SYNTHESIS OF DIACYLKETENE AND ALKOXYCARBONYL(ACYL)KETENE N,N-ACETALS BY THE REACTION OF β-DIKETONES AND β-KETOESTERS WITH MONOSUBSTITUTED CYANAMIDES

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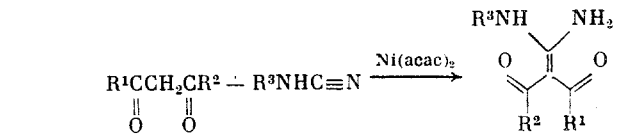
β-Diketones and β-ketoesters react with monosubstituted cyanamides in the presence of catalytic amounts of $Ni(acac)_2$ to form diacyl- and alkoxycarbonyl(acyl)ketene N,N-acetals (DKAs and AKAs, respectively). The interconversion of E and Z isomeric forms of AKAs was studied by means of ^1H and ^{13}C NMR spectroscopy.

The use of α-oxoketone S,S- and S,N-acetals in organic chemistry as three-carbon synthones is a generally accepted method (cf. [1]). The synthesis of heterocyclic systems from the appropriate N,N-acetals (ketenaminals) has recently been reported by several investigators [2-4]. However, the latter reagents are less readily available and have been investigated to a lesser extent. In particular, few data are available about diacylketene and alkoxycarbonyl(acyl)ketene N,N-acetals (DKAs and AKAs), since the available methods of obtaining these compounds have many limitations and, in general, are not very effective. Individual DKAs and AKAs have been synthesized by the reaction of amines with the appropriate S,S-acetals [5, 6], the reaction of aromatic acid chloranhydrides with 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine [7], and by addition of β-diketones to diphenylcarbodiimide [8].

We have found a convenient method for obtaining DKAs and AKAs from β-dicarbonyl compounds and cyanamides in the presence of nickel acetylacetonate $Ni(acac)_2$. In a previous communication we examined the reaction of acetylacetone with benzoylcyanamide, established the role of $Ni(acac)_2$ in this process, and determined the molecular and crystalline structure of the synthesized ketenaminal [9].

In the present work we endeavored to synthesize new DKAs and AKAs by the reaction of β-diketones and β-ketoesters with monosubstituted cyanamides (see [10]).

The addition of β-dicarbonyl compounds (I)-(IV) to cyanamides (V) and (VI) proceeded smoothly in boiling THF or benzene in the presence of 1-5 mole % $Ni(acac)_2$. (Reaction (1) with cyanamide (VII) was carried out using an excess of (I).) The yield of DKAs (VIIIa-d) and AKAs (IXa-d) was 50-90% (Table 1).

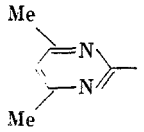


(1)

(I)—(IV) (V)—(VII) (VIIIa-d), (IXa-d)

$R^1 = R^2 = Me$ (I); $R^1 = R^2 = Ph$ (II); $R^1 = Me$, $R^2 = OEt$ (III);

$R^1 = Ph$, $R^2 = OEt$ (IV); $R^3 = Ph$ (V); PhCO (VI);



(VII).

Ketenaminals (VIIIa-d) and (IXa-d) are colorless or yellowish crystalline substances, readily soluble in acetone and poorly soluble in hexane. Compounds obtained from phenylcyanamide (V) are readily soluble in THF, Et_2O, $CHCl_3$, and benzene. The mass spectra of DKAs (VIIIa-d) and AKAs (IXa-d) contain intense $[M]^{+\cdot}$ molelcular ion peaks.

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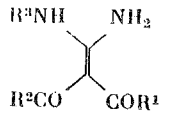
TABLE 1. Ketenaminals (VIIIa-d, g) and (IXa-d)



Reagent*	Reaction time,* h	Ketenaminal	R^1	R^2	R^3	Yield, %	Mp, °C	Found/Calculated, %			Empirical formula	Mass spectrum $[M]^{+\cdot}$, m/z	IR spectrum ($CHCl_3$, ν, cm^{-1})
								C	H	N			
(I)+(V)	4	(VIIIa)	Me	Me	Ph	78	55–56	65,86 66,03	6,41 6,47	12,83 12,84	$C_{12}H_{14}N_2O_2$	218	3470 (NH), 3300–2800 (NH, CH), 1608 (CO)
(II)+(V)	2	(VIIIb)	Ph	Ph	Ph	76	116–117	76,97 77,17	5,25 5,29	8,59 8,18	$C_{22}H_{18}N_2O_2$	342	3475 (NH), 3300–2900 (NH, CH), 1609 (CO)
(II)+(VI)	20	(VIIIc)	Ph	Ph	PhCO	50	223–224	74,34 74,57	4,89 4,90	7,52 7,56	$C_{23}H_{18}N_2O_3$	370	3360 (NH), 3250–2850 (NH, CH), 1685 (CON), 1643, 1633 (CO)
(I)+(VII)	0,5	(VIIId)	Me	Me	4,6-Dimethylpyrimidin-2-yl	67	172–173	58,19 58,05	6,39 6,49	22,64 22,57	$C_{12}H_{16}N_4O_2$	248	3260 (NH), 3300–2800 (NH, CH), 1620 (CO)
–	–	(VIIIg)	Ph	Ph	H	89	201–202	71,95 72,16	5,45 5,30	10,67 10,52	$C_{16}H_{14}N_2O_2$	266	3479 (NH), 3500–3100 (NH, CH), 1600 (CO)
(III)+(V)	2	(IXa)	Me	OEt	Ph	86	44–45	62,87 62,89	6,53 6,50	10,97 11,29	$C_{13}H_{16}N_2O_3$	248	3478 (NH), 3300–2850 (NH, CH), 1643, 1638, 1607 (CO)
(IV)+(V)	2	(IXb)	Ph	OEt	Ph	70	81–82	69,71 69,66	5,72 5,85	8,59 8,18	$C_{18}H_{18}N_2O_3$	310	3480 (NH), 3350–2850 (NH, CH), 1645, 1635, 1610 (CO)
(III)+(VI)	2	(IXc)	Me	OEt	PhCO	57	83–84	60,58 60,86	5,72 5,85	10,50 10,14	$C_{14}H_{16}N_2O_4$	276	3350 (NH), 3280–2800 (NH, CH), 1690 (CON), 1655, 1677 (CO)
(IV)+(VI)	3	(IXd)	Ph	OEt	PhCO	56	105–106	67,30 67,44	5,06 5,37	8,67 8,28	$C_{19}H_{17}N_2O_4$	338	3370 (NH), 3300–2800 (NH, CH), 1692 (CON), 1660, 1655, 1645, 1625 (CO)

*For reactions of compounds (I)-(IV) with compounds (V)-(VII).

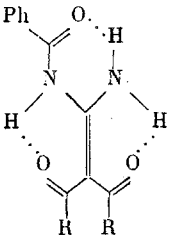
TABLE 2. PMR Spectra of Compounds (VIIIa-d, g) and (IXa-d)

Compound	Solvent	T, °C	δ, ppm			
			MeCO singlet	EtO quartet, triplet	Ph multiplet	NH broad singlet
(VIIIa)	$CDCl_3$	22	2,36	–	7,40–7,10	12,81; 10,63; 5,41
(VIIIb)	$CDCl_3$	22	–	–	7,52–6,97	12,43; 10,24; 5,55
(VIIIc)	$CDCl_3$	22	–	–	8,22–6,99	14,51; 10,60; 9,96
(VIIId)†	$CDCl_3$	22	2,38	–	–	13,70; 11,13; 10,40
(VIIIg)	$CDCl_3$	22	–	–	7,31–6,93	9,57; 6,15
(IXa)	$CDCl_3$	22	2,44	4,12; 1,33	7,44–7,16	11,44; 11,44; 5,36 13,55; 9,48; 5,36
		−50	2,41 2,43	4,18; 1,33 4,16; 1,31	7,45–7,15	11,40; 11,40; 5,58 13,46; 9,47; 5,47
(IXb)	$CDCl_3$	22	–	3,78; 0,63	7,51–7,25	11,10; 10,70; 5,38 12,82; 9,05; 5,38
		−30		3,78; 0,60 3,74; 0,58	7,51–7,26	10,93; 10,68; 5,48 12,74; 9,05; 5,43
(IXc)	$CDCl_3$	22	2,45 2,48	4,26; 1,34 4,29; 1,37	8,08–7,45	13,82; 11,81; 9,95 15,69; 10,01; 9,95
(IXd)	$(CD_3)_2SO$	22	2,32	4,17; 1,28	7,94–7,54	15,10; 10,13; 9,70
	$CDCl_3$	22		3,89; 0,66 3,86; 0,63	8,17–7,31	13,40; 10,88; 9,77 14,80; 9,89; 9,64
	$(CD_3)_2SO$	22	–	3,76; 0,55	8,01–7,33	13,50; 10,40; 9,43 14,60; 9,62; 9,62

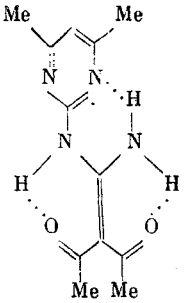
*Signals of the minor isomer are shown in the upper line.
†The spectrum also contains signals of the 4,6-dimethylpyrimidin-2-yl fragment (δ, ppm): 6.69 (CH=), 2.41 (2Me).

The structures of all synthesized compounds were also confirmed by means of IR and ^1H and ^{13}C NMR spectra (Tables 1-3, respectively).

Earlier [9] we showed (on the basis of spectral and x-ray diffraction data) that ketenaminal (VIIIe; $R^1 = R^2 = Me$, $R^3 = PhCO$) has a type A structure in solution and in the molten and crystalline states, with three stable intramolecular hydrogen bonds (IHBs).



(A)



(B)

The IR and PMR spectra of N-benzoylketenaminals (VIIIc) and (IXc, d) indicate that all C=O and NH groups in these compounds are involved in the formation of IHBs; consequently, these compounds also have an A-type structure. On the basis of the spectral data, structure B should be assigned to DKA (VIIId), in which one of the N atoms in the pyrimidine ring participates in the formation of IHBs.

Indeed, the IR spectra of DKAs (VIIIc, d) and AKAs (IXc, d) do not contain absorption bands of free NH groups even at high dilutions in $CHCl_3$ (in which the shape of the spectra does not change). As in the case of compound (VIIIe) [9], in the spectra of ketenaminals (VIIIc) and (Xc, d) the high-frequency bands at 3370-3350 cm^{-1} should be assigned to the weaker IHB N–H...O=C(Ph), and the bands at 1692-1685 cm^{-1} belong to the amide group. The broad, diffuse bands with maxima at 3250-2800 cm^{-1} characterize the remaining NH groups, which are bound to acyl (alkoxycarbonyl) groups (the latter appear as intense bands at 1660-1625 cm^{-1}). The IR spectrum of DKA (VIIId) contains an intense absorption band at 3260 cm^{-1}, a broad, low-intensity band with a maximum at 3200-2800 cm^{-1} (νNH), and a CO absorption band at 1620 cm^{-1}.

TABLE 3. ^{13}C NMR Spectra of Compounds (VIIIa-d, g) and (IXa-d) in $CDCl_3$

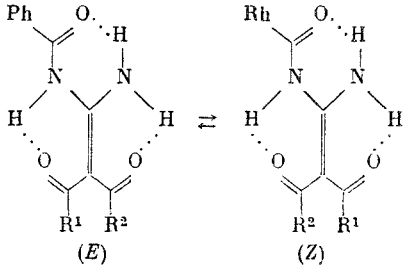
Compound	δ, ppm*								
	C¹	C²	COMe	COPh	NCOPh	CO_2Et	COMe	OEt	Ph
(VIIIa)	162,05	102,31	198,27	–	–	–	32,47	–	135,19; 130,11; 127,49; 125,97
(VIIIb)	161,78	97,98	–	197,43	–	–	–	–	143,66; 135,17; 130,22; 130,03; 129,08; 127,48; 125,79
(VIIIc)	161,79	98,58	–	198,06 197,86	169,52	–	–	–	143,00; 133,71; 132,29; 130,70; 130,57; 129,21; 128,90; 128,15; 127,72; 127,67
(VIIId)†	161,34	102,49	198,48	–	–	–	32,59	–	–
(VIIIg)	164,35	90,85	–	197,59	–	–	–	–	143,91; 130,16; 129,01; 127,67
(IXa)	162,73	88,36	197,35	–	–	171,36	32,58	59,64; 14,44	135,46; 130,01; 127,18; 125,93
(IXb)	162,10	87,20		195,60	–	171,68	–	59,78; 13,16	145,39; 135,40; 129,73; 128,57; 127,40; 127,14; 127,04
(IXc)	162,55 163,20	89,23 89,75	198,64 199,16	–	168,95 165,59	171,70 170,27	33,21 32,63	60,48; 14,35 60,12; 14,35	133,33; 132,56; 129,00; 128,06; 127,72
(IXd)	161,50 162,13	87,84 88,72	–	196,41 196,74	168,72 169,30	171,73 170,44	–	59,93; 13,08 59,61; 13,08	144,46; 144,26; 133,49; 132,32; 132,16; 129,63; 129,51; 129,04; 128,05; 127,75; 127,70; 127,64; 126,76; 126,61

*Signals of the minor isomer are shown in the upper line (except for signals of the Ph group, which are shown without referral).

†The spectrum also contains signals of the 4,6-dimethylpyrimidin-2-yl fragment (δ, ppm): 167.60 (C^4, C^6), 158.74 (C^2), 114.86 (C^5), 23.79 (Me).

The PMR spectra of compounds (VIIIc, d), as in the case of (VIIIe), contain three downfield signals of NH groups which participate in the formation of IHBs.

AKAs (IXc, d) theoretically can exist as E and Z isomers, which are interconvertible.



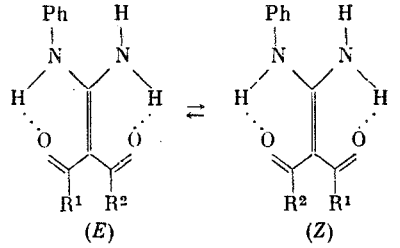
Indeed, the ^1H and ^{13}C NMR spectra of compounds (IXc, d) in $CDCl_3$ contain two sets of signals (Tables 2 and 3; the isomer ratio is 1.9:1 for (IXc) and 2:1 for (IXd), but a specific assignment of signals to E and Z isomers is difficult).

For DKAs containing two Me_2N groups the rotation barrier around the C=C bond is very low ($\Delta G \leq 8$ kcal/mole) [11]. This can be explained by a significant decrease in the double bond character of the C=C bond as a result of pronounced p–π conjugation in the ketenaminal molecules. The hindered rotation in the case of (IXc, d) may be explained by the presence of three IHBs in these molecules. In fact, in DMSO-d_6, which can rupture IHBs, the PMR spectra of AKAs (IXc, d) contain one set of signals each from acyl and alkoxycarbonyl groups.

The IR spectra of ketenaminals (VIIIa, b) and (IXa, b), which contain a PhNH group, also contain absorption bands of NH and CO groups at 3300-2800 and 1645-1608 cm^{-1} in addition to an absorption band of the free NH group at 3480-3470 cm^{-1}. The pattern of these spectra does not change at a 20-fold dilution of the solutions in $CHCl_3$. Thus both C=O groups in (VIIIa, b) and (IXa, b) take part in the formation of two IHBs.

The PMR spectra of DKAs (VIIIa, b) in $CDCl_3$ contain one free NH signal (δ 5.58-6.36 ppm) and two downfield signals of NH groups participating in the formation of IHBs.

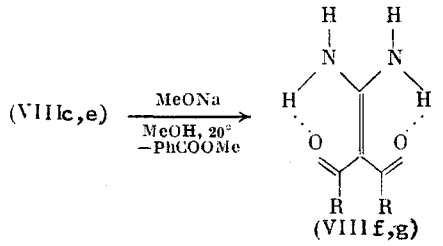
In contrast to (IXc, d), the spectra of AKAs (IXa, b) in $CDCl_3$ at 22°C have a double set of signals for NH groups participating in the formation of IHBs; only at −50°C is there a double set of signals for all proton groups. This indicates that compounds (IXa, b) exist as an equilibrium mixture of E and Z isomers (the isomer ratio is 1.5:1 for (IXa) and 1.6:1 for (IXb)).



(*E*) (*Z*)

The temperature-dependent changes of the spectra show that the interconversion process in (IXa, b), which takes place above −50 or −30°C, respectively, is relatively slow in the NMR time scale, since the signals of the NH groups, whose chemical shifts differ by hundreds of Hz units, do not average out even at +50°C.

The reactions of β-diketones and β-ketoesters with cyanamides (V)-(VII) can yield monosubstituted (with respect to nitrogen) DKAs and AKAs. Earlier, in an attempt to react unsubstituted cyanamide with acetylacetone, we obtained a mixture of ketenaminals from which unsubstituted DKA (VIIIf) was isolated in a low yield [12]. However, DKAs of this type can readily be obtained in high yields from the corresponding N-benzoyl derivatives (VIIIc, e) in the presence of MeONa:



(2)

R = Me (f), Ph (g).

Thus reactions (1) and (2) represent a straightforward method for synthesizing previously difficult to obtain DKAs and AKAs, including compounds unsubstituted with respect to nitrogen or containing a heteroamino group as a substituent.

EXPERIMENTAL

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

Ketenaminals (VIIIa-c) and (IXa-d). A mixture containing 0.01 mole β-dicarbonyl compounds (I)-(IV), 0.01 mole cyanamides (V) or (VI), and 1 mole % $Ni(acac)_2$ in 15 ml benzene (in the case of (V)) or 5 mole % $Ni(acac)_2$ in 15 ml THF (in the case of (VI)) was boiled in an atmosphere of dry Ar for 2-20 h (Table 1). In the experiments with compound (V) the mixture was filtered through SiO_2 (eluent, $CHCl_3$), the solvent was evaporated, and the residue was recrystallized from Et_2O–hexane (1:1, −78°C), yielding compounds (VIIIa, b) or (IXa, b). In syntheses with compound (VI), THF was evaporated, and the residue was recrystallized from EtOH, yielding compounds (VIIIc) or (IXc, d).

3-[N-(4,6-Dimethylpyrimidin-2-yl)diaminomethylene]pentane-2,4-dione (VIIId). A mixture containing 0.444 g cyanamide (VII) [13], 1.20 g compound (I), and 0.080 g $Ni(acac)_2$ was boiled for 30 min. The mixture was then cooled, and the crystalline precipitate was filtered

and washed with a small amount of EtOH, yielding compound (VIIId). An analytical product was prepared by recrystallization from EtOH.

Ketenaminals (VIIIf, g). A mixture containing 0.01 mole DKAs (VIIIc, d) and 0.01 mole MeONa in 20 ml MeOH was stirred at 20°C for 45 min, and 0.01 mole AcOH was added dropwise. The solvent was evaporated; $CHCl_3$ was added to the residue, which was filtered through SiO_2 (eluent, $CHCl_3$). The solvent was evaporated, and the crystalline residue was washed with hexane, yielding compounds (VIIIf, g). An analytical product was prepared by recrystallization from benzene. Compound (VIIIf) was obtained in a yield of 82% and was identical to the one synthesized earlier from acetylacetone and cyanamide [12].

The yields, elemental analysis data, and physicochemical characteristics of DKAs (VIIIa-d, g) and AKAs (IXa-d) are shown in Table 1; ^1H and ^{13}C NMR spectral data for these compounds are presented in Tables 2 and 3, respectively.

LITERATURE CITED

1. M. Dieter, Tetrahedron, 42, 3029 (1986).
2. V. Aggarwal, H. Ila, and H. Janjappa, Synthesis, 65 (1982).
3. Z.-t. Huang and Z.-r. Liu, Heterocycles, 24, 2247 (1986).
4. H. Grassivaro, E. Rossi, and R. Stradi, Synthesis, 1010 (1986).
5. E. Ericsson and J. Sandstrom, Acta Chem. Scand., 24, 3102 (1970).
6. M. Augustin, Ch. Groth, H. Kristen, et al., J. Prakt. Chem., 321, 205 (1979).
7. M. D. Nair, S. Rajappa, and J. Desai, Ind. J. Chem., 21B, 1 (1982).
8. R. Gompper and R. Kunz, Chem. Ber., 98, 1391 (1965).
9. V. A. Dorokhov, M. F. Gordeev, M. N. Bochkareva, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1134 (1989).
10. V. A. Dorokhov, M. F. Gordeev, V. S. Bogdanov, and Z. K. Dem'yanets, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1683 (1987).
11. J. Sandstrom, in: Topics in Stereochemistry, N. L. Allinger, E. L. Eliel, and S. H. Wilen (eds.), Vol. 14, Wiley, New York (1983), p. 83.
12. V. A. Dorokhov, M. F. Gordeev, and V. S. Bogdanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1431 (1988).
13. J. Birtwell, J. Chem. Soc., 1725 (1953).

N,N'-DIALKYL-N,N'-DINITROSULFODIAMIDES

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N,N'-dinitrosulfodiamides are formed in the nitration of sulfodiamides with concentrated nitric acid or nitronium borofluoride, and also on substitutional nitration of the corresponding N,N'-di-tert.-butyl derivatives with those reagents. Sulfuryl chloride reacts with the disodium salt of ethylene N,N'-dinitramine to produce 2,5-dinitro-1,2,5-thiadiazolidine-1,1-dioxide. The corresponding N-nitrosulfamides are formed when nitramine salts react with methane sulfochloride.

There is only scanty and conflicting published evidence on the preparation of N,N'-dinitrosulfodiamides (DNSDA). In [1], N,N'-dimethyl-DNSDA (IIa) was described as a solid substance, but in [2] it was considered to be a liquid. In [3], it was reported that a cyclic DNSDA had been made: 2,5-dinitro-1,2,5-thiadiazolidine-1,1-dioxide. It is doubtful whether that structure is correct however, since the compound claimed in [3] as 1,2,5-thiadiazolidine-1,1-dioxide has been shown [4] not to be such.

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