REACTIONS OF ASYMMETRIC CARBODIIMIDES WITH AZOIMIDE

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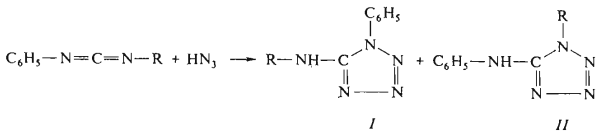
Reaction of asymmetric aliphatic-aromatic and diaryl carbodiimides with HN_3 leads to 1,5-disubstituted tetrazoles. Carbodiimides of general formula $C_6H_5—N=C=N—R$ (R = = alkyl) form an adduct at C=N bond exclusively at a less basic nitrogen, *i.e.* near phenyl whereas those with R = aryl afford a 1 : 1 mixture of products. ^{1}H-NMR spectroscopy revealed an aminotetrazole-iminotetrazoline tautomerism of the prepared 1-phenyl-5-alkylaminotetrazoles, which undergo isomerization to 1-alkyl-5-anilinotetrazoles.

One of possible preparations of 1,5-disubstituted tetrazoles involves reaction of carbodiimides with azoimide[1]. Cycloaddition to C=N bond of asymmetric carbodiimides can occur at both sides under formation of two various products. The ratio of those adducts depends on the dipolarophilic activity of both double bonds. The goal of this paper was to examine the behaviour of non-equivalent C=N bonds of the cumulated system of asymmetric carbodiimides towards azoimide.



I *II*

a, R = CH_3 *e*, R = cyclo-C_6H_{11}
b, R = i-C_3H_7 *f*, R = 4-CH_3—C_6H_4
c, R = i-C_4H_9 *g*, R = 4-CH_3O—C_6H_4
d, R = tert-C_4H_9

SCHEME 1

Therefore, a series of mixed aliphatic-aromatic and asymmetric diaryl carbodiimides was synthesized, which gave crystalline products with a benzene solution of azoimide in high yields at room temperature. Upon reaction of aliphatic-aromatic carbodiimides only 1-phenyl-5-alkylaminotetrazoles *I* were isolated (Scheme 1,

Table I). Spectroscopic search for the isomeric product *II* in the reaction mixture resulted in failure. The structural assignment was also evidenced by a double melting point[2], which is in accordance with values measured for *Ia* and *Ie*.

TABLE I

1-Phenyl-5-alkylaminotetrazoles

Compound	Formula (mol.w.)	Calculated/Found			M.p., °C yield, %	Time h
		% C	% H	% N		
Ia	$C_8H_9N_5$ (175·2)	54·84 54·80	5·18 5·00	39·98 38·87	133–134[a] 40[b]	0·5
Ib	$C_{10}H_{13}N_5$ (203·2)	59·09 59·28	6·44 6·44	34·45 34·45	118–119 78	2·5
Ic	$C_{11}H_{15}H_5$ (217·3)	60·80 60·94	6·95 6·96	32·23 32·40	142–143 90	0·5
Id	$C_{11}H_{15}N_5$ (217·3)	60·80 60·72	6·95 6·88	32·23 32·10	113–114 89	60
Ie	$C_{13}H_{17}N_5$ (243·3)	64·17 64·04	7·04 7·09	28·78 28·94	116–119[c] 82	60

[a] M.p. (ref.[2]) 133·5–136·5°C; [b] the lower yield of *Ia* is due to a rapid polymerization of the carbodiimide; [c] m.p. (ref.[2]) 120·5–121·5°C.

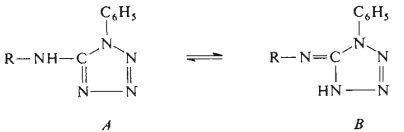
TABLE II

^{1}H-NMR Data[a] of 1-Phenyl-5-alkylaminotetrazoles

Compound	Amino form	Imino form	"NaOH"[b]
I	3·00 (d, 3 H, CH_3) $J_{CH_2,NH} = 4·81$	2·99 (s, 3 H, CH_3)	3·00 (s, 3 H, CH_3)
Ib	4·02 (m, 1 H, CH) $J_{CH_3,NH} = 7·60$	4·01 (m, 1 H, CH)	3·99 (m, 1 H, CH)
Ic	3·24 (q, 2 H, CH_2) $J_{CH_2,NH} = 6·00$	3·23 (d, 2 H, CH_2)	3·22 (d, 2 H, CH_2)

[a] δ, ppm, $(CD_3)_2CO$, J in Hz; [b] other chemical shift data except for NH were unaltered.

The synthesized compounds were characterized by a sharp singlet of aromatic protons (δ, ppm) in the 7·47–7·56 range (phenyl out of the tetrazole ring plane), by a broad singlet of the NH proton (5·97–6·21) and by signals of alkyl groups thus corroborating the existence of an aminotetrazole-iminotetrazoline tautomerism[3] (Table II). Resonation of the methyl group in *Ia* consisted of three peaks: of a singlet of the *B* form and a doublet of the tautometic *A* form (spin–spin interaction with the NH proton). The exchange rate of the proton is, under the given measurement conditions, low; nevertheless, addition of a few drops of 0·5M-NaOH considerably accelerates the tautomeric transformation. This interference results in a collapse of the methyl group resonances into a singlet of a time-averaging methyl signal. The methine proton of the isopropyl derivative *Ib* is represented by a complex multiplet of 21 peaks (14 of *A* form and 7 of *B* form), which, after addition of NaOH



SCHEME 2

solution collapsed into a septet. The signal of methylene group of *Ic* is formed by a quadruplet of *A* form and by a doublet of *B* form. The addition of NaOH is also associated with a collapse of the distinct methylene resonances to a doublet. Absorptions of the remaining alkyl protons of derivatives *Ib* and *Ic* were seen at 1·29 (d, 6 H, CH_3) and 0·92 (d, 6 H, CH_3) and at 2·01 (m, 1 H, CH). The ratio of tautomeric forms *A* : *B* 1 : 1 was found to be identic for compounds *Ia* and *Ic* on the basis of relative integrated intensities of the respective signals. Due to complexity of the multiplet of *Ib*, this ratio could not be determined. Derivatives *Id* and *Ie*, where the amino and imino forms cannot be distinguished, revealed following chemical shifts of alkyl groups: 1·41 (s, 9 H, CH_3), 1·07 (m, 10 H, CH_2) and 3·62 (m, 1 H, CH).

Both possible adducts were formed upon reaction of asymmetric aromatic carbodiimides with azoimide and their per cent representation was determined from the relative integrated intensities of methyl groups as follows: *If* : *IIf* = 1 : 1 (2·28, CH_3 in *I*; 2·45, CH_3 in *II*; total yield of both isomers 73%) and *Ig* : *IIg* = 1 : 1 (3·76, CH_3O in *I*; 3·90, CH_3O in *II*; total yield of both isomers 76%).

1-Phenyl-5-methylaminotetrazole and 1-phenyl-5-cyclohexylaminotetrazole were thermally isomerized at 180–200°C, ref.[2]; this transformation was applied to our compounds *I*, which afforded 1-alkyl-5-anilinotetrazoles *II* by this procedure. Differentiation between derivatives *I* and *II* by IR and UV was impossible, since

their absorption bands appeared almost at the same wavelengths. Exchange of substituents in positions 1 and 5 was significantly reflected in the ^{1}H-NMR spectrum (Table III). The original singlet of phenyl protons altered into a discernible multiplet of *o*-, *m*- and *p*-protons of the aniline moiety of the molecule, whereas signal of alkyl groups contracted their multiplicities and shifted down field. Basing upon these findings, we found the thermal range of isomerization of *Ic* to *IIc* to be 130–205°C.

EXPERIMENTAL

Melting points were determined on a micro hot-stage Boëtius, ^{1}H-NMR spectra, recorded with a Tesla BS 487 C apparatus operating at 80 MHz (internal reference substance hexamethyldisiloxane), are given in ppm (δ scale). Data listed in Tables II and III were obtained at a sweep width 50 Hz. The thermal interval of isomerization was determined in a cell heated to 160°C directly in the spectrometer; higher temperatures were attained by external heat. The starting carbodiimides were prepared by desulfuration of the corresponding thioureas with HgO (ref.[4]). A benzene solution of HN_3 was obtained according to[5].

1-Phenyl-5-alkylaminotetrazoles *Ia*–*Ie*

A 1M-solution of azoimide (20 ml, 20 mmol) was added to a solution of freshly prepared carbodiimide (10 mmol) in benzene (10 ml) and the mixture was allowed to stand at room tempera-

TABLE III
1-Alkyl-5-anilinotetrazoles

Compound	M.p., °C	Chemical shifts[a]			
		H_o	H_m	H_p	H-alkyl
IIa	185–186[b]	7·66	7·35	6·98	3·93 (s, 3 H, CH_3)
IIb	156–157[c]	7·71	7·34	6·98	1·51 (d, 6 H, CH_3) 4·89 (m, 1 H, CH)
IIc	147–148[d]	7·67	7·35	6·98	0·89 (d, 6 H, CH_3) 2·18 (m, 1 H, CH) 4·22 (d, 2 H, CH_2)
IId	177–178[e]	7·42	7·28	6·98	1·71 (s, 9 H, CH_3)
IIe	219–221[f]	7·65	7·34	6·98	2·30 (m, 10 H, CH_2) 4·50 (m, 1 H, CH)

[a] δ, ppm, $(CD_3)_2SO$; [b] m.p. (ref.[2]) 185·5–186·5°C; [c] for $C_{10}H_{13}N_5$ (203·2) calculated: 59·09% C, 6·44% H, 34·45% N; found: 59·20% C, 6·35% H, 34·53% N; [d] for $C_{11}H_{15}N_5$ (217·3) calculated: 60·80% C, 6·95% H, 32·23% N; found: 60·91% C, 6·90% H, 32·12% N; [e] for $C_{11}H_{15}N_5$ (217·3) found: 60·86% C, 6·80% H, 32·21% N; [f] m.p. (ref.[2]) 220·5–221·5°C.

ture. The product, precipitated within a time interval specified in Table I, was suction-filtered and crystallized from methanol jointly with the second crop obtained after concentration of the mother liquor.

1-Alkyl-5-anilinotetrazoles *IIa*—*IIe*

1,5-Disubstituted tetrazoles were heated in a glass autoclave for 1 h at 200—210°C. The melt was crystallized after cooling from methanol–acetone; the yields were quantitative.

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