Chemistry and Application of Organic Isocyanates. X [1]

Synthesis of Aliphatic Diisocyanates Containing Oxygen or Sulphur Bridge in Polymethylene Chain

Tadeusz Lesiak and Leszek Maciejewski

Toruń/Poland, Institute of Chemistry, Nicolaus Copernicus University

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One obstacle for continuation of our search reported in the last paper [1] (and the literature cited there), was the lack of commercially available new aliphatic diisocyanates. For that reason, we decided to synthesize some compounds of the type: $OCN(CH_2)_nO(CH_2)_nNCO$, as well as OCN $(CH_2)_nS(CH_2)_nNCO$ and $OCN-CH_2S(CH_2)_nSCH_2-NCO$.

Especially in this paper, we describe the syntheses of ether-diisocyanates of the formula given above, where n=2-4, or sulphido-diisocyanates where n=1 or 2. We prepared them by the method employed earlier by Lesiak et al. [2-4] based on the Curtius rearrangement. For identi-

fication purposes, the compounds were additionally transformed into urea derivatives by treatment with aniline or piperidine.

The starting compounds for the preparation of diisocyanates mentioned above were corresponding aliphatic diesters 2a - g, prepared from aliphatic diacids 1a - e and 1g or in case of diester 2f directly by condensation of thioglycolic acid, paraformaldehyde and ethanol. Compounds 2a - g have been subsequently transformed into dihydrazides 3a - g by treatment with hydrazine hydrate in ethanol. Dihydrazides obtained (3a - g) were converted into

Com- pound	Yield	M.p. or b.p./hP (°C)	Formula (molecular weight)	calcd./f C	ound H	N	i.r. film, cm ⁻¹	n.m.r. (TMS, CDCl ₃ , δ ppm)	n _D ²⁰
3a	85	145 – 146	C ₆ H ₁₄ N ₄ O ₃ (190.20)	37.89 37.85	7.42 7.67	29.46 29.16			
3 b	96	139 - 140	C ₈ H ₁₈ N ₄ O ₃ (218.26)	44.03 44.34	8.31 8.14	25.67 25.48			
3 c	77	141 - 142	C ₁₀ H ₂₂ N ₄ O ₃ (246.31)	48.76 48.38	9.00 8.88	22.75 22.40			
4 a	55	76-77/4	C ₆ H ₈ N ₂ O ₃ (156.14)	46.15 45.83	5.16 5.26	17.94 18.22	2275, 1130	3.3 – 3.5 (m, 4H, CH ₂ NCO) 3.5 – 3.7 (m, 4H, CH ₂ O)	1.4476
4c	61	114–115 /1.3	C ₁₀ H ₁₆ N ₂ O ₃ (212.25)	56.59 56.21	7.60 7.38	13.20 13.39	2270, 1100	1.64 (m, 8H, CH ₂ CH ₂ CH ₂), 3.3 (m, 4H, CH ₂ NCO), 3.42 (m, 4H, CH ₂ O)	1.4539
4 d	52	62 - 64/2.7	C ₄ H ₄ N ₂ O ₂ S (144.15)	33.33 33.24	2.80 2.90	19.43 19.54	2240	4.52 (s, 4H, CH ₂)	1.5170
4 e	58	94ª) /0.7-1.3	$C_6H_8N_2O_2S$ (172.21)	41.85 41.54	4.68 4.89	16.27 16.45	2260 2270	2.77 (t, 4H, CH ₂ S), 3.47 (t, 4H, CH ₂ NCO)	1.5102
4 f	51	118 – 124 /1.33	$C_5H_6N_2O_2S_2$ (190.24)	31.57 31.42	3.18 3.40	14.73 14.84	2270	3.98 (s, 2H, SCH ₂ S), 4.45 (s, 4H, CH ₂ NCO)	1.5600
4 g	60	142 – 144 /0.8	C ₆ H ₈ N ₂ O ₂ S ₂ (204.26)	35.28 35.12	3.95 4.04	13.71 13.68	2270	2.95 (s, 4H, CH ₂ CH ₂ CH ₂), 4.32, (s, 4H, CH ₂ NCO)	1.5663

Table 1 Physical constants and analytical data of dihydrazides 3a - c as well as diisocyanates 4a - g

^{a)} lit. [18] b.p. $100 - 120 \circ C/0.5 - 1 \text{ mm Hg}$

corresponding acyl diazides (reaction with acidified water solution of sodium nitrite). The latter compounds were converted *in situ* under Curtius rearrangement conditions, into diisocyanates 4a - g. These compounds are easily isolated and are not contaminated by any side products.

The treatment of diisocyanates 4a - g with aniline, or piperidine in benzene solution, yielded the appropriate N,N-disubstituted diureas 5a - g and 6a - g, respectively.

The structures of the compounds discussed above, shows the general formula "A" or "B".

$\begin{array}{ccc} R-(CH_2)_n-X-(CH_2)_n-R & \text{or} & R-CH_2-X-(CH_2)_m-X-CH_2-R \\ A & B \end{array}$

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Com- pound	R		x	n	m	Formula
1	СООН	a	0	2	_	А
2	COOEt	b	0	3	_	Α
3	CONHNH ₂	с	0	4	_	Α
4	NCO	d	S	1	_	Α
5	NHCONHC ₆ H ₅	е	S	2	_	Α
6	NHCONC ₅ H ₁₀	f	S	_	1	В
		g	S	_	2	В
		5	ļ			

The results of elementary analyses and physical constants of dihydrazides (3a-c) as well as diisocyanates (4a-g) are presented in the Table 1.

Among the compounds prepared, diisocyanates 4a, 4c, 4d, 4f and 4g and dihydrazides 3a, 3b and 3c as well as diurea derivatives 5a - g, and 6a - g are so far not reported in the literature.

Experimental

All melting points were not corrected. The IR spectra were determined with a Specord 71 R (Carl Zeiss Jena) spectrophotometer. The ¹H-NMR spectra were recorded on a Tesla BS-487C, 80 MHz instrument.

The starting aliphatic diacids 1a [5], 1b [6], 1c [7], 1d [8], 1e [9], and 1g [10], aliphatic diesters 2a [11], 2b [8], 2c [7], 2d [12], 2e [13], 2f [14], 2g [15] and bis(hydrazinocarbonylmethyl)sulphide (3d) [16], bis(β -hydrazinocarbonylmethyl)sulphide (3e) [16], bis(hydrazinocarbonylmethyl)thio)methane (3f) and 1,2-bis(hydrazinocarbonylmethyl-thio)ethane (3g) [17] have been prepared by similar methods reported in the literature cited.

Bis-γ-isocyanatopropyl ether (4b) Typical Procedure:

The agitated mixture of bis- γ -hydrazinocarbonylpropyl ether (**3b**) (17.5 g, 0.08 mol) and diluted hydrochloric acid (15 ml of conc. HCl and 70 ml of water) is cooled to 0 °C and a solution of sodium nitrite (10.7 g, 0.16 mol) in water (13 ml) is added at such a rate that the temperature does not exceed 15 °C. After addition of half of the sodium nitrite solution, benzene (25 ml) is added. After addition of the rest of sodium nitrite solution stirring is continued for 0.5 hour. Then the organic layer is separated and the aqueous layer extracted with benzene (3 × 10 ml). The combined benzene solution is dried over anhydrous calcium chloride, and carefully refluxed until evolution of nitrogen ceases (circa for one hour). From reaction mixture about 50 ml of benzene is distilled off and the residue purified by fractional distilla-

Table 2 Physical constants and analytical data of diureas 5a - g and 6a - g

Com-	M.p.	Formula	calcd./found				
pound	(°C)	(molecular weight)	С	Н	N		
5a	180 - 181	$\begin{array}{c} C_{18}H_{22}N_4O_3\\ (342.40)\end{array}$	63.14 63.20	6.48 6.33	16.36 16.08		
5 b	187 – 188	C ₂₀ H ₂₆ N ₄ O ₃ (370.46)	64.85 64.45	7.07 7.05	15.12 14.88		
5 c	189 - 190	C ₂₂ H ₃₀ N ₄ O ₃ (398.51)	66.31 66.80	7.59 7.36	14.06 14.42		
5 d	195 – 197	C ₁₆ H ₁₈ N ₄ O ₂ S (330.41)	58.16 58.04	5.49 5.60	16.96 16.80		
5 e	205 - 206	C ₁₈ H ₂₂ N ₄ O ₂ S (358.47)	60.31 60.40	6.19 6.36	15.63 15.78		
5 f	215 - 216	C ₁₇ H ₂₀ N ₄ O ₂ S ₂ (376.50)	54.23 54.06	5.35 5.48	14.88 14.62		
5 g	209 - 210	C ₁₈ H ₂₂ N ₄ O ₂ S ₂ (390.53)	55.36 55.51	5.68 5.76	14.35 14.21		
6 a	158 - 160	C ₁₆ H ₃₀ N ₄ O ₃ (326.44)	58.87 58.72	9.26 9.31	17.16 17.24		
6 b	106 - 107	C ₁₈ H ₃₄ N ₄ O ₃ (354.50)	60.99 60.98	9.67 9.90	15.80 15.74		
6 c	125 - 126.5	C ₂₀ H ₃₈ N ₄ O ₃ (382.55)	62.80 62.91	9.94 10.01	14.65 14.59		

Table 2(continued)

Com-	M.p.	Formula	calcd./fo	und		
pound	(°Č)	(molecular weight)	С	Н	N	
6 d	153.5 - 155	$C_{14}H_{26}N_4O_2S$	53.48	8.33	17.82	
		(314.45)	53.32	8.48	17.69	
6 e	130-131	$C_{16}H_{30}N_4O_2S$	56.11	8.83	16.63	
		(342.51)	56.23	8.79	16.14	
6 f	153 – 154	$C_{15}H_{28}N_4O_2S_2$	49.93	7.83	15.54	
		(360.54)	50.12	7.94	15.36	
6g	187 - 189	$C_{16}H_{30}N_4O_2S_2$	51.31	8.07	14.96	
-		(374.57)	51.24	8.28	14.82	

tion (under reduced pressure) to give 8.1 g (55%) of bis(γ -isocyanatopropyl)ether **4b**: b.p. $101 - 102 \degree C/5.3 hPa$ (lit. [18] 137 $\degree C/14 mm$ Hg), and n_D^{20} 1,4505.

IR (film, cm⁻¹): 2280 (NCO), 1120 (COC)

¹H-NMR (CDCl₃, TMS, δ ppm): 1.82 (m, 4H, CH₂CH₂CH₂), 3.38 (m, 4H, CH₂NCO), 3.5 (m, 4H, CH₂O).

Preparation of N,N-disubstituted diureas 5 a - g and 6 a - gFreshly distilled aniline or piperidine (0.03 mol) were added while stirring to 0.005 mol of appropriate diisocyanate 4a - g in 50 cm³ of anhydrous benzene, respectively. Then the reaction mixtures were boiled for 2 hours and afterwards the hot solutions were filtered off and allowed to crystallize. The precipitates obtained were refluxed with n-hexane and then recrystallized from methanol to constant melting points. Analyses and melting points of the diureas are given in the Table 2.

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Address for correspondence:

Prof. Dr. habil. T. Lesiak N. Copernicus University 7. Gagarin Street PL 87-100 Toruń, Poland