STRUCTURES OF THE PRODUCTS OF REACTION OF 1,5-DIKETONES WITH HYDROXYLAMINE

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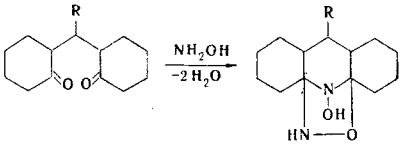
Alkylidenebis-2,2'-cyclohexanones react with two molecules of hydroxylamine to give 8-hydroxy-1,2,4,5-bistetramethylene-7-oxa-6,8-diazabicyclo[3.2.1]octanes, whereas 5,5'-methylene-2,2-dimethyl-4-pyrone and "semicyclic" and aliphatic-aromatic 1,5-diketones form dioximes.

2,2'-Alkylidenedicyclohexanones (Ia-c) react with 2 moles of hydroxylamine to give 8-hydroxy-1,2,4,5-bistetramethylene-7-oxa-6,8-diazabicyclo[3.2.1]octanes (IIa-c) rather than dioximes, as was previously assumed [1, 2]. Two stereoisomers of IIa corresponding to the two forms of diketone Ia were isolated. β-Isomer IVa is formed from the racemic form of Ia, whereas a mixture of the racemic and meso forms gives a mixture of two isomers, from which α-isomer IIa was isolated.

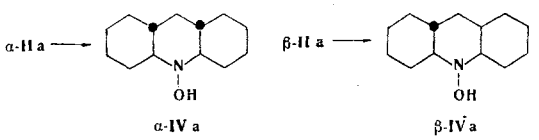


Ia-c IIa-c

I, II a R=H; b R=CH_3; c R=C_6H_5

Absorption of the C=N bond at 1600-1700 cm^{-1} is absent in the IR spectra of IIa-c; in addition to the absorption of an associated hydroxyl group at 3100-3200 cm^{-1}, there is a narrow peak at 3220 cm^{-1}, which is related to the NH group. A similar pattern is observed in the spectrum of the product of the reaction of glutaraldehyde with 1 mole of hydroxylamine, for which the 7,8-dioxa-6-azabicyclo[3.2.1]octane structure, which is similar to the structure of II, was established [3].

The corresponding O,N-diacetyl derivatives (α- and β-IIIa) are formed by the action of acetic anhydride in pyridine on the α- and β-isomers of IIa. Their IR spectra contain intense absorption bands of ester (1780 cm^{-1}) and amide (1670 cm^{-1}) carbonyl groups. Stereoisomeric N-hydroxyperhydroacridines IVa are formed in the reduction of the α- and β-isomers of IIa and IIIa with $NaBH_4$ in alcohol [4]. trans-syn-trans-Isomer α-IVa is formed from the α-isomers, whereas primarily trans-anti-cis-isomer β-IVa is formed from the β-isomers, along with a small amount of α-IVa. Their configurations were confirmed [4] by conversion to the α- and β-perhydroacridines, the configurations of which are known. The results obtained make it possible to propose a trans-syn-trans configuration for the α-isomer of IIa and a trans-anti-cis configuration for the β-isomer.



α-IV a β-IV a

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TABLE 1. Products of the Reaction of 1,5-Diketones with Hydroxylamine

Compound	mp, °C	Crystallization solvent	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
α-IIa	180—181 *	Dioxane	$C_{13}H_{22}N_2O_4$	65,6	9,2	11,8	65,5	9,2	11,8	7,8 *
β-IIa	160—161 †	Ethyl acetate	$C_{13}H_{22}N_2O_4$	65,5	9,4	12,0	65,5	9,2	11,8	87
IIb	180—182 ‡	Dioxane	$C_{14}H_{24}N_2O_2$	66,4	9,9	11,3	66,7	9,5	11,1	51
IIc	193—195	Methanol	$C_{19}H_{26}N_2O_2$	73,2	8,4	8,8	72,6	8,3	8,9	21
α-IIIa	140—141	40% Ethanol	$C_{17}H_{26}N_2O_4$	63,2	8,1	8,8	63,4	8,1	8,7	44
β-IIIa	173—174	Ethanol	$C_{17}H_{26}N_2O_4$	63,9	8,4	8,7	63,4	8,1	8,7	21
VI	200—202	Ethanol	$C_{15}H_{26}N_2O_4$	60,6	8,7	9,5	60,4	8,7	9,4	22
X	136—138	Benzene	$C_{15}H_{20}N_2O_2$	69,4	8,0	10,4	69,2	7,7	10,8	86
XI	180—181	Propanol	$C_{21}H_{24}N_2O_2$	74,5	7,6	8,2	75,0	7,1	8,3	95
XII	153—154 **	Benzene	$C_{23}H_{22}N_2O_2$	77,1	6,6	7,9	77,1	6,1	7,8	91

* Isolated by fractional crystallization from a mixture of α-IIa and β-IIa; mp 190-191° [1] and 179-183° [5].
† Literature mp 130° [1] and 159-164° [5].
‡ Literature mp 164-167° [2].
** Literature mp 163.5° [7].

5,5'-Methylenebis-2,2-dimethyl-4-pyrone (V) forms a dioxime (VI), evidently because of the fact that in the tetracyclic form analogous to structure II, 1,3-repulsion should develop between the axial CH_3 groups and the O—NH fragment.

"Semicyclic" 1,5-diketones, namely, 1-phenyl-3-2-oxocyclohexyl)-1-propanone (VII) and 1,3-diphenyl-3-(2-oxocyclohexyl)-1-propanone (VIII), and the aliphatic-aromatic benzylidenediacetophenone (IX) give dioximes (X-XII). Their IR spectra contain the absorption band of a C=N bond at 1650-1670 cm^{-1} but do not contain the narrow absorption peak of the NH bond at 3220 cm^{-1} characteristic for II.

EXPERIMENTAL

Condensation of 1,5-Diketones with Hydroxylamine. Diketone IIIc was synthesized by the method in [6]. A solution of 0.7 mole of hydroxylamine hydrochloride and 53 g of Na_2CO_3 in 100 ml of water was added to a solution of 0.35 mole of the diketone in 300 ml of ethanol. After 3 h,* the precipitate was removed by filtration, washed with ethanol and water, and recrystallized. See Table 1 for information concerning the products.

Reduction of α- and β-IIa and IIIa. A 0.01-mole sample of the compound in 90 ml of alcohol was reduced with 0.06 mole of sodium borohydride. According to thin-layer chromatography [Al_2O_3, petroleum ether-ethyl acetate (1:1), only α-IVa is formed from α-IIa and IIIa, whereas β-IVa and traces of α-IVa are formed from the β-isomers. The IR spectra of the products of the reduction of IVa were identical to the spectra of genuine samples.

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* Refluxing for 15 min and 6 h, respectively, is required for the preparation of dioximes VI and X.