sulting aminonitrile (II) ws identical to that described previously [3] (PMR spectrum, MH<sup>+</sup>, UV spectrum).

b) To 0.89 g (5 mmoles) of the cyanohydrin (VII) was added at 20°C with stirring over five minutes 0.37 g (5 mmoles) of diethylamine. The temperature of the mixture rose to 35-40°C, and after 30-45 min the mixture contained (II) alone (GLC and TLC). The product was separated as described above, the (II) obtained being identical to that previously described [3].

Purification of a small amount (1.46 g) of the aminonitrile (II) by vacuum distillation at 112.5-114°C (0.35 mm) over 15-20 min afforded a pure sample of (II),  $n_D^{20}$  1.5012 (cf. [3]) containing no thermal reaction products and identical with the material obtained above according to the IR and PMR spectra.

<u>Isomerization of (II) to (V)</u>. A solution of 1.17 g (5 mmoles) of (II) in 3 ml of acetonitrile (or toluene, or dioxane) was heated for a given length of time, completion of the reaction of (II) being followed by TLC and GLC. The solvent was evaporated, and the residue distilled in vacuo to give pure (V) as a pale yellow oil, bp 108-110°C (0.3 mm). UV spectrum:  $\lambda_{max}$  245 ( $\varepsilon$  7400) and  $\lambda_{pl}$  300 nm ( $\varepsilon$  670). IR spectrum, CCl<sub>4</sub>,  $\vee$ , cm<sup>-1</sup>: 2240 (CN) and 1655 (C=C). PMR spectrum ( $\delta$ , ppm, J, Hz): 1.05 t (6H, NCH<sub>2</sub>CH<sub>3</sub>), 1.32 s (3H, Me<sup>3</sup>), 1.57 s and 1.62 s (6H, Me<sup>7</sup> and Me<sup>8</sup>), 1.80-2.15 m (4H, CH<sub>2</sub>CH<sub>2</sub>), 2.92 q (4H, NCH<sub>2</sub>CH<sub>3</sub>), 3.65 d (1H, H<sup>2</sup>, J<sub>AB</sub> = 14), 4.94 m (1H, H<sup>6</sup>), 5.97 d (1H, H<sup>1</sup>, J<sub>AB</sub> = 14), in agreement with the data reported in [3].

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BENZOYLATION OF 1,4-DIAZA-1,3-BUTADIENES: SYNTHESIS OF REPRESENTATIVES OF A NEW CHEMICAL CLASS - 1,2-DIAMINO-1-CHLOROETHYLENES

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Trans-N,N'-dialkyl-N,N'-dibenzoyl-1,2-diamino-1-chloroethylenes - the first representatives of a new chemical class - and N,N'-dialkyl-N,N'-dibenzoyl-1,2-diaminoethylenes were obtained by benzoylation of N,N'-dialkyl-1,4-diaza-1,3-butadienes. On increase in pressure to 10,000 atm, the yields of the N,N'-dibenzoylated 1,2diamino-1-chloroethylenes increase, and those of the N,N'-dibenzoylated 1,2diaminoethylenes decrease.

The acylation of conjugated bis-amines has not been investigated whatsoever. The benzoylation of 1,4-diazabutadienes (I), undertaken in the present work, proceeds stereospecifically and results in the formation of new functional derivatives of ethylene

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TABLE 1. Products of Benzoylation of Compounds (Ic-e) with PhCOC1 in Benzene

Bis-imine (I)	Reaction products (mp, °C) <sup>a</sup> .	(III):(II) ratio, molarb
(Ic)	(IIc), 147–148	000
(Id)	(IId) 125-127 <sup>d</sup> (IIId)121-122,5 e	1:4
(Ie)	(IIe), 220,5–221 (IIIe), 232,5–234	1:3
<b>(</b> Ia)	(IIIa), 228-238	$_{\infty}f$

a) From MeOH.

b) Determined from PMR spectra of the reaction

mixture.

c) (IIIc) does not form at all.

d) Mixture of two diastereomers.

e) Mixture of meso- and dl-forms.

f) (IIa) is not formed at all.



R = t-Bu (a), Bu (b), i-Bu (c), sec-Bu (d), cyclohexyl (e).

The reaction of compounds (Ia-e) with PhCOCl was carried out in benzene in the presence of  $Et_3N$ . With aliphatic acid chlorides (MeCOCl, EtCOCl) or in more polar media (CHCl<sub>3</sub>, MeCN), no individual products could be isolated from the strongly resinified mixtures.

The specific nature of (I) is manifested not only in the conjugation of two imine groupings (the electronic factor), but also in the steric proximity of the latter, which renders the benzoylation reaction of (I) particularly sensitive to steric influences of radicals R. Compound (Ia) with bulky t-Bu groups did not change even on prolonged (20 h) boiling with PhCOC1, and the reaction between the reagents could be obtained only at high pressures. Bisimine (Ib) with inappreciable steric hindrances at the N-atoms, on the contrary, reacted with strong resinification, and the benzoylation products could not be isolated from the reaction mixtures. The benzoylation of (Ic-e) proceeded more smoothly and resulted in the readily crystallizable olefin derivatives (IIc-e) (yield 14-33%) and (IIId, e) (yield 6-7%). The ratio between (II) and (III) in the reaction mixtures depended on the volume of R: with increase in the steric hindrance the fraction of the reduction product (III) increased (Table 1).

The yield and ratio between (IId, e) and (IIId, e) are substantially influenced by pressure: the acylation of (Id, e) at 10,000 atm increases the yields of (IId, e) to 50%, while the fraction of (IIId, e) decreases to 2%, and the isolation of pure(IId, e) is considerably facilitated.

Olefins (IIc-e), (IIId-e) were obtained in geometrically individual forms (the PMR analysis of the reaction mixtures), which indicates a high steric selectivity of the acylation reaction of (Ic-e). The x-ray diffraction analysis (XRDA) [1] showed a trans configuration of (IIc), which in combination with the PMR data (the same values of the chemical shifts of HC= in (IIc-e)) makes it possible to assign the trans structure to other chloro derivatives also (IIc-e). The configuration of ethylenes (IIId-e) was not established.

The initial stage of the acylation reaction of conjugated (I) is, probably, the formation of a bis-adduct (VI), which reacts further along two specific paths: splitting of HCl leads to (II), while a partial reduction of the C=N bond with subsequent dehydrochlorination of (VII) leads to (III) (the molecule of the initial bis-imine (I) may play the role of a reducing agent)

$$\approx R - \dot{N} = CH - CH = \dot{N} - R$$

$$\downarrow COPh 2CI^{-} COPh$$

$$\downarrow (I1)$$

$$(VII)$$

$$(VII)$$

$$(I1)$$

$$(I1)$$

$$(I1)$$

$$(I1)$$

$$(I1)$$

$$(III)$$

$$(III)$$

$$(VII)$$

Compounds (IIc-e) containing the conjugated  $\sum_{N=C}^{1} = C = -N^{4}$  grouping are the first

representatives of a new chemical class — the 1,2-diamino-1-chloroethylenes. Using (IIc) as an example, it was found that the  $N^1-C^2$  bond is much shorter than an ordinary bond, the  $C^2$ -Cl bond is shorter than in MeCl, but longer than in  $CH_2$ =CHCl; the  $C^2$ -C<sup>3</sup> bond is somewhat shorter than in olefins, and approximately the same as in allenes. The  $C^3-N^4$  distance is approximately the same as in aliphatic amines [1]. According to the XRDA data, the benzoyl groups cause considerable steric hindrance and in particular strongly screen the C<sup>3</sup>-H proton. These structural features of 1,2-diamino-1-chloroethylenes conform with their usual chemical properties: under mild conditions (IIc) is stable toward alkalis (boiling in benzene with excess Et<sub>3</sub>N for 5 h or treatment with methanolic KOH at 20°C for 18 h), while under rigid conditions (boiling in a methanolic solution of KOH for 2 h) instead of the expected acetylene (IV), compound (V) is formed, which is a derivative of an ortho-form of glycine amide



## EXPERIMENTAL

The melting points were determined on a "Boetius" heating stage. The mass spectra were run on a "Varian MAT CH-6" spectrometer, the PMR spectra on a "Bruker WM-250" spectrometer and <sup>13</sup>C NMR spectra on a "Bruker AM-300" spectrometer (in CDCl<sub>3</sub>, the chemical shifts are given relative to TMS). Column chromatography was carried out on silica gel L 100  $\times$  160  $\mu$ , with elution with  $CH_2Cl_2$ , and then with a 1:1  $CH_2Cl_2$ -ether mixture. The course of the separation was monitored by TLC on Silufol, with development of the plate by iodine vapors. The elemental analysis of the previously not described compounds corresponded to the calculated values. The starting imines (Ia-c, e) were obtained according to [2]. The reactions under pressure were carried out in polyfluoroethylene ampuls, V = 1 ml. The mixture of the reagents was diluted by benzene to a volume of 1 ml, and then the ampuls were placed in a high-pressure reactor [3] and the conditions shown below were produced.

Di(sec-butylimino)ethane (Id). A 20.2 g portion (276 mmoles) of dl-2-aminobutane was added with stirring to 20 g (138 mmoles) of 40% glyoxal at <25°C. The mixture was extracted with ether, the extract was dried over  $Na_2SO_4$ , and compound (Id) was isolated by distillation. Yield 14.0 g (60%), bp 81-83°C (15 mm), mp 17.3°C. PMR spectrum (8, ppm): 0.65-1.8 m (16H, CH<sub>3</sub>, CH<sub>2</sub>), 3.18 m (2H, NCH), 7.90 s (2H, N=CH).

N,N'-Dibenzoyl-N,N'-di(isobutyl)-1,2-diamino-1-chloroethylene (IIc). A 1.41 g portion (10 mmoles) of PhCOCl was added dropwise, with stirring, to 0.84 g (5 mmoles) of a freshly distilled (Ic), 1.1 g (11 mmoles) of  $Et_3N$ , and 20 ml of benzene. The mixture was boiled for 30 min, evaporated, and 20 ml of CHCl, was added to the residue. The solution was washed with water, dried over Na2SO4 and evaporated to yield 0.68 g (33%) of (IIc). Mass spectrum m/z 414; 376 (M-HC1). PMR spectrum (δ, ppm): 0.60 d, 0.70 d (12H, CH<sub>3</sub>), 0.99 m (2H, (CH<sub>3</sub>)<sub>2</sub>. C<u>H</u>), 3.11 d, 3.32 d (4H, CH<sub>2</sub>), 6.07 s (1H, HC=), 7.2-7.7 m (10H, Ph). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 19.8 q (CH<sub>3</sub>), 25.8 d, 26.1 d ((CH<sub>3</sub>)<sub>2</sub>CH), 52.3 t, 53.1 t (CH<sub>2</sub>), 126.9 d, 128.0, 128.3 d, 129.8 d, 130.2 d, 130.5 d, 130.7 d, 132.5 s (CC1), 135.7 s, 136.7 s, 170.5 s (C=0), 170.7 s (C=0).

N,N'-Dibenzoyl-N,N'-di(cyclohexyl)-1,2-diaminoethylene (IIIe) and N,N'-Dibenzoyl-N,N'di(cyclohexyl)-1,2-diamino-1-chloroethylene (IIe). a) Benzoylation at Atmospheric Pressure. The benzoylation of (Ie) was carried out in a similar way. The reaction of 6.61 g (30 mmoles) of (Ie), 6.06 g (60 mmoles) of  $Et_3N$  and 8.43 g (60 mmoles) of PhCOC1 gave 3.77 g of a mixture of (IIe) and (IIIe), mp 223.5-226°C, which was separated chromatographically. Yield, 2.82 g (20%) of (IIe), R<sub>f</sub> 0.6 (benzene-ether, 1:1) and 0.90 g (7%) of (IIIe), R<sub>f</sub> 0.5 (the same system). Mass spectrum of (IIe): m/z 466. PMR spectrum of (IIe) (δ, ppm): 0.6-1.8 m (20H, CH<sub>2</sub> of cyclohexyl), 3.79 m, 3.98 m (2H, N-CH), 6.03 s (1H, HC=), 7.3-7.6 m (10H, Ph).

<sup>13</sup>C NMR spectrum of (IIe), (δ, ppm): 24.4 t, 24.6 t, 25.3 t, 25.7 t, 29.4 t (CH<sub>2</sub>), 57.5 d, 57.7 d (NCH), 126.9 d, 127.8 d, 127.9 d, 128.4 d, 129.9 d, 130.0 d, 134.0 s (CCl), 136.9 s, 137.7 s, 170.5 s (C=O). Mass spectrum of (IIIe): m/z 430. PMR spectrum of (IIIe) (δ, ppm): 0.7-1.7 m (20H, CH<sub>2</sub> of cyclohexyl), 4.07 m, (2H, NCH), 5.77 s (2H, HC=), 7.3-7.6 m (10H, Ph).

b) <u>Benzoylation at 10,000 atm</u>. A mixture of 220 mg (1 mmole) of (Ie), 281 mg (2 mmoles) of PhCOCl and 252 mg (2.5 mmoles) of  $Et_3N$  was heated for 1 h at 80°C. According to the PMR data, the reaction mixture contained 50% of (IIe) and 2% of (IIIe).

<u>N,N'-Dibenzoyl-N,N'di(sec-butyl)-1,2-diaminoethylene (IIId) and N,N'-Dibenzoyl-N,N'-di-(sec-butyl)-1,2-diamino-1-chloroethylene (IId). a) Benzoylation at Atmospheric Pressure.</u> The reaction of 3.36 g (20 mmoles) of (Id), 5.05 g (50 mmoles) of Et<sub>3</sub>N and 5.62 g (40 mmoles) of PhCOC1 gave 1.77 g of a mixture of (IId) and (IIId), mp 127.5-129°C, which was separated chromatographically. Yield 1.19 g (14%) of (IId) (mixture of two racemic diastereomers),  $R_f 0.7$  (benzene-ether, 1:1) and 0.48 g (6%) of (IIId) (mixture of meso- and dl-forms),  $R_f 0.6$  (the same system). PMR spectrum of (IId, ( $\delta$ , ppm): 0.5-1.6 m (16H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>), 3.7-4.2 (2H, N-CH), 5.98 s (1H, HC=), 7.2-7.6 m (10H, Ph). PMR spectrum of (IIId), ( $\delta$ , ppm): 0.5-1.5 m (16H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>), 4.0-4.4 (2H, N-CH) 5.90 s (2H, HC=), 7.2-7.6 m (10H, Ph).

b) <u>Benzoylation at 10,000 atm</u>. A mixture of 168 mg (1 mmole) of (Id), 281 mg (2 mmoles) of PhCOCl and 252 mg (2.5 mmoles) of  $Et_3N$  was heated for 1 h at 80°C. According to PMR data, the reaction mixture contained 50% of (IId) and 2% of (IIId).

<u>N,N-Dibenzoyl-N,N'-di(tert-butyl)-1,2-diaminoethylene (IIIa)</u>. A mixture of 168 mg (1 mmole) of (Ia), 281 mg (2 mmoles) of PhCOC1 and 252 mg (2.5 mmoles) of Et<sub>3</sub>N was diluted with benzene to 1 ml, held for 11 h at 80°C and 5000 atm, and diluted with 10 ml of CHCl<sub>3</sub>, washed with water, and dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated, and the residue was chromatographed to yield 15 mg (4%) of (IIIa), mp 228-238°C. PMR spectrum in CDCl<sub>3</sub> ( $\delta$ , ppm, relative to TMS): 0.92 s (18H, Me), 5.68 s (2H, HC), 7.3-7.6 m (10H, Ph). Mass spectrum: m/z 378.

<u>N,N'-Dibenzoyl-N,N'-di(isobutyl)-1,1-dimethoxy-1,2-diaminoethane (V)</u>. A mixture of 2.0 g (4.8 mmoles) of (IIc), 0.41 g (7.3 mmoles) of KOH and 20 ml of MeOH was boiled for 2 h to the disappearance of (IIc) (TLC control), evaporated, the residue was heated with 10 ml of benzene, filtered, and the filtrate was chromatographed. Yield 0.27 g (13%) of (V) in the form of an oil,  $R_f$  0.6 (benzene-ether, 2:1). Mass spectrum: m/z 440. PMR spectrum ( $\delta$ , ppm): 0.71 d, 0.92 d (12H,(CH<sub>3</sub>)<sub>2</sub>CH), 1.74 m, 2.00 m (2H, (CH<sub>3</sub>)<sub>2</sub>CH), 3.10 d (2H), 3.32 d (1H), 3.63 s (2H), 3.92 s (1H, NCH<sub>2</sub>), 3.71 s (3H, OCH<sub>3</sub>), 4.18 s (3H, OCH<sub>3</sub>), 7.25-7.40 (10H, Ph). <sup>13</sup>C NMR spectrum ( $\delta$ , ppm): 19.7 q (CH<sub>3</sub>), 27.0 d (CH), 46.7 t, 53.4 t, 57.2 t (CH<sub>2</sub>), 51.9 q (OCH<sub>3</sub>), 126.7 d, 128.2 d, 129.2 d, 130.8 s, 136.0 s, 169.4 s (C=0), 172.4 s (C=0).

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