Bis(5,5-dimethyl-1-oxide-4-oxo-2-phenylpyrrolin-1-yl-3)phenylmethane (XVb). A mixture of 0.4 g (2 mmoles) of pyrroline (Ib), 0.3 ml (3 mmoles) of benzaldehyde and 0.22 g (4 mmoles) of MeONa in 20 ml of MeOH was allowed to stand for 72 h at 20°C, and was then evaporated. Compound (XVb) was isolated by chromatography on a column with SiO_2, using $CHCl_3$ as eluent.

Bis(4-oxo-1-oxide-2,5,5-trimethyl-1-pyrrolin-2-yl-3)phenylmethane (XVa) was obtained under similar conditions from pyrroline (Ia).

LITERATURE CITED

1. V. A. Reznikov and L. B. Volodarskii, Khim. Geterotsikl. Soedin., No. 1, 120 (1990).
2. V. V. Martin and L. B. Volodarskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1336 (1980).
3. L. B. Volodarskii, I. A. Grigor'ev, and G. A. Kutikova, Zh. Org. Khim., 9, 1973 (1974).
4. I. A. Grigor'ev and L. B. Volodarskii, Zh. Org. Khim., 10, 118 (1974).
5. H. G. Aurich and W. Weis, Top. Curr. Chem., 59, 65 (1975).
6. V. A. Reznikov and L. B. Volodarskii, Inventor's Certificate No. 1,356,400 (USSR); Byull. Izobret., No. 24, 271 (1988).

SYNTHESIS OF ACYLKETENE N,N-ACETALS AND THEIR E,Z-ISOMERISM

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A method was proposed for the synthesis of acylketene N,N-acetals (AKA) by the action of methanol in the presence of Co^{2+} acetate on diacylketene N,N-acetals. Using ^1H and ^{13}C NMR spectroscopy, a restrainment of the internal rotation around the C=C bond of AKA was discovered, and the influence of solvation of the dynamic equilibrium of the E- and Z-isomers was studied.

Acylketene N,N-acetals (AKA) which are functionalized enaminoketones, are of interest as reagents for building up heterocyclic systems [1-3]. However, the methods of synthesis of these compounds either have been insufficiently developed or are limited in their possibilities. Thus, only in scattered cases can the AKA be synthesized by the reaction of amines with ketene S,S-acetals [4]. The synthesis of AKA by the action of ammonia and amines on 2-acylacetamidines appears to be more effective, but this method has until now been used quite rarely, and until [5], the structure of 2-acylacetamidines was ascribed to the reaction products. Individual representatives of AKA were obtained by acylation of 1,1-bis(piperidino)- or 1,1-bis(morpholino)ethene [6].

We have recently proposed a simple and effective method of synthesis of diacylketene acetals (DKA) by the reaction of monosubstituted cyanamides with β-diketones in the presence of 1-10 mole % of Ni^{2+} acetylacetonate [7-9]. In turn, the protolytic deacylation of DKA can obviously be used for the preparation of AKA, since it is well known that β-dicarbonyl compounds readily undergo acid [10] or alkaline [11] splitting. However, previously only two examples of the DKA → AKA transformation have been reported: by the action of aqueous H_2SO_4 on 2-(dibenzoylmethylene)-1-methylhexahydropyrimidine [12] and of MeSH on 2-(diacetylmethylene)-1-methylimidazolidine [13].

It was shown in the present work that the reaction of MeOH with DKA (Ia-e) in the presence of 5 mole % of $Co(OAc)_2 \cdot 4H_2O$ results in the formation of AKA (IIa-e) in high yields (Table 1).

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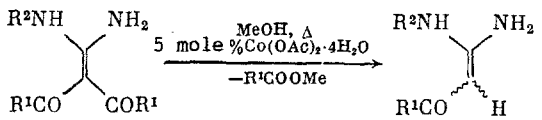
TABLE 1. Acylketene N,N-Acetals (IIa-e)

AKA	Time of synthesis, h	Yield, %	Mp, °C*	Found/Calculated, %			Empirical formula	Mass spectrum $[M]^{+\cdot}$, m/z	IR spectrum in $CHCl_3$, ν, cm^{-1}
				C	H	N			
(IIa)	1	82	131–133	68.45 68,16	6.80 6.86	15.65 15,90	$C_{10}H_{12}N_2O$	176	3527, 3485, 3422 (NH), 3350–2800 (NH, CH), 1625, 1615, 1598 (CO, C=C)
(IIb)	15	62	164–166	75.55 75,60	6.03 5,92	11.81 11,75	$C_{15}H_{14}N_2O$	238	3526, 3480, 3422 (NH), 3300–2800 (NH, CH), 1625 1615 ‡, 1597, 1580 (CO, C=C)
(IIc) †	3	75	143–144	–	–	–			3505, 3340 (NH), 3450–2800 (NH, CH), 1705 ‡, 1696 (CON), 1645 ‡, 1630, 1590 (CO, C=C)
(IId)	12	85	163–164	64.79 64,69	5.96 5,92	13.71 13,72	$C_{11}H_{12}N_2O_2$	204	3505, 3460–2700 (NH, CH), 1680 (CON), 1630, 1580 (CO, C=C)
(IIe)	6,5	90	188–189	58.51 58,23	6.73 6,84	27.38 27,17	$C_{10}H_{14}N_4O$	206	3501, 3440 (NH), 3400–2800 (NH, CH), 1631, 1602, 1570 (CO, C=N, C=C)

*The following solvents for recrystallization were used: (IIa, e), benzene; (IIb), benzene–hexane (4.5:1); (IIc), benzene–hexane (3:1); (IId), benzene–hexane (1:1).
†The compound is identical to that isolated from the products of the reaction of cyanamide with acetylacetone [14].
‡Shoulder.



(Ia–e) (IIa–e) (1)

R^1 = Me, R^2 = Ph (a); $R^1 = R^2$ = Ph (b); R^1 = Me, R^2 = Me CO (c); R^1 = Me, R^2 = =PhCO (d); R^1 = Me, R^2 = 4,6-dimethylpyrimidin-2-yl (e).

Salts of transition metals were previously used as catalysts of the alcoholysis of alkenyl-β-dicarbonyl compounds [15]. It should be noted however that our attempts to use Ni^{2+} and Mn^{2+} acetates instead of Co^{2+} acetate were unsuccessful [compound (II) was formed in inappreciable amounts].

It can be assumed that in a similar way as in [15], process (1) includes the formation of chelate complexes (III) and (IV) formed by Co^{2+} with ligands (I) and (II). (The possibility of formation of chelates of DKA with the M^{2+} salts was shown by us in [8].)

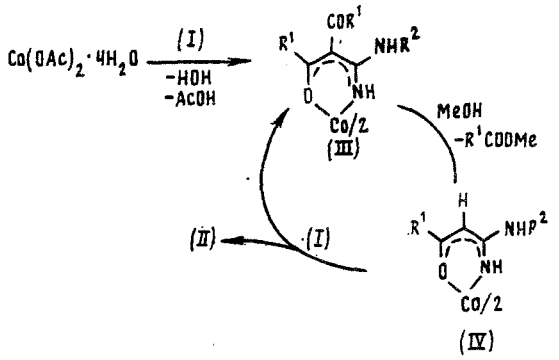


TABLE 2. PMR Spectra of AKA (IIa-e) and DKA (V)

Compound	Solvent	T, °C	Ratio of isomers	δ, ppm*				
				=CH	CH_3CO	CH_3CON	NH	remaining protons
(IIa)	$CDCl_3$	22	1 : 2	4,83 4,79	1,98 2,04	–	12,74; 4,70	7,45–7,14 (Ph)
	$(CD_3)_2SO$	22	1 : 1,9	4,75	1,84	–	13,0; 8,75; 6,69	7,44–7,10 (Ph)
(IIb)	$CDCl_3$	22	1 : 1,3	5,47	–	–	13,30; 4,71	7,92–7,16 (Ph)
	$(CD_3)_2SO$	22	1 : 1,7	5,50 5,44	–	–	13,45; 10,52; 9,03; 6,95	7,80–7,10 (Ph)
	$(CD_3)_2SO$	80	1 : 1,7	5,45	–	–	13,45; 8,70; 6,72	7,83–7,11 (Ph)
(IIc)	$CDCl_3$	22	1 : 3,2	4,69 4,75	2,14 2,20	1,98 2,00	13,68; 9,30	–
	C_5D_5N	22	1 : 1,5	5,08 5,00	2,02 2,03	2,00	14,32; 11,32; 10,85; 9,05; 8,70	–
	C_5D_5N	105	–	4,97	2,08	2,02	14,10; 10,50; 9,60; 8,00	–
	$(CD_3)_2SO$	22	1 : 2,5	4,74	2,10 2,04	1,84 1,85	13,71; 10,21; 9,90; 8,30; 8,00 7,70	– –
(IId)	$CDCl_3$	22	1 : 15,5	4,93 4,86	2,05	–	14,80; 8,80	8,14–7,33 (Ph)
	CD_3CN	22	1 : 9,8	5,00 4,91	2,21	–	15,03; 8,87	8,10–7,47 (Ph)
	C_5D_5N	22	1 : 12,2	5,29 5,20	2,05 2,08	–	15,60; 11,00; 8,95	8,35–7,30 (Ph)
	$CDCl_3$ – $(CD_3)_2SO$, 1 : 1	22	1 : 6,2	5,14 4,86	1,97	–	14,90; 10,15; 8,50; 8,30	8,03–7,28 (Ph)
	$(CD_3)_2SO$	22	1 : 3,7	5,23 4,92	1,90 1,92	–	15,05; 10,38; 10,10; 8,40; 8,30	8,03–7,48 (Ph)
	$(CD_3)_2SO$	120	1 : 3,7	5,30 4,95	1,97	–	13,57; 10,03; 9,02; 7,80	8,04–7,47 (Ph)
(IIe)	$CDCl_3$	22	1 : 1,6	4,69 4,74	2,00 2,02	–	13,50; 10,53; 9,40; 7,49	6,65, 6,59 (CH of pyrimidine ring), 2,36, 2,34 (2 Me)
	$(CD_3)_2SO$	22	1 : 1,9	4,93 4,76	1,81 1,87	–	13,57; 9,82; 7,67; 10,42; 10,02; 9,23	6,85, 6,88 (CH), 2,39 (2Me)
	$(CD_3)_2SO$	110	–	5,14–4,67 †	1,88	–	13,48; 9,56; 7,93	6,81 (CH); 2,39 (2Me)
(V)	C_5D_5N	22	–	–	2,45	–	10,74; 7,72	–

*The signals of the minor isomer are given in the upper row (except for the signals of the Ph and NH groups which are given without assignment.

†Broad signals (ω ~ 30 Hz).

Deacylation of DKA by the action of MeOH in the presence of catalytic amounts of Co^{2+} acetate is a more suitable and universal method, compared with methods using alkaline and acid reagents. Thus, while compounds (IIa, b, e) are readily formed by the action of equimolar amounts of MeONa in MeOH on the corresponding DKA (Ia, b, e), compounds (IIc, d) cannot be obtained in this way, since the reaction proceeds with splitting off of the N-acyl group. (In the preceding article we described the synthesis of 3-(diaminomethylene)pentane-2,4-dione (V) from (Id) by the action of MeONa [9].)

Deacylation of (Id) with Bu_2NH in boiling BuOH proceeds nonselectively with the formation of a mixture of (IId) and (V), which were separated by column chromatography in yields of 30 and 55%, respectively.

Acid splitting of (Id) by a solution of aqueous H_2SO_4 in MeCN, and subsequent treatment of the reaction mixture with NH_4OH give a low yield of (IId). Substantially better results are obtained by using 57% $HClO_4$. Compounds (IId, e) were synthesized in this way. 2-Acetyl-

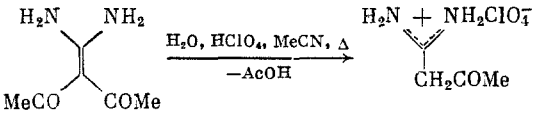
TABLE 3. ^{13}C NMR Spectra of AKA (IIa-e) in $(CD_3)_2SO$

AKA	δ, ppm*						
	CO	CON	NCN	=CH	CH_3CO	CH_3CON	Ph
(IIa)	189.41 187.85	–	159.32	79.73 80.79	28.82 28.20	–	138.03; 137.50; 129.52; 129.29; 128.30; 124.57; 124.12; 122.84
(IIb)	183.43 181.99	–	160.75	77.65 78.78	–	–	141.86; 141.50; 137.99; 137.70; 131.32; 131.23; 129.63; 128.42; 128.15; 128.19; 125.05; 124.62; 123.34; 123.19
(IIc)	192.96 192.16	172.58 172.25	156.58 157.87	81.73 82.00	28.94 28.74	24.15 24.76	–
(IId)	192.81 193.41	167.63 168.66	158.56 156.60	83.14	28.69 29.25	–	133.25; 132.72; 132.63; 129.17; 128.58; 128.01; 127.56
(IIe) †	189.64 190.44	–	158.32	81.33	28.56	–	–

*The signals of the minor isomer are given in the lower row (except for the signals of the Ph group which are given without assignment).

†The spectrum also contains the signals of 4,6-dimethylpyrimidin-2-yl group (δ, ppm): 167.43 (C^2), 158.16 (C^4 and C^6), 113.91 (C^5 of the predominant isomer), 113.51 (C^5 of the minor isomer), 23.16 (2Me).

acetamidinium perchlorate (VI) was obtained by the action of $HClO_4$ on (V). Compounds (I) are not deacylated by acetic acid.

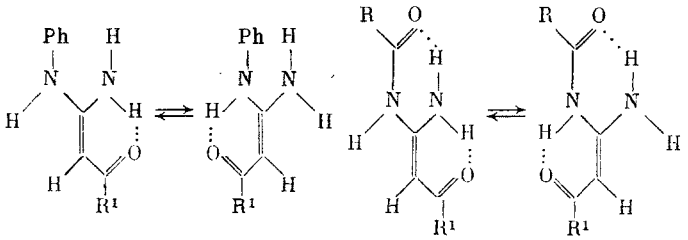


(V) (VI)

An attempt to carry out the hydrolysis of DKA over SiO_2 (similarly to the transformation of 3-[(1-amino-1-methylthio)methylene]pentane-2,4-dione [16]) did not produce positive results.

The structure of AKA was confirmed by IR, ^1H and ^{13}C NMR, and mass spectrometric methods. The mass spectra of (IIa-e) contain intense peaks of molecular ions. In the IR spectra of (IIa-e), absorption bands are observed of both free and bound NH groups. The form of the spectra in $CHCl_3$ does not change on high dilution, i.e., as in the case of AKA (Ia-e) [9], the formation of strong intramolecular hydrogen bonds (IHB) is characteristic for these compounds. The amide groups in (IIc) and (IId) have absorption bands at 1705 and 1680 cm^{-1}, respectively (compare: in (Ic) in $CHCl_3$ – 1710 cm^{-1} [16] and in (Id) in CCl_4 – 1680 cm^{-1} [8]).

The ^1H and ^{13}C NMR spectra of compounds (IIa-e) in various solvents exhibit double sets of signals of the separate groups of atoms (Tables 2, 3). This indicates the existence of the AKA (Ia-e) in the form of an equilibrium of E- and Z-isomers. As known, for DKA containing two Me_2N groups, the rotation barrier around the C=C bond is very low ($\Delta G^{\neq} < 10$ kcal/mole) [17]. We have previously shown for N,N-acetals of alkoxycarbonyl(acyl)ketenes that the restrainment of the rotation around the C=C bond increases because of the presence of the IHB [9]. It can be assumed that a similar effect in the case of (IIa-e) is also attributable to the existence of IHB in these compounds.



E *Z* *E* *Z*

Signals of the two isomers are observed in a ratio of 1:1.5 in the PMR spectrum of (IIc) in C_5D_5N, while in the spectrum of (IId) in the same solvent, they occur in a ratio of 1:12.2. The weakest-field signal of the minor isomer (IIc) with δ 14.32 ppm should be assigned to a proton of an amide group, which participates in the formation of IHB [compare with signals at δ 14.2 ppm in the spectrum of (Ic) in C_5D_5N]. In the spectrum of compound (V) which does not contain an amide group, the weakest-field NH signal has a chemical shift of 10.74 ppm. It follows from this that the minor isomer (IIc) has a Z-configuration. This assignment is confirmed by a double resonance experiment, which reveals the presence of a spin–spin interaction between the methine proton of the E-isomer (a signal with δ 5.00 ppm is in the form of a broadened triplet) and the NH group protons (δ 10.85 and 9.05 ppm).

Similar considerations lead us to conclude that in (IId) in C_5D_5N, the Z-isomer is predominant [the weakest-field signal with δ 15.60 ppm belongs to this isomer; compare with the signal with δ 15.35 ppm in the spectrum of (Id) in C_5D_5N].

The ratio of the isomers in AKA (IIc, d) is substantially dependent on the solvent. Thus, for example, in the spectrum of (IIc) in $(CD_3)_2SO$, the ratio of E- and Z-isomers is 2.5:1, while on the contrary, in $CDCl_3$ the Z-isomer predominates (1:3.2). These data indicate a strong influence of solvation on the dynamic equilibrium of the AKA isomers. In the preceding article [9], we showed that in $(CD_3)_2SO$, the interconversion of the E- and Z-isomers of alkoxycarbonyl(acyl)ketene N,N-acetals is facilitated by partial cleavage of the IHB. The effect of the influence of solvents on the rate and position of the dynamic equilibrium is well known and is often interpreted by using an empirical parameter E_t scale as a measure, which makes allowance for both the polarity of the solvent and its ability to produce hydrogen bonds [18]. It may be assumed that increase in the content of the E-isomer of the AKA with increase in the value of E_t of the solvent, is due to some extent to both the facilitation of the IHB cleavage in the Z-isomer, and the prefered solvation of the E-isomer by a polar solvent having a free NH group of the amide function. However, the data obtained also indicate that the E_t scale has to be used cautiously for the interpretation of the dynamic equilibrium of AKA [thus, the content of the E-isomer for (IId) in CD_3CN (E_t 46.0) is lower than in $(CD_3)_2SO$ (E_t 45.0)].

According to the PMR spectral data, in the case of AKA (IIa, b, e) the ratio of the isomeric forms also changes on changing the solvent, but for these compounds it was difficult to assign the signals specifically to the E- or Z-isomers.

It should be noted that the rate of the dynamic equilibrium of AKA (IIa-e) is substantially dependent on the nature of the substituent at the N atom. Thus, a slow interconversion on the NMR time scale of the isomers of (IIa) in $(CD_3)_2SO$ takes place even at 20°C (one set of the Me and CH group signals is observed in the PMR spectrum, but double sets of signals are seen in the ^{13}C NMR spectrum). This process becomes rapid above 76°C [smoothening out of signals of the (IIa) isomers in the ^{13}C NMR spectrum]. A coalescence of CH group signals in the PMR spectrum of (IIb) in $(CD_3)_2SO$ is reached at 80°C. Indications of interconversion of the isomers are observed in the PMR spectra: for (IIc) in C_5D_5N at 105°C, and for (IIe) in $(CD_3)_2SO$ above 100°C. The strongest restrainment of the rotation around the C=C bond occurs in the case of (IId). The coalescence of the CH group signals in the PMR spectra of (IId) in $(CD_3)_2SO$ is not reached even at 120°C (the ratio of the E- and Z-isomers is retained unchanged under these conditions).

EXPERIMENTAL

The PMR spectra were recorded on a "Bruker WM-250" spectrometer and the ^{13}C NMR spectra on a "Bruker AM-300" spectrometer. The IR spectra were run on a UR-20 spectrometer. The mass spectra were obtained on a "Varian MAT CH-6" mass spectrometer.

The diacylketene N,N-acetals (Ia, b, d, e) were obtained according to [9].

3-[(N-Acetyl)diaminomethylene]pentane-2,4-dione (Ic). A mixture of 0.600 g of (V) [5] and 0.454 g of Ac_2O in 12 ml of benzene was boiled for 1.5 h. The solvent was distilled off, and the residue was recrystallized from hexane. Yield 0.660 g (84%) of (Ic), mp 59-60°C. The product was identical with that previously synthesized by us from NH_2CN and acetylacetone [14].

Acylketene N,N-acetals (IIa-e). a) A mixture of 20 mmoles of (Ia-e) and 1 mmole of $Co(OAc)_2 \cdot 4H_2O$ in 40 ml of MeOH was boiled for 1-15 h (see Table 1). The solvent was distilled off (1 torr), $CHCl_3$ was added to the residue, and the mixture was filtered through SiO_2 (L 40/100 μm, eluent – $CHCl_3$). Chloroform was distilled off, the residue was recrystallized from a suitable solvent, and compounds (IIa-e) were obtained.

The yields, the elemental analysis data, and the physicochemical characteristics of AKA (IIa-e) are given in Table 1, while the ^1H and ^{13}C NMR spectral data of these compounds are given in Tables 2 and 3, respectively.

b) A mixture of 2 mmoles of (Ia, b), 4.5 ml of MeOH, and 2.4 mmoles of MeONa was stirred at 50°C for 1 h. Acetic acid (2.4 mmoles) was added at 20°C to the reaction mixture, which was then stirred for 15 min. The solvent was distilled off, $CHCl_3$ was added to the residue, and the mixture was filtered through SiO_2 (L 40/100 μm, eluent – $CHCl_3$). Chloroform was distilled off, and the residue was recrystallized from benzene (IIa) or a benzene–hexane (4.5:1) mixture (IIb). Yield, 1.74 mmoles (87%) of (IIa) or 1.48 mmoles (74%) of (IIb).

c) A mixture of 0.500 g of (Id) and 0.268 g of Bu_2NH in 5 ml of BuOH was boiled for 6 h. The solvent was distilled off, and the residue was chromatographed on a column with SiO_2 (L 40/100 μm, eluent benzene–EtOH). The solvent was distilled off, and 0.120 g (30%) of (IId) was obtained from the fraction with R_f 0.29 (eluent benzene–EtOH, 20:1), while from the fraction with R_f 0.13 (benzene–EtOH, 10:1), 0.160 g (55%) of (V) was obtained. Compound (V) was identical to that which we previously obtained from (Id) and MeONa [9].

d) A mixture of 1 mmole of (Id) or (Ie) with 4 ml of MeCN and 0.12 ml of 57% aqueous $HClO_4$ was boiled for 4.5 (Id) or for 1.5 h (Ie). The solvent was distilled off, and the residue was treated with 13 ml of 6% NH_4OH, and extracted with 4 × 20 ml of $CHCl_3$. The organic layer was separated, dried over $MgSO_4$, and $CHCl_3$ was distilled off. Yield, 0.72 mmole (72%) of (IId) or 0.96 mmole (96%) of (IIe).

2-Acetylacetamidinium Perchlorate (VI). A mixture of 0.400 g of (V) with 8 ml of MeCN and 0.5 ml of a 57% aqueous $HClO_4$ was boiled for 2.5 h. The solvent was distilled off. The crystalline residue was dissolved in 1 ml of EtOH and salted out with 25 ml of Et_2O. Yield 0.330 g (59%) of (VI), mp 78-79°C. Mass spectrum (m/z): 100 $[M - HClO_4]^{+\cdot}$. Found, %: C 24.18, H 4.89, N 13.93, Cl 17.87. $C_4H_8N_2O \cdot HClO_4$. Calculated, %: C 23.95, H 4.52, N 13.96, Cl 17.67. IR spectrum (KBr, ν, cm^{-1}): 3500-3140 (NH), 1728 (CO), 1686 (C=N). PMR spectrum [$(CD_3)_2SO$, δ, ppm): 8.60-8.10 br. s ($2NH_2$), 4.05 s (CH_2), 2.27 s (Me). ^{13}C NMR spectrum [$(CD_3)_2SO$, δ, ppm): 200.55 (CO), 166.21 (NCN), 46.11 (CH_2), 29.90 (Me).

LITERATURE CITED

1. V. Aggarwal, H. Ila, and H. Junjappa, Synthesis, 65 (1982).
2. Zh.-t. Huang and Zh.-r. Lin, Heterocycles, 24, 2247 (1986).
3. H. Grassivaro, E. Rossi, and R. Stradi, Synthesis, 1010 (1986).
4. M. Augustin, Ch. Groth, H. Kristen, et al., J. Prakt. Chem., 321, 215 (1979).
5. Zh.-t. Huang and Zh.-r. Lin, Synthesis, 357 (1987).
6. A. A. Armati, P. De Ruggieri, E. Rossi, R. Stradi, Synthesis, 573 (1986).
7. V. A. Dorokhov, M. F. Gordeev, Z. K. Demyanets, and V. S. Bogdanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1683 (1987).
8. V. A. Dorokhov, M. F. Gordeev, M. N. Bochkareva, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1134 (1989).
9. V. A. Dorokhov, M. F. Gordeev, Z. K. Dem'yanets, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1806 (1989).
10. H. Adkins and H. Kutz, J. Am. Chem. Soc., 52, 3212 (1930).
11. H. Kutz and H. Adkins, J. Am. Chem. Soc., 52, 4036 (1930).
12. M. D. Nair, S. Rajapa, J. A. Desai, Ind. J. Chem., 21B, 1 (1982).
13. Zh.-t. Huang and L.-h. Tsai, Chem. Ber, 119, 2208 (1986).
14. V. A. Dorokhov, M. F. Gordeev, and V. S. Bogdanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1431 (1988).

15. K. Uehara, F. Kitumara, and M. Tanaka, Bull. Chem. Soc., Jpn., 49, 493 (1976).
16. V. A. Dorokhov and M. F. Gordeev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 941 (1988).
17. J. Sandstrom, Topics in Stereochemistry, Vol. 14, H. L. Alinger, E. Eliel, and S. H. Willen (eds.), John Wiley, N.Y. (1983), p. 83.
18. G. Reichardt, Angew. Chem. Int. Ed., 18, 98 (1979).

CYCLOADDITION OF α-DIALKYLBORYLAMINO-N-HETEROCYCLES TO CYANAMIDES

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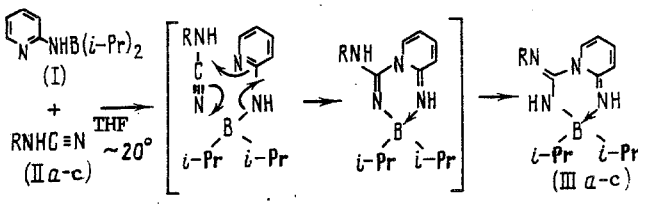
α-Diisopropylaminopyridine and 2-dipropylborylamino-1-methylbenzimidazole react with cyanamides to give chelate [4+2]-cycloadducts. X-ray crystallography has been used to establish the molecular and crystal structure of the product of the reaction of α-diisopropylaminopyridine and benzoylcyanamide.

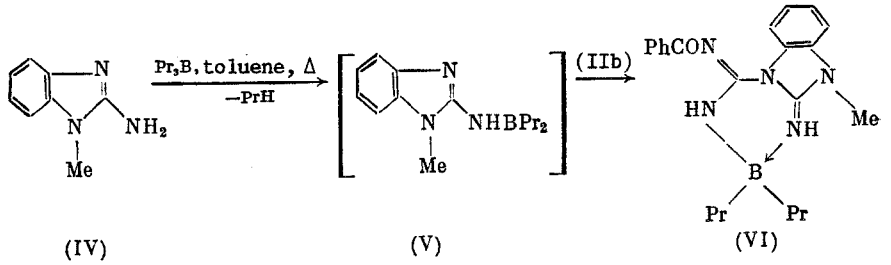
We have previously found that borylated α-amino-N-heterocycles (BAH) undergo a unique [4+2]-cycloaddition to isocyanates [1-3], isothiocyanates [2, 4], diphenylcarbodiimide [5], malononitrile [5], ethyl cyanoacetate [6], and ethoxyacetylene [7]. In these reactions, the BAH undergoes attack of the reagent on the double bond at boron and the terminal nitrogen, rather than at the B–N bond, such as occurs in aminoboration [8].

We have now examined the reaction of BAH with cyanamides. It was found that 2-diisopropylborylaminopyridine (I) adds smoothly to phenylcyanamide (IIa), benzoylcyanamide (IIb), and (benzimidazol-2-yl)cyanamide (IIc) in THF at ~20°C to give the yellow, crystalline [4+2]-cycloadducts (IIIa-c), isolated in yields of 78-85%.



R = Ph(a); R = PhCO (b); R- benzimidazol-2-yl (c).

Similarly, 2-dipropylborylamino-1-methylbenzimidazole (V) reacts with (IIb) to give the [4+2]-cycloadduct (VI) (the BAH (V) was obtained by boiling 2-amino-1-methylbenzimidazole (IV) with tripropylborane in toluene, and was used without isolation; cf. the borylation of α-amino-N-heterocycles in [8-11]).



(IV) (V) (VI)

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