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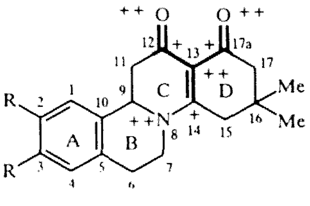
INTERACTION OF 8-AZA-D-HOMOGONA-1,3,5(10),13-TETRAENE-12,17a-DIONES WITH ACETIC ANHYDRIDE — NEW DIRECTIONS IN THE TRANSFORMATION OF CONFORMATIONALLY RESTRICTED α-ACYL-β-AMINOVINYL KETONES

O. V. Gulyakevich, A. S. Lyakhov, and A. L. Mikhal'chuk

The interaction of 16,16-dimethyl-8-aza-D-homogona-1,3,5(10),13-tetraene-12,17a-diones with acetic anhydride has been investigated. In the presence of fused sodium acetate, the major products are 11-vinyl-16,16-dimethyl-8-aza-D-homogona-1,3,5(10),9(11),13-pentaene-12,17a-dione; minor products are 16,16-dimethyl-8-aza-D-homogona-1,3,5(10),9(11),13,17-hexaen-12-ones. In the absence of sodium acetate, the reaction stops at the 11-acetyl-16,16-dimethyl-8-aza-D-homogona-1,3,5(10),13-tetraene-12,17a-dione derivative. In the case of 2,3-demethoxy-8-aza-D-homogonane, a different principal product is formed, regardless of whether or not sodium acetate is present; this is a compound that results from the formation of a bond between the original homogonane and 8-aza-D-homogona-1,3,5(10),9(11),13,17-hexaen-12-one (which is formed during the course of the reaction) at positions 9 and 4, respectively. The structure of the compounds that were obtained has been verified by a set of physicochemical data (IR and UV spectra, PMR, and x-ray diffraction). A probable scheme is proposed for the basic directions of the reaction.

8-Aza-D-homogonanes are the most extensively and intensively studied series of 8-azasteroid derivatives [1], owing to their accessibility and also the great interest in their medical-biological properties [2, 3] and physicochemical properties [4, 5]. These properties are apparently related to the presence of the conformationally restricted α-acyl-β-aminovinylcarbonyl (AAVC) fragment in the structure (indicated in the formula for Ia,b by heavy lines). We had previously studied the conversions of 8-aza-D-homogonanes in reactions with aromatic and heteroaromatic aldehydes [6], esters [7], copper bromide [8], and certain other compounds [9, 10]. It is known that aliphatic and alicyclic β-aminovinylcarbonyl compounds, depending on their structure and the conditions, may act as N-, O-, or C-nucleophiles [11], a property that is used in their conversions to (for example) derivatives containing the AAVC fragment, upon interaction with acylating agents [12]. At the same time, this aspect of the reactivity of AAVC compounds, including representatives with the structure I, had not been studied previously. All that has been reported in the literature is one case of formation of O-acyl derivatives of AAVC compounds of the 2-acylcyclohexane-1,3-dione series as byproducts in the acylation of 3-amino-2-cyclohexen-1-ones [12].



Ia, b

a) R = H, b) R = OMe

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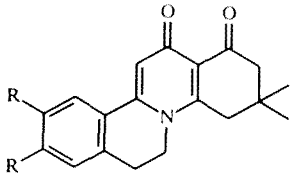
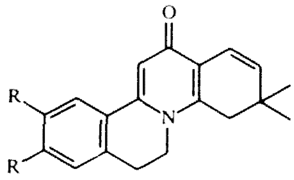
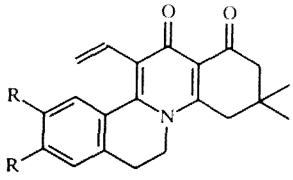
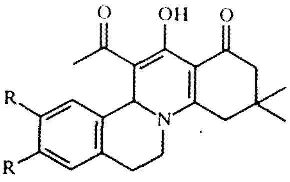
The AAVC fragment is a strongly polarized bifunctional system that is capable of manifesting both electrophilic and nucleophilic properties. Because of this property, with further consideration of data reported in [11, 12], we were interested in studying the interaction of 8-aza-D-homogonanes (Ia,b) with certain electrophiles such as acetic anhydride, with the aim of developing a probable approach to O-acyl derivatives or products of O,C-isomerization of the latter (through the Claisen—Haas reaction [13]) to the corresponding C-acyl derivatives.

Compounds Ia,b were obtained by annelation of 3,4-dihydroisoquinolines with 2-acetyldimedones as described previously [14, 15].

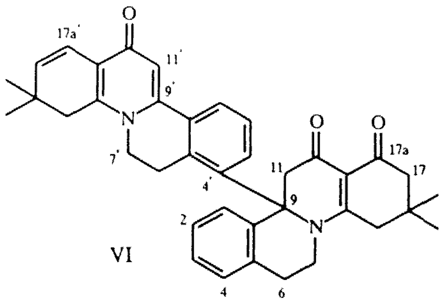

IIa, b


IIIa, b


IV, b


Va, b

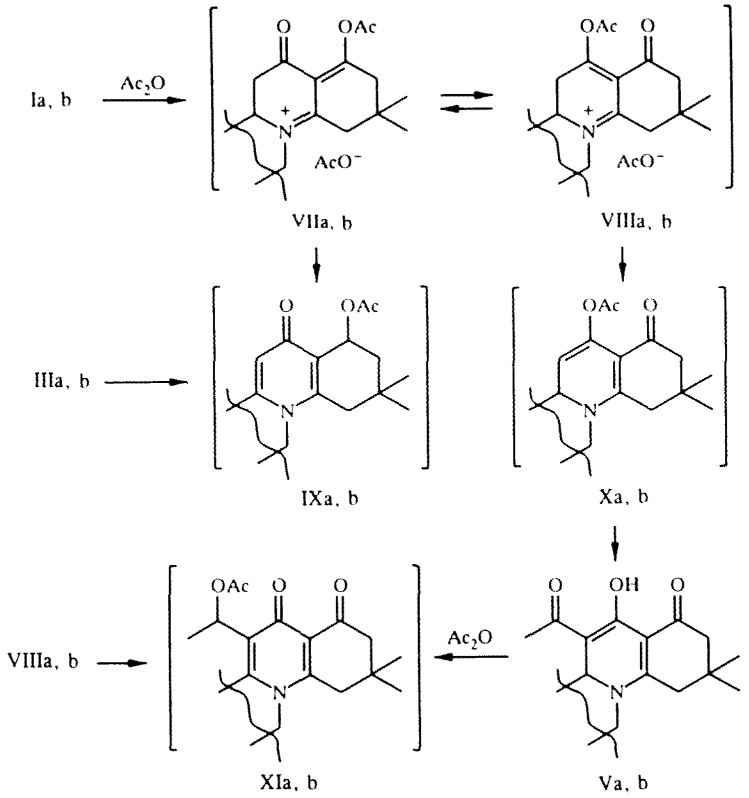
a R = H, b R = OMe


VI

The interaction of the 8-aza-D-homogonanes Ia,b with acetic anhydride was carried out by heating a mixture of the reactants in an argon atmosphere, with the aim of eliminating any possible oxidative processes involving atmospheric oxygen. The reactions were performed with and without fused sodium acetate; the sodium acetate was selected for investigation because of its known catalytic properties in processes of acylation and probable O,C-isomerization. On the basis of the TLC process-monitoring data, we concluded that these reactions are accomplished through several intermediate compounds, leading ultimately to the products IIa,b, IIIa,b, IVa,b, Va, and VI. Let us note that we did not make any special attempts to isolate or establish the structure of the intermediates in these studies. Nonetheless, certain preliminary judgements on the probable reaction path are fully justified, on the basis of the results reported here, data from our previous studies [6-10], other data reported in the literature [11, 12, 16], and views and concepts given in [17, 18].

Thus, as a result of the interaction of the 8-aza-D-homogonane Ia with acetic anhydride in the presence of sodium acetate, we obtain the derivatives IVa and VI as the main products, and the 9(11)-dehydro derivative IIa as a minor product of the reaction. In the absence of sodium acetate, the main reaction products proved to be compounds Va and VI, with compound IIIa as a minor product. Since the reaction mixtures were quite complex, certain minor products may have been lost in the separation process. Nonetheless, from a comparison of the ratio of the principal products IVa and VI (in the presence of AcONa) and the ratio of V and VI (without AcONa), we can judge the role of sodium acetate as a catalyst of the conversion Ia → IVa. This observation is obviously preliminary in character and will require a more detailed test, including tests on other analogs of the homogonanes I.

The interaction of the 8-aza-D-homogonanes Ia,b with acetic anhydride can be represented in generalized form by the following scheme:



Of course, this scheme reflects only one of the basic direction of the reactions; it does not take into account, and does not explain, the paths of formation of all of the products that have been recovered (for example, IIa,b and VI), these products representing the results of other processes that are not yet fu 828 nderstood. When we consider the data of [12] and the well-known fact that vinylogs of amides, including compound I, are protonated preferentially at the oxygen atoms [11], we can postulate as the key primary intermediates of the interaction with acetic anhydride the enoliminium derivatives VII, VIII, which may be the result of both a direct reaction and acylotropic interconversion [17]. Retrosynthetic analysis of the closest predecessors of the derivatives IIIa,b, in turn, leads to the γ-pyridone derivative IX, which is essentially the result of redox disproportionation of the intermediates VII. On the other hand, retrosynthetic analysis of the closest predecessors of the vinyl derivatives IVa,b points successively to the γ-pyridones XI that arise in acylation and redox disproportionation of the acetyl derivatives of V, which in turn are the products of Claisen—Haas O,C-isomerization [13] of the intermediate compounds X. The acetyl-substituted compound Va, which is recovered as one of the products of the reaction without the presence of sodium acetate, is essentially one of the intermediates, supporting the validity of these hypotheses. Thus, the overall sequence of conversions of the 8-aza-D-homogonanes Ia,b in the interaction with acetic acid as represented by the reaction scheme we have shown does not present any significant contradictions.

The formation of the minor products IIa,b (2-5% of theoretical) may be the result of a side process of dehydrogenation of the original homogonanes Ia,b, initiated by the elevated temperature.

Somewhat unexpected was the detection of the derivative VI among the products of interaction of compound Ia with acetic anhydride, either with or without sodium acetate; the formation of this product may be due to a secondary process of alkylation of IIIa by a $C_{(9)}$-carbonium ion that is generated under the reaction conditions from the substrate Ia (Friedel-Crafts reaction [13]). The generation of carbonium ions from compounds having benzyl protons is a rather general condition of ion-radical processes [18]. Since the yield of the derivative VI is approximately half of the total product yield, we are justified in concluding that the process of its formation is another general direction in the conversion of 8-aza-D-homogonane substrates Ia,b under the described conditions. Here it is remarkable that in the case of the 2,3-dimethoxy derivative Ib, no products of the type of VI were detected. This may be explained by the action of steric and electronic factors due to the presence of the two methoxy groups.

The formation of the known 9,11-dehydro derivatives IIa,b was confirmed by the coincidence of their physicochemical characteristics with data reported in the literature [19], and also by comparison with known samples. The structures of the

TABLE 1. Characteristics of Compounds IIIa,b, IVa,b, V, and VI

Compound	Empirical formula	Found, %			Calculated, %			mp, °C	M⁺	IR spectrum, ν, cm⁻¹	UV spectrum, λ_{max}, nm (and ε)	Yield, %
		C	H	N	C	H	N					
IIIa	$C_{19}H_{19}NO$	82,09	6,92	5,01	82,28	6,90	5,05	96...99	277	1638, 1612, 1602, 1581, 1560...1520, 1492	270,9 (21040)	5,0*
IIIb	$C_{21}H_{23}NO_3$	74,51	6,89	4,26	74,75	6,87	4,15	254...257	337	1637, 1604, 1590, 1559, 1510, 1462, 1353, 1273, 1224, 1158, 1032, 848	228,3 (18675), 280,0 (23740)	10,0
IVa	$C_{21}H_{21}NO_2$	78,77	6,62	4,39	78,97	6,63	4,39	217...220	319	1670, 1615, 1580, 1480, 1470, 1455, 1386, 1324, 1243, 1086, 772	277,1 (28580)	40,0
IVb	$C_{23}H_{25}NO_4$	72,57	6,57	3,63	72,80	6,64	3,69	277...281	379	1675, 1620, 1610, 1585, 1524, 1491, 1470...1445, 1272, 1145	266,4 (40910), 292,0 (41405)	46,8
V	$C_{21}H_{23}NO_3$	74,69	6,80	4,17	74,75	6,87	4,15	233...236	337	1705, 1643, 1615...1580, 1510...1480, 1462, 1370, 1335, 1246	251,6 (15360), 318,9 (20170), 376,6 (6510)	43,0*
VI	$C_{38}H_{38}N_2O_3$	79,93	6,99	4,91	79,97	6,71	4,91	182...186	570	1698, 1640, 1614, 1603, 1582, 1530, 1495	270,9 (45546)	40,0, 24,7*

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*Reaction performed without sodium acetate.

TABLE 2. PMR Spectra of Compounds III-VI

Compound	Chemical shifts δ, in ppm, and SSCC (J), in Hz								
	16-gem-Me	15-H	6-H	7-H	17a-H	17-H	11-H	H_{arom}	other protons
IIIa,	1,13 (6H, s)	2,73 (2H, s)	3,06 (2H, t, J = 6,0)	4,10 (2H, t, J = 6,0)	5,66 (1H, d, J = 10,0)	6,84 (1H, d, J = 10,0)	6,94 (1H, s)	7,26 (1H, m, 4-H), 7,39 (2H, m, 2- & 3-H), 7,72 (1H, m, 1-H)	
IIIb	1,12 (6H, s)	2,71 (2H, s)	3,00 (2H, t, J = 6,0)	4,06 (2H, t, J = 6,0)	5,65 (1H, d, J = 10,0)	6,85 (1H, d, J = 10,0)	6,83 (1H, s)	6,74 (1H, s, 4-H); 7,18 (1H, s, 1-H)	
IVa	1,10 (6H, s)	2,76 (2H, s)	3,08 (2H, t, J = 6,0)	3,98 (2H, t, J = 6,0)	–	2,36 (2H, s)	–	7,30...7,46 (3H, m, 2-, 3- & 4-H); 7,72 (1H, m, 1-H)	3,91 (3H, s) OMe); 3,94 (3H, s, OMe)
IVb	1,11 (6H, s)	2,76 (2H, s)	3,01 (2H, t, J = 6,0)	3,94 (2H, t, J = 6,0)	–	2,36 (2H, s)	–	6,87 (1H, s, 4-H), 7,25 (1H, s, 1-H)	5,50 (1H, dd, J = 3,0, 11,0, 11-$\underline{CH}$-CH_2), 6,42 (1H, dd, J = 11,0, 17,5, 11-CH-$\underline{CH_2}$), 6,57 (1H, d. d, J = 3,0, 17,5, 11-CH-CH_2)
V	1,04 (3H, s), 1,10 (3H, s)	2,38 (1H, d, J = 17,5, H_B), 2,50 (1H, d, J = 17,5, H_A)	3,14 (2H, m)	3,97 (2H, m)	–	2,18 (1H, d, J = 16,5, H_B); 2,30 (1H, d, J = 16,5, H_A)	–	6,90 (1H, m, 7,04...7,21 (3H, m),	3,83 (3H, s, OMe), 3,96 (3H, s, OMe), 5,63 (1H, d. d, J = 5,0, 9,0, 11-$\underline{CH}$-CH_2), 6,55 (2H, m, J = 1,0, 9,0, 11-CH-$\underline{CH_2}$)
VI*	1,17 (3H, s), 2,10 (3H, s), [1,10 (6H, s)]	2,61 (2H, dd, J = 17, H_AH_B), [2,74 (2H, s)]	3,04 (2H, m), [3,04 (2H, m)]	3,76 (1H, m), 4,15 (1H, tt) J = 4,0, 4,0, 14,0), [4,10 (2H, t, J = 6,0)]	– [5,66 (1H, d, J = 10,0]	2,26 (2H, s), [6,85 (1H, d, J = 10,0]	3,08 (1H, d. J = 16,5, H_B), 3,48 (1H, d, J = 16,5, H_A), [6,92 (1H, s)]	7,10 (1H, m), 7,23 (2H, m), 7,40 (2H, m), 7,70 (1H, m), 7,90 (1H, m),	–

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*Values listed in brackets are for signals from protons of hexaenone residue IIIa (H').

TABLE 3. Coordinates and Equivalent Thermal Parameters of Nonhydrogen Atoms in Structure of 8-Aza-D-homogonane IVa

Atom	x/a	y/b	z/c	B(eq)
$C_{(1)}$	0,0903(3)	0,4272(2)	1,2778(2)	3,95(6)
$C_{(2)}$	0,0565(3)	0,4116(3)	1,3807(2)	5,08(8)
$C_{(3)}$	0,1597(4)	0,3776(3)	1,4611(2)	5,54(9)
$C_{(4)}$	0,2955(3)	0,3547(3)	1,4393(2)	4,93(8)
$C_{(5)}$	0,3324(3)	0,3701(2)	1,3360(2)	3,82(6)
$C_{(6)}$	0,4685(3)	0,3368(3)	1,3014(2)	4,25(7)
$C_{(7)}$	0,3968(3)	0,2394(2)	1,1901(2)	3,69(6)
$C_{(9)}$	0,2689(2)	0,4199(2)	1,1456(1)	2,99(5)
$C_{(10)}$	0,2314(2)	0,4096(2)	1,2560(1)	3,35(5)
$C_{(11)}$	0,2473(2)	0,5199(2)	1,0801(1)	3,10(5)
$C_{(12)}$	0,2626(2)	0,5046(2)	0,9657(1)	3,01(5)
$C_{(13)}$	0,2730(2)	0,3664(2)	0,9261(1)	2,93(5)
$C_{(14)}$	0,3117(2)	0,2795(2)	0,9989(1)	2,84(5)
$C_{(15)}$	0,3435(2)	0,1450(2)	0,9631(2)	3,46(6)
$C_{(16)}$	0,2585(3)	0,0737(2)	0,8433(2)	3,74(6)
$C_{(17)}$	0,2977(3)	0,1979(2)	0,7727(2)	4,23(7)
$C_{(17a)}$	0,2432(2)	0,3185(2)	0,8065(2)	3,45(6)
$C_{(18)}$	0,3298(3)	-0,0381(3)	0,8108(2)	5,09(8)
$C_{(19)}$	0,0680(3)	-0,0089(2)	0,8281(2)	4,98(7)
$C_{(20)}$	0,2171(3)	0,6470(2)	1,1247(2)	3,96(6)
$C_{(21)}$	0,1661(3)	0,7387(3)	1,0713(2)	5,04(8)
$O_{(1)}$	0,2677(2)	0,6031(1)	0,9084(1)	4,04(5)
$O_{(2)}$	0,1743(2)	0,3702(2)	0,7375(1)	5,19(6)
$N_{(1)}$	0,3219(2)	0,3126(2)	1,1084(1)	3,00(4)

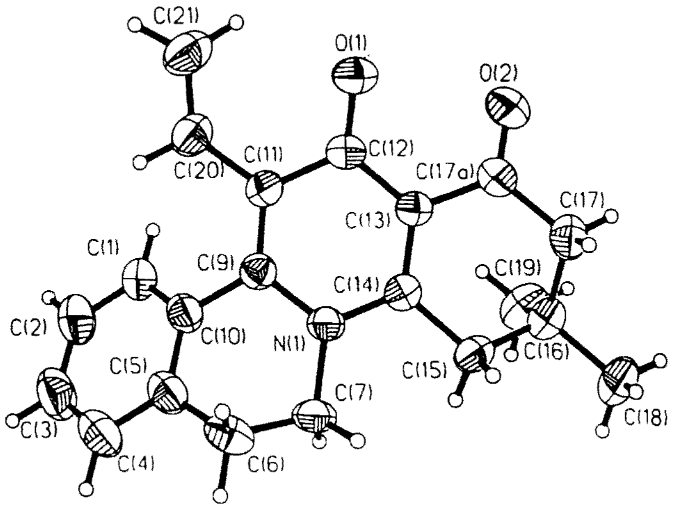

Fig. 1. Geometry of molecule of 8-aza-D-homogonane IVa.

products IIIa,b, IVa,b, V, and VI are consistent with their physicochemical characteristics (Table 1); in the case of the derivative IVa, the structure was also confirmed by x-ray structure analysis. Thus, IR and UV spectroscopic data on the derivatives IIIa,b and VIa,b, which contain the γ-pyridone fragment (ring C), correlate with the literature data for related compounds [20, 21]. At the same time, in the PMR spectra of the products IIIa,b and IVa,b, extremely characteristic signals of vinyl groupings are observed, the $C_{(17)}{=}C_{(17a)}H$ group for IIIa,b, and $CH{=}CH_2$ in position 11 for the IVa,b. A characteristic, distinctive feature of the derivative V is the presence of a downfield signal in the PMR spectrum from the enol proton; another feature is the resonance signal of the methyl group of the acyl substituent at $C_{(11)}$. Analysis of the PMR spectrum of the derivative VI provides evidence for the presence of a fragment corresponding to the structure IIIa, and also

TABLE 4. Bond Lengths of Nonhydrogen Atoms in Molecule of 8-Aza-D-homogonane IVa

Bond	d, Å	Bond	d, Å
$C_{(1)}-C_{(2)}$	1,385(3)	$C_{(1)}-C_{(10)}$	1,399(3)
$C_{(2)}-C_{(3)}$	1,378(4)	$C_{(3)}-C_{(4)}$	1,377(5)
$C_{(4)}-C_{(5)}$	1,399(3)	$C_{(5)}-C_{(6)}$	1,495(3)
$C_{(5)}-C_{(10)}$	1,393(3)	$C_{(6)}-C_{(7)}$	1,509(3)
$C_{(7)}-N_{(1)}$	1,490(3)	$C_{(9)}-C_{(10)}$	1,485(3)
$C_{(9)}-C_{(11)}$	1,369(2)	$C_{(9)}-N_{(1)}$	1,398(2)
$C_{(11)}-C_{(12)}$	1,470(2)	$C_{(11)}-C_{(20)}$	1,471(3)
$C_{(12)}-C_{(13)}$	1,456(2)	$C_{(12)}-O_{(1)}$	1,236(2)
$C_{(13)}-C_{(14)}$	1,377(2)	$C_{(13)}-C_{(17a)}$	1,483(3)
$C_{(14)}-C_{(15)}$	1,511(3)	$C_{(14)}-N_{(1)}$	1,368(2)
$C_{(15)}-C_{(16)}$	1,529(3)	$C_{(16)}-C_{(17)}$	1,525(3)
$C_{(16)}-C_{(18)}$	1,532(4)	$C_{(16)}-C_{(19)}$	1,527(3)
$C_{(17)}-C_{(17a)}$	1,506(3)	$C_{(17a)}-O_{(2)}$	1,217(3)
$C_{(20)}-C_{(21)}$	1,322(3)		

TABLE 5. Bond Angles of Nonhydrogen Atoms in Structure of 8-Aza-D-homogonane IVa

Angle	ω, deg	Angle	ω, deg
$C_{(2)}-C_{(1)}-C_{(10)}$	119,6(2)	$C_{(1)}-C_{(2)}-C_{(3)}$	120,4(2)
$C_{(2)}-C_{(3)}-C_{(4)}$	120,5(3)	$C_{(3)}-C_{(4)}-C_{(5)}$	120,1(2)
$C_{(4)}-C_{(5)}-C_{(6)}$	124,2(2)	$C_{(4)}-C_{(5)}-C_{(10)}$	119,4(2)
$C_{(6)}-C_{(5)}-C_{(10)}$	116,2(2)	$C_{(5)}-C_{(6)}-C_{(7)}$	108,8(2)
$C_{(6)}-C_{(7)}-N_{(1)}$	110,9(2)	$C_{(10)}-C_{(9)}-C_{(11)}$	124,7(2)
$C_{(10)}-C_{(9)}-N_{(1)}$	114,8(2)	$C_{(11)}-C_{(9)}-N_{(1)}$	120,5(2)
$C_{(1)}-C_{(10)}-C_{(5)}$	119,9(2)	$C_{(1)}-C_{(10)}-C_{(9)}$	121,3(2)
$C_{(5)}-C_{(10)}-C_{(9)}$	118,6(2)	$C_{(9)}-C_{(11)}-C_{(12)}$	119,8(2)
$C_{(9)}-C_{(11)}-C_{(20)}$	120,5(2)	$C_{(12)}-C_{(11)}-C_{(20)}$	119,6(2)
$C_{(11)}-C_{(12)}-C_{(13)}$	115,1(2)	$C_{(11)}-C_{(12)}-O_{(1)}$	121,9(2)
$C_{(13)}-C_{(12)}-O_{(1)}$	123,0(2)	$C_{(12)}-C_{(13)}-C_{(14)}$	120,6(2)
$C_{(12)}-C_{(13)}-C_{(17a)}$	120,2(2)	$C_{(14)}-C_{(13)}-C_{(17a)}$	119,3(2)
$C_{(13)}-C_{(14)}-C_{(15)}$	122,6(2)	$C_{(13)}-C_{(14)}-N_{(1)}$	120,3(2)
$C_{(15)}-C_{(14)}-N_{(1)}$	117,1(2)	$C_{(14)}-C_{(15)}-C_{(16)}$	113,9(2)
$C_{(15)}-C_{(16)}-C_{(17)}$	108,1(2)	$C_{(15)}-C_{(16)}-C_{(18)}$	108,6(2)
$C_{(15)}-C_{(16)}-C_{(19)}$	110,7(2)	$C_{(17)}-C_{(16)}-C_{(18)}$	110,3(2)
$C_{(17)}-C_{(16)}-C_{(19)}$	110,1(2)	$C_{(18)}-C_{(16)}-C_{(19)}$	109,0(2)
$C_{(16)}-C_{(17)}-C_{(17a)}$	113,0(2)	$C_{(13)}-C_{(17a)}-C_{(17)}$	117,0(2)
$C_{(13)}-C_{(17a)}-O_{(2)}$	122,4(2)	$C_{(17)}-C_{(17a)}-O_{(2)}$	120,5(2)
$C_{(11)}-C_{(20)}-C_{(21)}$	128,8(2)	$C_{(7)}-N_{(1)}-C_{(9)}$	119,0(2)
$C_{(7)}-N_{(1)}-C_{(14)}$	120,4(2)	$C_{(9)}-N_{(1)}-C_{(14)}$	120,5(2)

a fragment of the original Ia without a benzyl proton at $C_{(9)}$. Here it is remarkable that one of the methyl groups undergoes a rather significant downfield shift (~200 Hz), apparently as a result of the anisotropic influence of the environment. In the 5.0-8.0 ppm region in the spectrum of VI, we observe resonance signals of 10 protons, of which one is manifested in the form of a singlet (11-H), two in the form of coupled spin—spin interaction of doublets (17-H and 17a-H), and the others in the form of multiplets that are characteristic for a substituted benzene ring, with an overall integral intensity corresponding to seven protons. Conclusive support for the structure of the vinyl derivatives IVa,b was obtained by means of x-ray structural investigation of compound IVa (see Fig. 1 and Tables 3-5). The x-ray diffraction data fully support the structure established for this production on the basis of the spectroscopic data; the x-ray data also provide information on its steric structure that was not evident from the spectroscopic data. The most important features of the structure of the derivative IVa are as follows:

a) The C ring is flattened — the average deviation of its constituent rings from the average plane is no greater than 0.098 Å, and the lengths of its constituent bonds are equalized, thus confirming the γ-pyridone structure. Here, the alternation of bond orders clearly indicates its quasiaromatic nature.

b) The plane of the aromatic ring A is rotated 43° relative to the average plane of ring C, practically eliminating any significant electronic interactions between these rings, and pointing out the unsoundness of the conclusion drawn in [21] as to conjugation of rings A and C with delocalization of electron density through the AC fragment of 8-azasteroids having a γ-pyridone ring C.

c) The bond angles $C_{(13)}-C_{(12)}-O_{(1)}$ and $C_{(13)}-C_{(17a)}-O_{(2)}$ are increased (Table 4) in comparison with the statistically average observed values [22]; this can apparently be explained by Coulomb repulsion of the like-charged oxygen atoms $O_{(1)}$ and $O_{(2)}$.

d) The vinyl group at $C_{(11)}$ lies very nearly in the same plane as the carbonyl group $C_{(12)}=O_{(1)}$, probably because of the very significant deformation of the bond angle $C_{(11)}-C_{(20)}-C_{(21)}$, which amounts to almost 9°C.

In view of the conformational rigidity of the tetracyclic 8-aza-D-homogonane skeleton and the insignificant influence of the alkyl and alkenyl substitutes on its geometric parameters, we can conclude that the x-ray diffraction results obtained on compound IVa can be extended with a high degree of probability to other 8-aza-D-homogona-12,17a-diones with a γ-pyridone C ring [19], and that these results can be used in studying specific properties of these compounds [20, 21].

A more detailed discussion of the experimental data and the results of the x-ray diffraction studies of the structure of the derivative IVa will be presented in a separate article.

Thus, the results presented in this article lead to the conclusion that we have found a new process for the conversion of cyclic compounds containing an AAVC fragment when subjected to the action of acetic anhydride. One of the directions of this process, in terms of the overall result that is achieved, may be defined as redox deoxogenation. The basically new direction we have found in structural-functional transformations of condensed nitrogen-containing carbonyl compounds may be general in character (see also data reported in [16]).

EXPERIMENTAL

The course of the reactions and the purities of the products were monitored by TLC on standard Silufol UV-254 plates with chloroform—methanol eluent (9.5:0.5), development in UV light or by iodine vapor, with subsequent holding at 250-350°C. Melting points were determined on a Boetius heating stage. IR spectra were taken on a UR-20 instrument in KBr tablets. Electronic absorption spectra were obtained in a Specord M-400 spectrophotometer for solutions of the compounds in methanol. PMR spectra were recorded in a Bruker AC-200 spectrometer (200 MHz) in $CDCl_3$, internal standard TMS. Mass spectra were measured in a Varian MAT-311 mass spectrometer, energy of ionizing radiation 70 eV.

Elemental analyses of the new compounds IIIa,b, IVa,b, V, and VI for C, H, and N matched the calculated values (see Table 1).

X-Ray Structure Analysis of Compound IVa. A three-dimensional set of x-ray diffraction data was obtained in a Nicolet $R3_m$ automatic four-circle diffractometer (Mo Kα radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max} = 60°$). Compound IVa crystallizes in the triclinic system, space group PI, z = 2. The elementary cell parameters are: a = 8.857 (3) Å, b = 9.821 (3) Å, c = 12.547 (3) Å, α = 93.89 (2)°, β = 100.92 (3)°, γ = 112.91 (2)°, V = 947.9 (5) $Å^3$. The structure was resolved by the direct method and refined in the anisotropic approximation for the nonhydrogen atoms, R = 6.24, R_w = 6.62 (3387 independent reflections with $F > 3\sigma/F/$).

Interaction of 8-Aza-D-Homogonanes Ia,b with Acetic Anhydride. A. A mixture of 1.54 g (5.2 mmoles) of the homogonane Ia, 0.27 g (3.3 mmoles) of fused sodium acetate, and 15 ml of acetic anhydride was refluxed in an argon atmosphere for 4 h. Then the reaction mass was boiled down; the residue was treated with a mixture of chloroform and water; the organic phase was separated, washed with water, dried with sodium sulfate, and evaporated down; the residue was chromatographed on 5/40μ silica gel with eluent 1:1 chloroform—hexane, then chloroform. Recovered 0.08 g of compound IIa, 0.66 g of 11-vinyl-16,16-dimethyl-8-aza-D-homogona-1,3,5(10),9(11),13-pentaene-12,17a-dione IVa, and 0.59 g of 9-(16',16',8'-aza-D-homogona-1',3',5(10),9(11)',13',17'-hexaen-12'-on-4'-yl)-16,16-dimethyl-8-aza-D-homogona-1,3,5(10),13-tetraene-12,17a-dione VI. The product IIa was chromatographically identical to a known sample; mp 249-250°C; literature mp 247-250°C [19].

B. A mixture of 1.51 g (5.1 mmoles) of the homogonane Ia and 20 ml of acetic anhydride was refluxed in an argon atmosphere for 2.5 h. Then the reaction mixture was boiled down, and the residue was held in a vacuum desiccator over KOH for complete removal of the acetic acid; as a result of subsequent separation by flash chromatography on 5/40μ silica gel (eluent 1:1 chloroform—hexane), two fractions were obtained. The first fraction yielded 0.74 g of 11-acetyl-16,16-dimethyl-8-aza-D-homogona-1,3,5(10),13-tetraene-12,17a-dione V. Rechromatographing of the second fraction yielded 0.36 g of the derivative VI and 0.07 g of 16,16-dimethyl-8-aza-D-homogona-1,3,5(10),9(11),13,17-hexaen-12-one IIIa.

C. A mixture of 1.77 g (5.0 mmoles) of the homogonane Ib, 0.41 g (5.0 mmoles) of fused sodium acetate, and 20 ml of acetic anhydride was refluxed in an argon atmosphere for 8 h. Then the reaction mixture was treated by procedure A; after chromatographing, obtained 0.17 g of 16,16-dimethyl-2,3-dimethoxy-8-aza-D-homogona-1,3,5(10),9(11),13,17-hexaen-12-one IIIb, 0.89 g of 11-vinyl-16,16-dimethyl-2,3-dimethoxy-8-aza-D-homogona-1,3,5(10),9(11),13-pentaene-12,17a-dione IVb, and also 0.08 g (4.5%) of the 9(11)-dehydro derivative IIb, chromatographically identical with a known sample, mp 284-287°C, literature mp 286°C [19].

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