmol) of **2a** in 10 ml of ether was kept at room temperature for 5 days. Then the solvent was evaporated and the products **9**, **10**, **11b** were isolated by preparative TLC using ethyl acetate/petroleum ether (1:2). See Tables 1, 2. Additional data for **9**, **10**, **11b**, and **11a** (m.p. 117°C; ref.[22] 112–117°C), which was synthesized[23] for comparison:

9: ^{13}C NMR ($CDCl_3$): δ = 29.0, 29.8 (NMe), 121.1–129.6 (aryl-C), 150.4, 150.9, 154.1 (2C=O, C=N). – MS (70 eV): *m/z* (%) = 234 (38, $M^+ + 1$), 233 (71, M^+), 120 (49), 119 (100, PhNCO), 83 (85), 77 (55), 70 (40), 65 (45), 56 (58), 51 (55), 39 (56).

10: ^{13}C NMR ($CDCl_3$): δ = 21.8 (aryl-Me), 120.8–145.9 (aryl-C), 150.4 (C=O). – MS (70 eV): *m/z* (%) = 352 (12, $M^+ - 93$), 248 (80), 197 (23, $M^+ - 248$), 157 (22), 155 (100, Tos), 94 (38, PhOH), 93 (16, PhO), 91 (92, C_7H_7), 65 (80).

11a: ^{13}C NMR ($CDCl_3$): δ = 21.5 (aryl-Me), 121.1–149.1 (aryl-C), 149.7 (C=O).

11b: MS (70 eV): *m/z* (%) = 305 (2, M^+), 248 (74), 212 (4, M^+ – PhO), 157 (12), 156 (20), 155 (95, Tos), 93 (5), 92 (22), 91 (100, C_7H_7), 65 (63).

Reaction of Imido(thio)carbonates **1** (**12**) *with Isothiocyanate* **2b**: To a solution of 2–3 mmol of **1** or **12** in a few ml of ether the equimolar amount of **2b** in 5 ml of ether was added dropwise at room temperature. Spontaneous crystallization occurred for **8a–c**, **19a** and allowed isolation by filtration, whereas, to get **19b–d**, the reaction mixtures had to be concentrated. Because of the lability of the products, some analytical data are not satisfactory (Table 1). *C-{[(Ethylthio)methoxymethylene]methylammonio}-N-(tosyl)-thioformamidate* (**19b**, 60%, m.p. 49°C) and *C-{[Ethoxy-(ethylthio)methylene]methylammonio}-N-(tosyl)thioformamidate)* (**19d**, 30%, oil) were too unstable for elementary analysis. See Tables 1, 2.

Reaction of Imidothiocarbonates **12** *with Isocyanate* **2a**: Samples of 2.0 mmol of **12** and 0.40 g (2.0 mmol) of **2a** were stirred at 80–90°C for 40 h without a solvent. The products **14a–d**, **18**, **23a,b** were obtained by preparative TLC, eluent ethyl acetate/petroleum ether (1:1, 1:2, or 1:3). See Tables 1, 2. Additional data:

14a: ^{13}C NMR ($CDCl_3$): δ = 13.6 (SMe), 21.7 (aryl-Me), 34.9 (NMe), 128.6–145.1 (aryl-C), 155.7 (urea C=O), 171.0 (SC=O).

23a: ^{13}C NMR ($CDCl_3$): δ = 12.7, 14.0 (NCH_2CH_3, SMe), 21.5 (aryl-Me), 37.0 (NMe), 44.9 (NCH_2), 127.0–145.0 (aryl-C), 151.8

(C=N), 169.5 (C=O). – MS (70 eV): *m/z* (%) = 468 (7, $M^+ - 15$), 328 (15, $M^+ - 155$), 264 (45, $M^+ - 155 - SO_2$), 159 (37), 155 (98, Tos), 102 (38), 91 (100, C_7H_7), 75 (20), 65 (36).

23b: MS (70 eV): *m/z* = 454 (24, $M^+ - 29$), 264 (27, $M^+ - 155 - SO_2$), 159 (13), 155 (95, Tos), 102 (45), 91 (100, C_7H_7), 65 (31), 44 (29).

Hydrolysis of **14a**: 200 mg (0.63 mmol) of **14a** was suspended in 20 ml of dioxane/water/conc. hydrochloric acid (1:1:2), and the mixture was refluxed for 2.5 h. Workup was carried out by extraction with chloroform. The organic layers were dried over sodium sulfate and *S-methyl methyl[(methylamino)carbonyl]thiocarbamate* (**17**, 31%, oil, data in Table 2) isolated by preparative TLC (eluent ethyl acetate/petroleum ether 1:2). Tosylamide could not be detected.

Rearrangement of **15** *to Thiourethane* **18**: Imidothiocarbonate **15** was obtained by Delépine's method[18] (64%, m.p. 106°C; ref.[24] m.p. 112°C). In an NMR tube, a sample was heated in 1,2-dichlorobenzene at 150°C for 3 h. According to the ^{1}H-NMR spectroscopic evidence, conversion into **18** was then complete (Table 2).

Dipoles **25a, b** *from Isocyanate* **2a** *and Isoureas* **24a, b**: To a solution of 2.0 mmol of **24** in a few ml of ether the equimolar amount of **2a** was added dropwise at room temperature. Products **25a, b** spontaneously precipitated from the solution and were isolated by filtration. *1,2,3,3-Tetramethylisouronium-1-(N-tosylcarboxamidate)* (**25a**, 83%, Table 2) was too unstable for m.p. determination or elementary analysis. For **25b**, see Tables 1, 2.

Reaction of Isocyanate **2a** *with Isourea* **24c**: At 0°C, 1.97 g (10.0 mmol) of **2a** was added to a solution of 1.78 g (10.0 mmol) of **24c** in 40 ml of dry ether. A colorless precipitate separated and gradually dissolved again. Concentration of the solution and addition of petroleum ether provided crystals of **27** (2.50 g, 98%, m.p. 99°C; ref.[25] m.p. 98–100°C); phenyl isocyanate was detected in the solution.

Reaction of Isothiocyanate **2b** *with Isoureas* **24a, b**: To a solution of 2.0 mmol of **24** in a few ml of ether 0.43 g (2.0 mmol) of **2b** was added dropwise at room temperature. The precipitates, which separated, gradually disappeared again. Starting from **24a**, on prolonged standing **28** separated from the reaction mixture (Tables 1, 2). To isolate **31b** (59%, b.p. 203°C; ref.[26] b.p. 82.6°C/10 Torr), preparative TLC had to be employed (eluent ethyl acetate/petroleum ether 1:2).

Reaction of Isothiocyanate **2b** *with Isourea* **24c**: The synthesis of **32** was carried out by analogy with the reaction of the corresponding isothiourea[3c] (see Tables 1, 2); **31a** was detected in the mother liquor. Heterocycle **32** decomposed in acetonitrile to give oligomeric **30b**[3c].

Cross-over Experiment: 2.0 mmol each of **12b** and **c** were mixed with 0.79 g (4.0 mmol) of **2a** and the mixture stirred at 80°C for 41 h. Separation of the products **14a** (10%), **14b** (12%), **14c** (4%), and **14d** (7%) was achieved by preparative TLC with ethyl acetate/petroleum ether (1:5).

CAS Registry Numbers

1a: 106115-04-2 / **1b**: 106115-05-3 / **1c**: 106115-06-4 / **1d**: 22313-55-9 / **1e**: 6263-07-7 / **1f**: 13997-51-8 / **1g**: 33842-03-4 / **2a**: 4083-64-1 / **2b**: 1424-52-8 / **5a**: 106115-29-1 / **5b**: 106115-75-5 / **5c**: 106115-08-6 / **5d**: 106115-09-7 / **5e**: 106115-10-0 / **6**: 13063-51-9 / **7**: 106115-11-1 / **8a**: 106115-12-2 / **8b**: 106115-13-3 / **8c**: 106115-14-4 / **9**: 106115-15-5 / **10**: 106115-16-6 / **11a**: 18303-09-8 / **11b**: 106115-17-7 / **12a**: 18802-92-1 / **12b**: 89915-57-1 / **12c**: 106115-30-4 / **12d**: 89915-60-6 / **14a**: 106115-18-8 / **14b**: 106115-19-9 / **14c**: 106115-20-2 / **14d**: 106115-21-3 / **15**: 21569-18-6 / **17**: 106115-31-5 / **18**: 106115-22-4 / **19a**: 106115-23-5 / **19b**: 106115-32-6 / **19c**: 106139-06-4 / **19d**: 106115-33-7 / **23a**: 106115-24-6 / **23b**: 106115-25-7 / **24a**: 61373-14-6 / **24b**: 74448-05-8 / **24c**: 30543-43-2 / **25a**: 106115-34-8 / **25b**: 106115-26-8 / **27**: 27049-57-6 / **28**: 106115-27-9 / **31a**: 16703-45-0 / **31b**: 17996-38-2 / **32**: 106115-28-0 / $MeN=CCl_2$: 5652-90-4 / $MeNHCO_2Me$: 6642-30-4 / MeNCS: 556-61-6 / $MeNHCONMe_2$: 632-14-4 / *N*-cyclohexylimidocarbonyl dichloride: 2666-80-0

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