Synthesis of *N,N*′-Bis[1-chloroalkyl]carbodiimides

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We have found that *N,N*′-bis[alkylidene]ureas **1** react with phosphorus(V) chloride to give a good yield of previously unknown *N,N*′-bis[1-chloroalkyl]carbodiimides **4**.

Chlorination of **1** is carried out in boiling toluene and is complete within 1 h (cf. Ref. [1]). Apparently, the reaction proceeds through formation of addition products **2** that transform into diazadienes **3** under cleavage of phosphoryl chloride. This transformation may be facilitated by the six-membered cyclic transition state. Obviously, the diazadiene structure is not sufficiently stabilized by the substituents R^1, R^2, R^3, R^4 used here and undergoes rearrangement

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Table 1. *N*,*N'*-Bis[1-chloroalkyl]carbodiimides **4a–d**

Product No.	R^1	R^2	R^3	R^4	Yield [%]	b.p./torr	n_D^{20}	Molecular formula[a]	I.R. (CCl_4) $\nu_{N=C=N}$ [cm^{-1}]	^1H-N.M.R. (CCl_4) δ [ppm]	^{19}F-N.M.R. (CCl_4) δ [ppm]
4a	C_6H_5	CF_3	CF_3	C_6H_5	85	115°/0.05	1.5045	$C_{17}H_{10}Cl_2F_6N_2$ (427.2)	2165	7.65–7.92 (m, 4H); 7.13–7.42 (m, 6H)	0.31
4b	C_6H_5	CF_3	t-C_4H_9	t-C_4H_9	70	125°/0.03	—	$C_{18}H_{23}Cl_2F_3N_2$ (395.3)	2171	7.98–8.12 (m, 2H); 7.55–7.66 (m, 3H); 1.58 (s, 9H); 1.52 (s, 9H)	−1.21
4c	C_6H_5	t-C_4H_9	t-C_4H_9	C_6H_5	70	172°/0.03	—	$C_{23}H_{28}Cl_2N_2$ (403.4)	2165	7.82–8.0 (m, 4H); 7.42–7.63 (m, 6H); 1.33 (s, 9H); 1.28 (s, 9H)	—
4d	C_6H_5	t-C_4H_9	t-C_4H_9	t-C_4H_9	70	145°/0.03	—	$C_{21}H_{32}Cl_2N_2$ (383.4)	2167	7.82–7.93 (m, 2H); 7.43–7.55 (m, 3H); 1.55 (s, 9H); 1.48 (s, 9H); 1.36 (s, 9H)	—

[a] The microanalyses were in satisfactory agreement with the calculated values (C ±0.4, H ±0.5, Cl ±0.35).

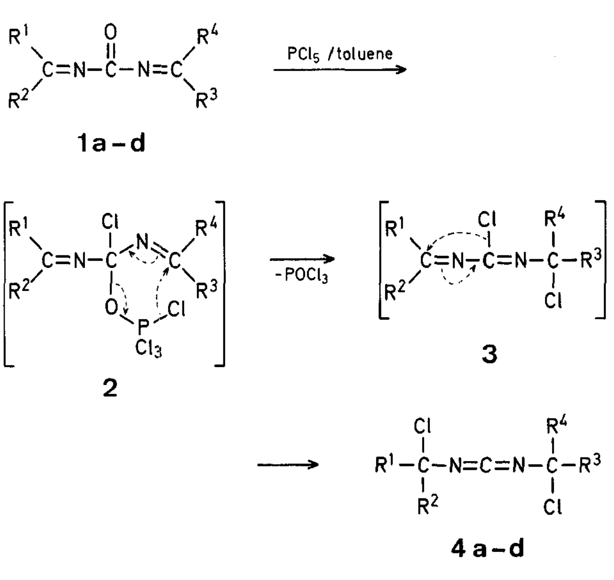
Table 2. *N*,*N'*-Bis[alkylidene]ureas **1a–d**

Product No.	R^1	R^2	R^3	R^4	Yield [%]	m.p. (hexane)	Molecular formula[a]	I.R. (CCl_4) $\nu_{C=O}$, $\nu_{C=N}$ [cm^{-1}]	^1H-N.M.R. (CCl_4) δ [ppm]	^{19}F-N.M.R. (CCl_4) δ [ppm]	M.S. (70 eV) m/e (M^+)
1a	C_6H_5	CF_3	CF_3	C_6H_5	70	96–98°	$C_{17}H_{10}F_6N_2O$ (372.3)	1720, 1670	7.68–7.95 (m, 10H)	10.9	372
1b	C_6H_5	CF_3	t-C_4H_9	t-C_4H_9	85	64–65°	$C_{18}H_{23}F_3N_2O$ (340.4)	1708, 1660	7.57–7.83 (m, 5H)	9.81	340
1c	C_6H_5	t-C_4H_9	t-C_4H_9	C_6H_5	60	151–153°	$C_{23}H_{28}N_2O$ (348.5)	1685, 1640	7.51–7.73 (m, 10H); 1.48 (s, 9H); 1.43 (s, 9H)[b]	—	348
1d	C_6H_5	t-C_4H_9	t-C_4H_9	t-C_4H_9	85	80–81°	$C_{21}H_{32}N_2O$ (328.5)	1695, 1650	7.40–7.55 (m, 5H); 1.48 (s, 18H); 1.43 (s, 9H)	—	328

[a] The microanalyses were in satisfactory agreement with the calculated values (C ±0.25, H ±0.45, N ±0.3).

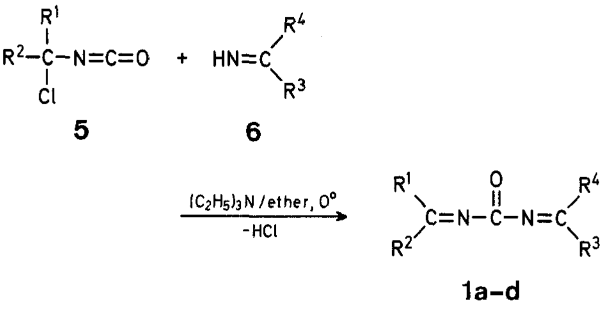
[b] $CDCl_3$ solution.

with migration of the chlorine atom in the C=N–C system. Similar migrations were found in a series of α-chloroalkyl isocyanates previously[2].



The *N*,*N'*-bis[1-chloroalkyl]carbodiimides **4** are colourless oils which are stable in dry air. Their structure is confirmed by microanalysis, I.R. and ^1H-N.M.R. spectroscopic data (Table 1).

The *N*,*N'*-bis[alkylidene]ureas **1** are obtained by reaction of the α-chloroalkyl isocyanates **5** with ketimines **6**.



Compounds **1a–d** are colourless crystalline substances which are stable in dry air. Their structure is confirmed by microanalysis, I.R. and N.M.R. spectroscopic data (Table 2).

The I.R. spectra were measured with a UR-20 infrared spectrometer. The ^1H-N.M.R. spectra were measured with a Tesla BS467 N.M.R. spectrometer using hexamethyldisiloxane as internal standard. The ^{19}F-N.M.R. spectra were measured with a Tesla BS 487B N.M.R. spectrometer using trifluoroacetic acid as internal standard.

_N,N'_-Bis[alkylidene]ureas 1a–d; General Procedure:

To a stirred solution of the α-chloroalkyl isocyanate **5** (0.1 mol) in anhydrous ether, a solution of ketimine **6** (0.1 mol) and triethylamine (0.1 mol) in ether is added dropwise. After the addition, the reaction mixture is heated at 30° and stirred during 3 h. Then triethylamine hydrochloride is filtered, washed with ether, and the filtrate is evaporated. Compounds **1a–d** are crystallized from hexane (Table 2).

***N,N'*-Bis[1-chloroalkyl]carbodiimides 4a–d; General Procedure:**
A solution of the urea **1a–d** (0.05 mol) and phosphorus(V) chloride (0.06 mol) in anhydrous toluene (50 ml) is heated under reflux for 1 h. After cooling, the reaction mixture is treated with sulfur dioxide to remove an excess of phosphorus(V) chloride. The solvent is evaporated and compounds **4a–d** are distilled in vacuo (Table 1).

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