REACTION OF 2-SUBSTITUTED 5,5-DIMETHYL-4-OXO-1-PYRROLINE-1-OXIDES WITH ELECTROPHILIC REAGENTS

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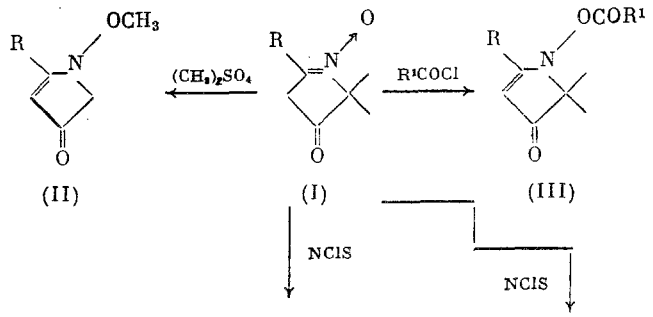
The reaction of β-oxonitrones, derivatives of pyrroline, with electrophilic reagents can proceed either at the oxygen atom of the nitrone group in the composition of the heterocyclic ring, or at the carbon atom between the carbonyl and nitrone group.

It was shown previously that the recyclization of enaminoketones, derivatives of imidazoline, proceeding in an acid medium, leads to pyrrolines (I), cyclic β-oxonitrones, which exist in the form of a mixture of two tautomeric forms – the oxonitrone and enhydroxylaminoketonic forms [1]. It could therefore be expected that compounds (I) would have the properties of carbonyl compounds, nitrones or enaminoketones. Thus, the reaction with electrophilic reagents can proceed at one of the three reaction centers – the oxygen atoms of the nitrone or carbonyl groups and the carbon atom between these two groups. In the study of the alkylation and nitrosation of β-oxonitrones, derivatives of 3-imidazoline-3-oxides, it was shown that the reaction proceeds at the carbon atom between the carbonyl and nitrone groups [2]. In the case of β-oxonitrones, derivatives of pyrroline, in the presence of hydrogen atoms at the α-carbon atom of substituent R^2, it could be expected that the reactions with electrophilic reagents would proceed at this center also (cf. [3, 4]).

The aim of the present work was to study the reaction of pyrrolines (I) with electrophilic reagents.

The alkylation reaction of pyrrolines (I) with dimethyl sulfate leads to O-alkylation products at the nitrone group (II), the structure of which was established by comparison with authentic samples [1]. The acylation reaction of compounds (I) with benzoyl or acetyl chloride proceeds similarly; as a result O-acylation products (III) are formed. The path of the reaction was established on the basis of the similarity of the UV and PMR spectra of compounds (II) and (III). In the reaction of pyrroline (Ib) with an equimolar amount of N-chlorosuccinimide, a monochloro derivative (IV) is formed, which according to the IR and UV spectral data exists in enhydroxylamino-ketonic form. Compound (IV) is also formed as the result of the recyclization reaction of the chloro-substituted enaminoketone (V) (cf. [1]). The action of an excess of N-chlorosuccinimide on pyrrolines (Ia-c) causes the formation of dichloro derivatives (VI). It should be noted that in the reaction of (Ia) with N-chlorosuccinimide the formation of the substitution product at 2-CH_3 group was not observed (cf. [4]).



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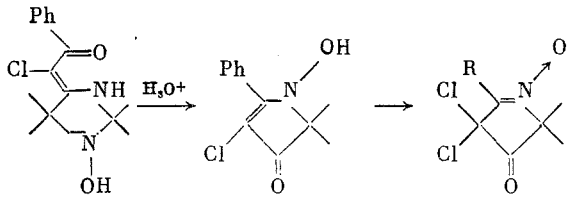
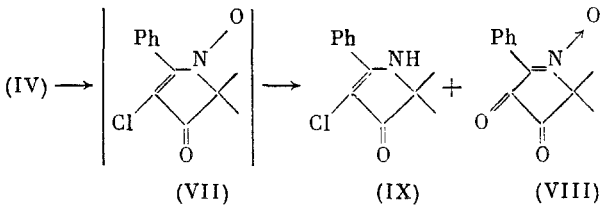


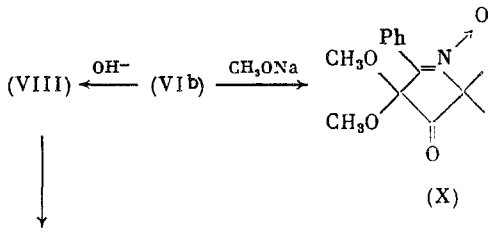
(V) (IV) (VI)

R = CH_3 (Ia), (IIa), (IIId), (VIa); C_6H_5 (Ib), (IIb), (IIIa, c), (VIb); CF_3 (Ic), (IIc), (VIc); $C(CH_3)_3$ (Id), (IIIb). $R^1 = CH_3$ (IIIa, b), C_6H_5 (IIIc, d).

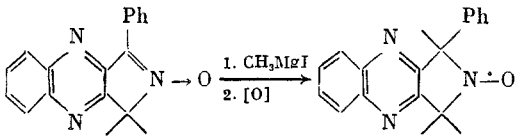
When solutions of the monochloro derivative (IV) are held in aqueous methanol in the presence of bases, first a nitroxyl radical (VII) is formed, which cannot be isolated because of its low stability, but according to the EPR data (triplet, a_N = 7.10 Oe) it can be assumed that compound (VII) has the structure of a vinylog of acylnitroxyl radical (cf. [5]). When attempts were made to isolate compound (VII) or increase the reaction time, its disproportionation to diketone (VIII) and enaminoketone (XI) took place. Diketone (VIII) is also formed during the alkaline hydrolysis of dichloro derivative (VIb): by the reaction of (VIb) with sodium methylate, dimethyl ketal (X) is formed.



(VII) (IX) (VIII)



(X)



(XI) (XII)

Condensation of diketone (VIII) with o-phenylenediamine leads to compound (XI), the reaction of which with methylmagnesium iodide, and subsequent oxidation leads smoothly to a stable nitroxyl radical (XII).

Nitrosation of pyrrolines (I) also proceeds at the carbon atom at the 3-position of the heterocyclic ring with the formation of diketone monooximes (XIII). It should be noted that oximes (XIII) are formed in the form of a mixture of E- and Z-isomers, which can be separated in the case of compound (XIIIa). Compounds (XIIIa) and (XIIIa*) are stereoisomers, since they may convert into one another on heating in an alcoholic solution. The shift of the absorption band of the carbonyl group in the IR spectrum of compound (XIIIa) relative to this band in compound (XIIIa*) by 15 cm^{-1} to the short-wave region is probably due to the presence of an intramolecular hydrogen bond. Based on this, the structure of a Z-isomer was ascribed to compound (XIIIa). In the reaction of monooxime (XIIIb) with hydroxylamine, dioxime (XIV) is formed.

The reaction of pyrroline (Ib) with benzaldehyde leads to compound (XVb), which according to the elemental analysis data is a product of the condensation of a molecule of benzaldehyde with two molecules of pyrroline. In the PMR spectrum (DMSO-d_6) of compound (XVb), proton signals of four methyl groups are observed at 0.33 (3H), 1.30 (3H), and 1.57 ppm (6H), a signal of two protons at the 3-position of the heterocyclic ring of pyrroline at 3.74 ppm (2H) and a multiplet of protons of three phenyl groups in the 6.9-8.1 ppm region. In the

TABLE 1. Characteristics of Synthesized Compounds

Compound	Yield, %	Mp, °C	Found/Calculated, %			Formula	IR spectrum (KBr), ν, cm^{-1}	UV spectrum, (ethanol) λ_{max}, nm (log ε)
			C	H	N			
(IIIa)	80	78–80	68,5 68,5	6,1 6,1	5,4 5,7	$C_{14}H_{15}NO_3$	1780 (OCO_6H_5), 1700 (C=O), 1610, 1590, 1575 (C=C)	254 (4,13), 303 (4,17), 342 (3,62)
(IIIb)	80	77–78	64,4 64,0	8,3 8,5	6,1 6,2	$C_{12}H_{19}NO_3$	1790 ($OCOCH_3$), 1700 (C=O)	284 (3,97), 317 (3,66)
(IIIc)	70	92–94	74,4 74,3	5,5 5,5	4,3 4,6	$C_{19}H_{17}NO_3$	1770 ($OCOC_6H_5$), 1710 (C=O), 1610, 1595, 1575 (C=C)	237 (4,25), 257 (4,12), 302 (4,16), 343 (3,58)
(IIId)	75	Oil	68,2 68,5	6,0 6,1	6.0 5,7	$C_{14}H_{15}NO_3$	1765 ($OCOC_6H_5$), 1700 (C=O), 1590 (C=C)	235 (4,12), 283 (4,05), 313 (3,98)
(IV)	75	110–112	60,2 60,6	5,1 5,1	5,8 5,9	$C_{12}H_{12}ClNO_2$	1660 (C=O), 1610 (C=C)	257 (4,01), 306 (3,60), 366 (3,75)
(V)	90	164–165	61,1 61,1	6,6 6,5	9,8 9,5	$C_{15}H_{19}ClN_2O_2$	1600 (C=O), 1545 (C=C)	241 (4,04), 282 (4,15)
(VIa)	90	Oil	40,4 40,0	4,4 4,3	6,3 6,6	$C_7H_9Cl_2NO_2$	1790 (C=O), 1575 (C=N)	236 (4,19), 282 (4,15)
(VIb)	60	90–91	53,2 52,9	4,1 4,0	5,2 5,2	$C_{12}H_{11}Cl_2NO_2$	1790 (C=O), 1535 (C=N)	298 (4,19),
(VIc)	45	55–56	32,0 31,6	2,7 3,0	5.0 5,3	$C_7H_6Cl_2F_3NO_2$	1805 (C=O), 1575 (C=N)	254 (4,0)
(VIII)	60	82–83	66,3 66,3	5,1 5,1	6,4 6,4	$C_{12}H_{11}NO_3$	1760, 1700 (C=O), 1525 (C=N)	245 (4,28) 314 (4,06)
(IX)	20	190–191	64,6 65,0	5,4 5,4	6,5 6,3	$C_{12}H_{12}ClNO$	1660 (C=O), 1610, 1595 (C=C), 3240 (NH)	247 (4,15), 356 (3,93)
(X)	85	84–85	63,7 63,9	6,5 6,5	5,1 5,3	$C_{14}H_{17}NO_4$	1765 (C=O), 1545 (C=N)	293 (4,20)
(XI)	75	198–199	74,5 74,7	5,2 5,2	14,5 15,5	$C_{18}H_{15}N_3O$	1530, 1570, 1620 (C=C, C=N)	243 (4,22), 262 (4,32), 327 (3,98), 365 (3,89), 379 (3,86)
(XII)	80	71–73	74,7 75,0	5,9 5,9	13,5 13,8	$C_{19}H_{18}N_3O$	1605 (C=N)	242 (4,34), 325 (3,85)
(XIIIa)	30	188–190	49,3 49,4	5.9 5,9	16,3 16,5	$C_7H_{10}N_2O_3$	1760 (C=O), 1625, 1570 (C=N)	272 (3,95), 321 (3,79)
(XIIIa) *	30	172–174	49,5 49,4	5,9 5,9	16,2 16,5	$C_7H_{10}N_2O_3$	1775 (C=O), 1620, 1545 (C=N)	276 (4,04), 326 (3,97)
(XIIIb)	70	228–229	62,2 62,2	5,1 5,2	12,1 12,1	$C_{12}H_{12}N_2O_3$	1755 (C=O), 1600, 1540 (C=N, C=C)	232 (4,19), 304 (4,10)
(XIV)	95	248–250	58,0 58,2	5,3 5,2	16,9 17,0	$C_{12}H_{13}N_3O_3$	1555, 1660 (C=N)	233 (4,24) 303 (4,08)
(XVa)	25	184–186	65,3 65,0	7,0 7,2	7,0 7,2	$C_{21}H_{26}N_2O_4 \cdot H_2O$	1790 (C=O), 1580 (C=C)	240 (3,89) 290 (3,89)
(XVb)	30	260–262	70,6 70,5	6,0 6,1	5,1 5,3	$C_{31}H_{30}N_2O_4 \cdot H_2O$	1770, 1790 (C=O), 1560 (C=N)	292 (4,04)

Note. Compounds (IIIa-c), (VIb), (VIII), (X) were purified by recrystallization from hexane, (IV), (V), (IX), (XVb) – from an ethyl acetate–hexane mixture, (XI), (XIV), (XVa) – from alcohol, (XIIIa-b) – from ethyl acetate. Compounds (IIId), (VIa) were purified by chromatography, (VIc) – by sublimation. Found/Calculated Cl, %: 14.6/14.9 (IV), 12.0/12.0 (V), 33.4/33.8 (VIa), 26.2/26.1 (VIb), 26.4/26.7 (VIc), 16.0/16.0 (IX). Found/Calculated F, %: 21.5/21.4 (VIc).

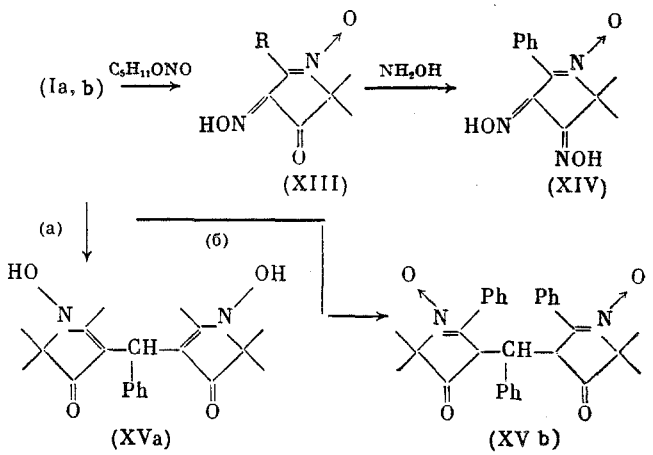
IR spectrum of compound (XVb) absorption bands of two carbonyl groups are observed at 1765 and 1790 cm^{-1} and a band of the C=N bond at 1560 cm^{-1}, while in the UV spectrum an absorption with λ_{max} 290 nm is observed, which is characteristic for the phenylnitrone grouping. On the basis of these data, the structure of bis(5,5-dimethyl-4-oxo-1-oxide-2-phenylpyrrolin-1-yl-3)phenylmethane was ascribed to compound (XVb). In a similar way, in the reaction of

TABLE 2. PMR Spectra of Synthesized Compounds

Compound	δ, ppm
(IIIa) *	1,35 (6H, 5-$(CH_3)_2$), 1,94 (3H, CH_3CO), 5,72 (1H, –CH=), 7,5 m (5H, C_6H_5)
(IIIb) *	1,17 (6H, 5-$(CH_3)_2$), 1,23 (9H, $C(CH_3)_3$), 2,10 (3H, CH_3CO), 5,26 (1H, –CH=)
(IIIc) *	1,36 (6H, 5-$(CH_3)_2$), 5,73 (1H, –CH=), 7,5 m (10H, $2C_6H_5$)
(IIId) †	1,26 (6H, 5-$(CH_3)_2$), 2,14 (3H, 2–CH_3), 5,25 (1H, –CH=), 7,7 m (5H, C_6H_5)
(VIa) *	1,51 (6H, 5-$(CH_3)_2$), 2,24 (3H, 2–CH_3)
(VIb) †	1,64 (6H, 5-$(CH_3)_2$), 7,8 m (5H, C_6H_5)
(VIII) †	1,57 (6H, 5-$(CH_3)_2$), 7,6 m (5H, C_6H_5)
(IX) †	1,36 (6H, 5-$(CH_3)_2$), 7,7 m (5H, C_6H_5)
(X) †	1,52 (6H, 5-$(CH_3)_2$), 3,35 (6H, 3-$(OCH_3)_2$), 7,7 m (5H, C_6H_5)
(XIIIb) ‡	1,42 (6H, 5-$(CH_3)_2$), 7,8 m (5H, C_6H_5)
(XIV) ‡	1,58 (6H, 5-$(CH_3)_2$), 7,8 m (5H, C_6H_5), 12,4 br.s (2H, =NOH)
(XVa) ‡	0,64 (6H), 1,25 (6H, 5-$(CH_3)_2$), 2,45 (6H, 2-(CH_3)), 7,4 m (5H, C_6H_5), 5,23 (1H, –CH–)
(XVb) ‡	0,33 (3H), 1,30 (3H), 1,57 (6H, 5-$(CH_3)_2$), 3,74 (2H, 3-CH–), 6,43 (1H, –CH–), 6,9–8,1 m (15H, $3C_6H_5$)

*The spectra were recorded in CCl_4.
†In $CDCl_3$.
‡In DMSO-d_6.

pyrroline (Ia) with benzaldehyde, compound (XVa) is formed, a product of condensation of two molecules of pyrroline with a benzaldehyde molecule (XVa), which, in contrast to compound (XVb), according to the PMR data, exists in the enhydroxylamino-ketonic tautomeric form



EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in KBr tablets (concentration 0.35%) and in CCl_4 solutions (concentration 5%) and the UV spectra on a "Specord UV-VIS" spectrophotometer in alcohol. The PMR spectra were run on a "Varian A-56-60A" spectrometer in DMSO-d_6, CCl_4, and $CDCl_3$ (concentration 7-10%). The results of the elemental analysis, melting points, yields, the IR and UV spectral data of the synthesized compounds are given in Table 1, and the PMR spectral data in Table 2.

1-Acetoxy-5,5-dimethyl-4-oxo-2-phenyl-2-pyrroline (IIIa). A solution of 0.25 ml (3 mmoles) of AcCl in 2 ml of THF was added dropwise, with stirring, to a solution of 0.4 g (2 mmoles) of pyrroline (Ib) and 0.55 ml (4 mmoles) of Et_3N in 10 ml of THF. The mixture was stirred for 15 min, the $Et_3N \cdot HCl$ precipitate was filtered off, and the solution was evaporated. Compound (IIIa) was separated by chromatography on a column with SiO_2 in an ethyl acetate–hexane (1:3) system.

In a similar way, 1-acetoxy-5,5-dimethyl-4-oxo-2-tert-butyl-2-pyrroline (IIIb) and 1-benzoyloxy-4-oxo-2,5,5-trimethyl-2-pyrroline (IIId) were obtained by the action of AcCl on pyrroline (Id) in $CHCl_3$ and BzCl on pyrroline (Ia) in THF, respectively.

1-Benzoyloxy-5,5-dimethyl-4-oxo-2-phenyl-2-pyrroline (IIIc). A 0.28 ml portion of BzCl was added dropwise, with stirring, to a solution of 0.4 g (2 mmoles) of pyrroline (Ib) and 0.16 g (4 mmoles) of NaOH in 10 ml of water. The mixture was stirred for 12 h at 20°C, the precipitate of compound (IIIc) that separated out was filtered off, washed with water, and dried.

1-Hydroxy-4-(2-oxo-2-phenyl-1-chloroethylidene)-2,2,5,5-tetramethylimidazolidine (V) was obtained by reducing 4-(2-oxo-2-phenyl-1-chloroethylidene)-2,2,5,5-tetramethylimidazolidine-1-oxyl with zinc, similarly as described in [6].

5,5-Dimethyl-4-oxo-2-phenyl-3-chloro-1-pyrroline-1-oxide (IV). A suspension of 0.4 g (2 mmoles) of pyrroline (Ib) and 0.29 g (2.2 mmoles) of N-chlorosuccinimide in 10 ml of CCl_4 was stirred for 30 min, and evaporated. Compound (IV) was separated by chromatography on a column with SiO_2 in an ethyl acetate–hexane (1:1) system. In a similar way, by the action of 5 mmoles of N-chlorosuccinimide on 2 mmoles of pyrrolines (Ia-c), 3,3-dichloro-4-oxo-2,5,5-trimethyl-1-pyrroline-1-oxide (VIa), 5,5-dimethyl-3,3-dichloro-4-oxo-2-phenyl-1-pyrroline-1-oxide (VIb), and 5,5-dimethyl-3,3-dichloro-4-oxo-2-trifluoromethyl-1-pyrroline-1-oxide (VIc) were obtained. The monochloro derivative (IV) can be obtained by recyclization of enaminoketone (V), similarly as described in [1], in a yield of 80%.

5,5-Dimethyl-3,4-dioxo-2-phenyl-1-pyrroline-1-oxide (VIII) and 5,5-Dimethyl-4-oxo-2-phenyl-3-chloro-2-pyrroline (IX). A solution of 0.25 g (1 mmole) of pyrroline (IV) and 0.1 ml of morpholine in 10 ml of MeOH was allowed to stand for 48 h at 20°C, and then was evaporated. Compounds (VIII) and (IX) were separated by chromatography on a column with SiO_2, using $CHCl_3$ as eluent. First, 0.11 g (50%) of diketone (VII) was eluted, and then 0.06 g (24%) of the starting pyrroline (IV) and 0.045 g (20%) of enaminoketone (IX).

Diketone (VIII) forms during an alkaline hydrolysis of dichloro derivative (VIb) in an 80% yield.

5,5-Dimethyl-3,3-dimethoxy-4-oxo-2-phenyl-1-pyrroline-1-oxide (X). A solution of 0.27 g (1 mmole) of dichloro derivative (VIb) in 20 ml of MeOH was held for 48 h at 20°C, and then evaporated. The residue was diluted with a small amount of hexane, and the precipitate of compound (X) was filtered off.

1,1-Dimethyl-3-phenyl-1H-3,3-pyrrolo[3,4-b]quinoxaline-2-oxide (XI). A solution of 0.34 g (1.6 mmoles) of diketone (VIII) and 0.18 g (1.7 mmoles) of o-phenylenediamine in 10 ml of ethanol was allowed to stand for 24 h at 20°C. The precipitate of compound (XI) was filtered off, the filtrate was evaporated, the residue was washed with a small amount of ethanol and an additional amount of compound (XI) was obtained.

2,3-Dihydro-1,1,3-trimethyl-3-phenyl-1H-pyrrolo[3,4-b]quinoxaline-2-oxyl (XII). A solution of 0.4 g (1.38 mmoles) of compound (XI) in dry ether was added dropwise, with stirring, to a solution of methylmagnesium iodide prepared from 1.4 g (9.7 mmoles) of MeI and 0.17 g (6.9 mmoles) of Mg in 30 ml of dry ether. The mixture was stirred for 3 h, 10 ml of water was added, the ether layer was separated, and the aqueous layer was extracted with ether (3 × 20 ml). The combined ether extract was dried over $MgSO_4$, 2 g of MnO_2 was added to the solution, and the mixture was stirred for 1 h at 20°C. The excess of the oxidant was filtered off and the filtrate was evaporated. Compound (XII) was isolated by chromatography on a column with SiO_2, using $CHCl_3$ as eluent.

5,5-Dimethyl-3-oximino-4-oxo-2-phenyl-1-pyrroline-1-oxide (XIIIb). A solution of 1.02 g (5 mmoles) of pyrroline (Ib), 0.81 g (15 mmoles) of MeONa, 1.34 ml (10 mmoles) of amyl nitrite in 40 ml of MeOH was allowed to stand for 6 h at 20°C, and then evaporated. The residue was dissolved in 25 ml of water, washed with ether (3 × 15 ml), neutralized with a 5% HCl solution and extracted with $CHCl_3$ (4 × 50 ml). The extract was dried over $MgSO_4$, the solution was evaporated, and oxime (XIIIb) was obtained.

Under similar conditions, by the action of amyl nitrite on pyrroline (Ia), a mixture of E- and Z-isomers of 3-oximino-4-oxo-2,5,5-trimethyl-1-pyrroline-1-oxides (XIIIa) and (XIIIa*) was obtained, which was separated by chromatography on a column with SiO_2 in a $CHCl_3$–MeOH (40:1) system.

5,5-Dimethyl-3,4-dioximino-2-phenyl-1-pyrroline-1-oxide (XIV). A solution of 0.12 g (0.52 mmole) of compound (XIIIb), 0.15 g (2.6 mmoles) of $NH_2OH \cdot HCl$ and 0.1 g (1.6 mmoles) of MeONa in 15 ml of ethanol was boiled for 20 min, and then evaporated. The residue was diluted with 5 ml of water, and the precipitate of dioxime (XVI) was filtered off.

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).

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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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