CYCLIZATION OF N-ALKYLAZINIUM CATIONS WITH BISNUCLEOPHILES.

4.* REGIO- AND STEREOSPECIFICITY OF THE REACTIONS OF β-DIKETONES WITH QUINOXALINIUM SALTS AND THEIR AZA AND BENZO ANALOGS

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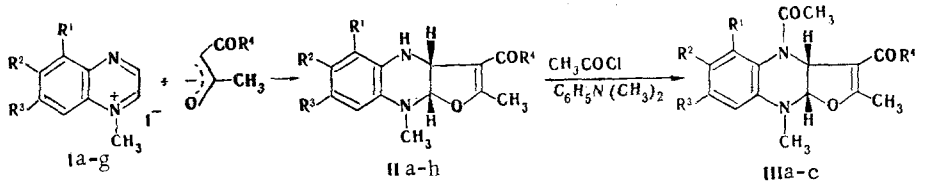
The reactions of substituted quinoxalinium, benzo[g]- and benzo[f]quinoxalinium, and pyrido[2,3-b]pyrazinium salts with anions of β-dicarbonyl compounds give furo-[2,3-b]-annelated systems with strictly determined regio- and stereoorientations.

In previous papers [1 , 2] we reported the cyclization of anions of β-diketones with N-alkylquinoxalinium salts (I), which leads to the formation of 3a,4,9,9a-tetrahydro-cis-furo-[2,3-b]quinoxalines (II). The observed regio- and stereospecificity of the reaction made it possible to assume that the reaction has concerted character [1]. In the present research we studied the effect of substitution in the benzene ring of quinoxaline on the cyclization. An investigation of the effects induced by substituents with various electronic effects gives additional information as to whether the reaction is a stepwise process or a pericyclic synchronous process [3].

The behavior of quaternary salts obtained by quaternization of quinoxalines that contain donor methyl groups (Ia), halogens (Ic-f), a condensed benzene ring (Ib, g), and an aza grouping (IV) in reactions with β-diketones was investigated. According to the PMR data, mixtures of 6- and 7-substituted salts Ic, d and Ie, f in ratios of ~1:1 are formed in the quaternization of 6-chloroquinoxaline and 6-bromoquinoxaline. Because of the similarity in their spectral characteristics, the precise compositions of the mixtures cannot be determined on the basis of the PMR spectral data. Mixtures of the isomers were subjected to reaction with acetylacetone. An analysis of the PMR spectra of the reaction mixtures showed that both isomeric salts form the corresponding furoquinoxalines II with the same stereo- and regioorientations as unsubstituted quinoxalinium salts [1, 2]. Mixtures of two substances consisting primarily of 6-halo-substituted 3a,4,9,9a-tetrahydro-cis-furo[2,3-b]quinoxalines, which can be isolated as individual substances IIc, e (Table 1), were also isolated preparatively from the reaction solutions. Linear and angular benzo annelation and the concerted effect of two methyl groups (the 5,7-dimethylquinoxalinium salt) also do not change the orientation of the reagents, and this indicates, with a high degree of probability, synchronous cycloaddition [3]. The only products established both preparatively and from the PMR spectra of the reaction mixtures were 3a,4,9,9a-tetrahydro-cis-furo[2,3-b]quinoxalines (IIa-h) (Table 1). The reaction of cations Ia-g with diketones was carried out over the same temperature range (from −50 to +25°C) as the reaction of unsubstituted quinoxalinium salts [1, 2]. The preparative yields of the resulting IIa-h varied over a wide range (30-80%); this was due to their low



I—III a $R^1=R^3=CH_3$, $R^2=H$; b,h $R^1=H$, $R^2=R^3=$ benzo: c $R^1=R^3=H$, $R^2=Cl$; d $R^1=R^2=H$, $R^3=Cl$; e $R^1=R^3=H$, $R^2=Br$; f $R^1=R^2=H$, $R^3=Br$; d $R^1=R^2=$ benzo, $R^3=H$; for IIb $R^4=OC_2H_5$, for the remaining compounds $R^4=CH_3$

*See [1] for Communication 3.

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TABLE 1. Physical Constants of II and III

Compound	mp, °C	R_f	PMR spectra: chemical shifts, δ, ppm: 3a-H	PMR spectra: chemical shifts, δ, ppm: 9a-H (11a)	PMR spectra: SSCC, $J_{3a9a(11a)}$	PMR spectra: SSCC, J_{3a}, CH_3	UV spectra in ethanol, λ_{max}, nm (log ε)	IR spectra, ν, cm^{-1}: NH	IR spectra, ν, cm^{-1}: C=C, C=O
IIa	92—94 (dec.)	—	5,17	5,84	9,3	1,0	220 (4,51); 253 (4,26); 282 (4,01)		
IIb	114—116 (dec.)	—	5,06	5,86	9,3	1,0	218 (4,35); 250 (4,82); 344 (3,75)	3362	1643, 1680
IIc	97—99 (dec.)	—	5,07	5,81	9,1	0,9	222 (4,54); 257 (4,28); 309 (3,74)	3337	1622
IIe	127—129 (dec.)	—	5,09	5,81	9,0	1,0	224 (4,52); 257 (4,30); 309 (3,70)	3341	1596, 1620
IIg	125—127 (dec.)	—	5,33	5,92	9,2	0,9	218 (4,37); 256 (4,56); 324 (3,46); 357 (3,51)	3374	1602, 1626
IIh	128—130 (dec.)	—	5,06	5,99	9,0	1,0	219 (4,30); 252 (4,70); 343 (3,73)	3360	1603, 1613, 1642
IIIa	144—145	0,60	In the aromatic region 6,95	5,93	9,3	1,1	218 (4,35); 248 (4,12); 282 (3,94)	—	1595, 1604, 1665
IIIb	199—200	0,64		5,76	9,6	1,2	218 (4,35); 250 (4,68); 341 (3,36)	—	1650, 1670, 1696
IIIc	146—147	0,59		5,80	9,6	1,6	224 (4,35); 252 (4,40)	—	1595, 1605, 1666

TABLE 2. Characteristics of IX

Compound	mp, °C	R	PMR spectra: chemical shifts, δ, ppm: 3a-H	11a-H	8-H	9-H	SSCC, Hz: J_{3a11a}	J_{3a, CH_3}	J_{89}	UV spectra in ethanol, λ_{max}, nm (log ε)	IR spectra, ν, cm^{-1}
IXa	268—270	CH_3	5,32	6,22	6,34	6,79	7,3	1,0	7,3	224 (4,22), 258 (4,50), 323 (3,75)	1662, 1675 (CCl_4)
IXb	187—188	OC_2H_5	5,27	6,20	6,42	6,72	7,0	1,0	7,2	216 (4,45), 243 (4,58), 315 (3,90)	1666, 1713 (CCl_4)
IXc	173—174	$CH_2CH—(CH_3)_2$	5,30	6,21	6,44	6,74	7,3	1,0	7,3	216 (4,39), 243 (4,59), 314 (3,87)	1670, 1697, 1713 (CCl_4)

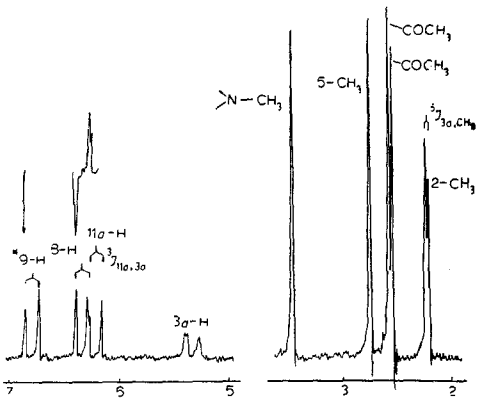


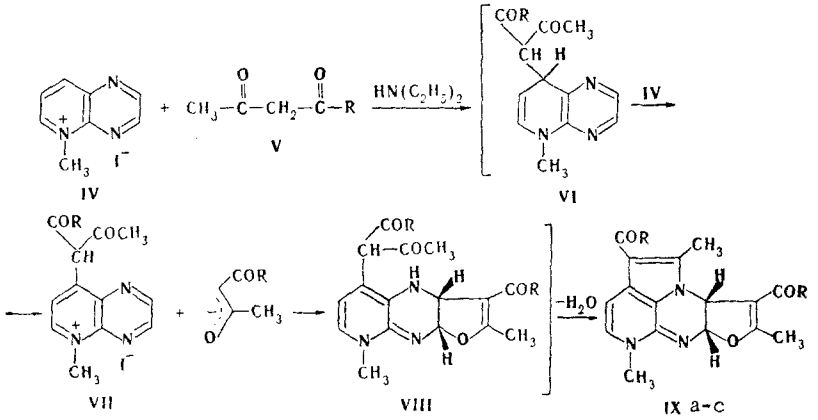
Fig. 1. INDOR spectrum of IXa in deuterochloroform.

stabilities. However, according to the PMR spectral data, mixing of the reagent in methanol CD_3OD at room temperature leads to the quantitative formation of furo-[2,3-b]quinoxalines (IIa-h).

The structure of IIa-h was proved by means of the PMR spectra (Table 1), which, upon the whole, are similar to the spectra of II, which do not have substituents in the benzene ring and are characterized by close values of the chemical shifts and spin—spin coupling constants (SSCC) [1]. It was demonstrated by x-ray diffraction analysis [1] that cycloadducts II in the crystalline state have endo-structure II with a cis orientation of the 3a-H and 9a-H atoms. The regioorientation of the furan ring relative to the N-methylpyrazine ring was proved by the fact that of the two signals of protons of the angular atoms, the

stronger field 3a-H signal is shifted markedly ($\Delta = \sim 2$ ppm) to weak field after acetylation, while the chemical shift of the 9a-H (11a-H) proton, which is attached to the carbon atom between the two heteroatoms, changes only slightly (compare the PMR spectra of IIa and IIIa, IIb, and IIIb, and IIc and IIIc).

The introduction of an aza grouping changes the reactivity of the quinoxalinium ion substantially. A distinctive feature of its aza analog, viz., the pyrido[2,3-b]pyrazinium cation (IV), in reactions with β-diketones is the fact that the cycloaddition of the enolate anion to the pyrazine ring is evidently preceded by the addition of the carbanion of the diketone to the 4 position of the pyridine ring, and the resulting dihydro compound VI is oxidized by starting cation IV to cation VII, as has been frequently observed in reactions involving nucleophilic substitution of hydrogen in azinium cations [4]. Cation VII undergoes cycloaddition with a second molecule of the diketone, after which the amino groups undergoes intramolecular condensation with the acetyl carbonyl group in VIII to give 3a,4,10,11a-tetrahydro-cis-fuor[3,2-b]pyrrolo[3,2,1-ij]pyrido[2,3-b]pyrazines (IXa-c) (Table 2). The reverse order of the steps is less likely, since cycloaddition of the enolate to the pyrazine ring converts it to a donor fragment that contains two amino groups and has decreased electrophilicity of the pyridine fragment.



R = CH_3, OC_2H_5, $CH_2CH(CH_3)_2$

The structure of IXa-c was proved by means of the ^1H and ^{13}C NMR and mass spectra. The protons of the pyridine and pyrazine rings form two independent AB spin systems, the choice between which was made by the INDOR internuclear method (Fig. 1).

One of the atoms of the pyrazine ring in IXa-c is a "pyridine" atom, and this is reflected in the weaker-field (as compared with II) chemical shifts of the 3a-H protons, as well as in the chemical shift of the methyl group of the furan ring (Table 2). The lower $^3J_{3a,11a}$ value (Table 2) can also be explained by the effect of the aza group, since it is known that acceptor substituents lower the magnitude of the vicinal constant [5]. Let us also note that, in contrast to II, the nitrogen atoms of the pyrazine ring in IX lie in a single plane, and this cannot be reflected in the $^3J_{3a,11a}$ SSCC. Considering this, as well as the related character of the starting substances, viz., quinoxalinium salts Ia-g and their aza analog IV, we assigned a cis-adduct structure to IX.

The mass spectra of IXa, b are characterized by intense molecular-ion peaks (M^+) and high-intensity peaks of $[M - 1]^+$ and $[M - 2]^+$ ions formed as a result of dehydrogenation (Table 2), the stabilities of which are due to the cyclic structure of IX.

The participation of the pyrido[2,3-b]pyrazinium ion in cyclization with enolates of diketones makes it possible to conclude that the reaction under consideration is applicable not only to 1,4-pyrazinium salts but also to uncharged pyrazines that are activated by a strong acceptor substituent. The reaction may evidently serve as a general method for the synthesis of furo[2,3-b]-annelated systems with strictly determined regio- and stereoorientations.

EXPERIMENTAL

The UV spectra were obtained with a Specord spectrophotometer. The IR spectra were recorded with a UR-20 spectrometer. The PMR spectra were recorded with Perkin-Elmer R-12B (60 MHz) and Bruker HX-90 spectrometers with tetramethylsilane and hexamethyldisiloxane as

the internal standards. The ^{13}C NMR spectra were obtained with a Bruker HX-90 spectrometer. The mass spectra were obtained with a modified MKh-1303 mass spectrometer with a system for direct introduction of the samples into the ion source at an accelerating voltage of 3.6 kV, an ionizing-electron energy of 30 eV, an emission current of 1.5 mA, and sample-vaporization temperatures of 190-220°C. Thin-layer chromatography (TLC) was carried out on Silufol UV-254 (elution with ethanol).

The starting quinoxalines were obtained from the corresponding o-diamines by the method used in [6, 7], the benzoquinoxalines were obtained by the method in [9]. Quaternary salts Ia,b,g were synthesized by dissolving the corresponding bases in a threefold excess of methyl iodide with subsequent separation of the salt crystals. The 6-chloro- and 6-bromoquinoxalines were quaternized at an appreciable rate only when they were heated in a mixture of methyl iodide with dimethyl sulfoxide (DMSO) (4:1) at 60°C for 24 h and gave mixtures of isomeric cations Ic,d and Ie,f, respectively. 5-Methylpyrido[2,3-b]-pyrazinium iodide was synthesized by the method in [10].

2,5,7,9-Tetramethyl-3-acetyl-3a,4,9,9a-tetrahydro-cis-furo[2,3-b]quinoxaline (IIa). A 2-ml (0.02 mole) sample of acetylacetone was added to a suspension of 2 g (0.007 mole) of 1,5,7-trimethylquinoxalinium iodide (Ia) in 4 ml of ethanol, after which 2 ml (0.019 mole) of diethylamine was added with stirring, during which the starting salt dissolved, and the reaction mixture became warmer. After 10-15 min, the resulting colorless precipitated IIa was removed by filtration and washed with ethanol and ether to give 0.7 g (38%) of colorless needles (from ethanol) with mp 92-94°C (dec.). PMR spectrum ($CDCl_3$): 3.07 (s, NCH_3); 2.10 (d, CH_3); 2.05 (s, $COCH_3$); 4.82 (NH); 2.23 (s, 6H, two methyl groups of the benzene ring); 5.17 (dq, 3a-H); 5.84 (d, 9a-H); 6.44, 6.53 ppm (d, 6-H and 3-H). Found: C 70.8; H 7.4; N 10.5%. $C_{16}H_{20}N_2O_2$. Calculated: C 70.6; H 7.4; N 10.3%.

2,5,7,9-Tetramethyl-3,4-diacetyl-3a,4,9,9a-tetrahydro-cis-furo[2,3-b]-quinoxaline (IIIa). A 2-g (7.4 mmole) sample of IIa was dissolved by heating in 14 ml of acetic anhydride, and the mixture was heated at 80°C for 5 min. It was then poured over 50 g of ice, and the mixture was allowed to stand overnight. Compound IIIa was extracted three times with chloroform, and the combined extracts were dried with sodium sulfate. The solvent was evaporated, and the residue was recrystallized from ethanol to give 0.4 g (36%) of a product with mp 144-145°C. PMR spectrum [$(CD_3)_2CO$]: 3.00 (s, NCH_3), 1.97 (d, CH_3), 2.30 (s, $NCOCH_3$), 1.78 (s, $COCH_3$), 5.93 (d, 3a;H), 2.20 (s, 6H, two methyl groups of the benzene ring), and 6.6-7.1 ppm (m, 9a-H, 6-H, and 8-H). Found: C 69.1; H 7.1; N 8.7%. $C_{18}H_{22}N_2O_3$. Calculated: C 68.8; H 7.1; N 8.9%.

6-Chloro-2,9-dimethyl-3-acetyl-3a,4,9,9a-tetrahydro-cis-furo[2,3-b]-quinoxaline (IIc). A 4-ml (0.038 mole) sample of diethylamine was added with stirring and cooling to −35°C was added to a suspension of 4 g (0.018 mole) of a mixture of salts Ic,d in 8 ml of ethanol and 4 ml (0.04 mole) of acetylacetone in such a way that the temperature did not rise above −10°C.* The starting mixture of salts dissolved; after 10-15 min, the mixture of IIc,d, from which individual IIc could be isolated after two crystallizations, was removed by filtration. The yield of product with mp 97-99°C (dec.) was 1.35 g (37%). PMR spectrum ($CDCl_3$): 3.02 (s, NCH_3), 2.12 (d, CH_3), 2.25 (s, $COCH_3$), 4.87 (NH), 5.07 (dq, 3a-H), 5.82 (d, 9a-H), and 6.5-6.9 ppm (m, 3H of the benzene ring). Found: C 60.1; H 5.6; N 9.8%. $C_{14}H_{15}ClN_2O_2$. Calculated: C 60.3; H 5.4; N 10.1%.

6-Bromo-2,9-dimethyl-3-acetyl-3a,4,9,9a-tetrahydro-cis-furo[2,3-b]-quinoxaline (IIe). This compound was similarly obtained in 29% yield as colorless needles (from ethanol) with mp 127-129°C (dec.). PMR spectrum ($CDCl_3$): 3.03 (s, NCH_3), 2.14 (d, CH_3), 2.26 (s, $COCH_3$), 4.84 (NH), 5.09 (dq, 3a-H), 5.81 (d, 9a-H), and 6.3-7.1 ppm (3H of the benzene ring). Found: C 52.4; H 4.9; N 8.7%. $C_{14}H_{15}BrN_2O_2$. Calculated: C 52.0; H 4.7; N 8.7%.

6-Chloro-2,9-dimethyl-3,4-diacetyl-3a,4,9,9a-tetrahydro-cis-furo[2,3-b]-quinoxaline (IIIc). A 1.5-ml (12 mmole) sample of dimethylaniline was added to a solution of 2 g (7.2 mmole) of IIc in 100 ml of benzene, after which 0.6 ml (8.4 mmole) of acetyl chloride was added with stirring, and the reaction mixture was allowed to stand for 2 h. The solution was filtered through a thin layer of silica gel (L40/100), the benzene was evaporated, and

*Products with different structures, to which a separate communication will be devoted, were formed in reactions of salts Ic,d and Ie,f with acetylacetone at temperatures above 0°C.

the residue was recrystallized to give 1.0 g (44%) of colorless needles (from ethanol) with mp 146-147°C. PMR spectrum ($CHCl_3$): 2.97 (s, NCH_3), 2.08 (d, CH_3), 2.18 (s, $COCH_3$), 2.08 (s, $NCOCH_3$), 5.80 (d, 9a-H), and 6.7-7.5 ppm (m, 3a-H, 3H of the benzene ring). Found: C 60.2; H 5.4; N 8.9%. $C_{16}H_{17}ClN_2O_3$. Calculated: C 59.9; H 5.3; N 8.7%.

2,11-Dimethyl-3-acetyl-3a,4,11,11a-tetrahydro-cis-furo[2,3-b]benzo[g]-quinoxaline (IIh). A 3-ml (0.029 mole) sample of diethylamine was added to a suspension of 3 g (0.01 mole) of N-methylbenzo[g]quinoxalinium iodide (Ib) in 6 ml of ethanol and 3 ml (0.029 mole) of acetylacetone heated to 50°C, and the reaction mixture was then cooled to 20°C. The resulting precipitate of IIh was removed by filtration and washed with ethanol and ether to give 2.54 g (70%) of colorless needles (from ethanol) with mp 128-130°C (dec.). PMR spectrum ($CDCl_3$ + d_6-DMSO): 3.17 (s, NCH_3), 2.11 (d, CH_3), 2.25 (s, $COCH_3$), 5.44 (NH), 5.06 (dq, 3a-H), 5.99 (d, 11a-H), and 6.8-7.9 ppm (m, 6H of the benzene rings). Found: C 73.3; H 6.3; N 9.3%. $C_{18}H_{18}N_2O_2$. Calculated: C 73.5; H 6.2; N 9.5%.

A similar reaction with ethyl acetoacetate gave IIb in 47% yield as colorless needles (from ethanol) with mp 99-100°C (dec.). PMR spectrum ($CDCl_3$): 3.13 (s, NCH_3); 2.04 (d, CH_3); 1.23 (t) and 4.23 (q, $COOC_2H_5$); 4.93 (NH); 5.06 (dq, 3a-H); 5.86 (d, 11a-H); 6.8-7.9 ppm (m, 6H of the benzene rings). Found: C 69.9; H 6.2; N 9.0%. $C_{19}H_{20}N_2O_3$. Calculated: C 70.4; H 6.2; N 8.7%.

2,11-Dimethyl-3-acetyl-3a,4,11,11a-tetrahydro-cis-furo[2,3-b]benzo[f]-quinoxaline (IIg). This compound was synthesized in 79% yield from N-methylbenzo[f]quinoxalinium iodide (Ig) and acetylacetone in the presence of diethylamine by the method used to prepare IIh. The colorless needles (from ethanol) had mp 125-126°C (dec.). PMR spectrum ($CDCl_3$): 3.18 (s, NCH_3), 2.01 (d, CH_3), 2.16 (s, $COCH_3$), 5.71 (NH), 5.33 (dq, 3a-H), 5.92 (d, 11a-H), and 7.0-8.0 ppm (m, 6H of the benzene rings). Found: C 73.4; H 6.1; N 9.9%. $C_{18}H_{18}N_2O_2$. Calculated: C 73.5; H 6.2; N 9.5%.

Ethyl 2,11-Dimethyl-4-acetyl-3a,4,11,11a-tetrahydro-cis-furo[2,3-b]benzo[g]quinoxaline-3-carboxylate (IIIb). This compound, with mp 199-200°C, was obtained in 58% yield by the method used to prepare IIIc. PMR spectrum ($CDCl_3$): 3.09 (s, NCH_3), 2.00 (d, CH_3), 1.28 (t), 3.9-4.5 (m, $COOC_2H_5$), 2.16 (s, $NCOCH_3$), 6.95 (dq, 3a-H), 5.76 (d, 11a-H), and 7.1-8.0 ppm (m, 6H of the benzene rings). Found: C 69.0; H 6.2; N 7.6%. $C_{21}H_{22}N_2O_4$. Calculated: C 68.8; H 6.1; N 7.7%.

2,5,10-Trimethyl-3,6-diacetyl-3a,4,10,11a-tetrahydro-cis-furo[3,2-b]-pyrrolo[3,2,1-ij]-pyrido[2,3-b]pyrazine (IXa). A 3-ml (0.029 mole) sample of diethylamine was added at room temperature to a suspension of 3 g (0.012 mole) of N-methylpyrido[2,3-b]pyrazinium iodide (IV) in 9 ml of ethanol. The starting salt dissolved, and the solution was allowed to stand overnight. The precipitated IXa was removed by filtration and washed with ethanol and ether to give 0.5 g (30%) of colorless needles (from ethanol) with mp 268-270°C. PMR spectrum ($CDCl_3$): 3.46 (s, NCH_3); 2.23 (d, 2-CH_3); 2.76 (s, 5-CH_3); 2.54, 2.56 (s, 3-$COOCH_3$, 6-$COCH_3$); 5.32 (dq, 3a-H); 6.22 (d, 11a-H); 6.34 (d, 8-H); 6.79 ppm (d, 9-H). ^{13}C NMR spectrum: 12.1 (2-CH_3); 14.7 (5-CH_3); 29.8 and 31.0 (3-$COCH_3$ and 6-$COCH_3$); 36.1 (NCH_3); 62.5 (3a-CH); 81.6 (8-CH); 98.3 (11a-CH); 116.6 and 121.5 (3-C and 6-C); 132.3 (9-CH); 140.6 and 144.6 (5-C and 7-C); 165.2 (2-C); 179.5 and 180.7 (4a-C and 10a-C); 192.3 and 194.1 ppm (3-$COCH_3$ and 6-$COCH_3$). Mass spectrum, m/z (I≥30%): 28 (33.9); 43 (36.6); 44 (47.3), 45 (43.6); 240 (39.9); 254 (31.5); 278 (41.3); 280 (68.8); 281 (30.2); 282 (93.5); 283 (56.6); 310 (50.3); 323 (76.0); 324 (30.0); 325 (100.0); 326 (51.0). Found: C 66.5; H 5.9; N 12.8%. $C_{18}H_{19}N_3O_3$. Calculated: C 66.5; H 5.9; N 12.9%.

Compound IXb, with mp 187-188°C, was similarly obtained in 40% yield by reaction with ethyl acetoacetate. PMR spectrum ($CDCl_3$): 3.46 (s, NCH_3); 2.21 (d, 2-CH_3); 2.73 (s, 5-CH_3); 1.36 (t), 4.35 (q), 1.40 (t), and 4.37 (q, 6.72 ppm (d, 9-H). Mass spectrum, m/z (I 30%): 27 (34.2); 28 (98.4); 29 (48.7); 31 (49.2); 43 (48.0); 44 (77.2); 45 (48.0); 125 (32.9); 242 (58.4); 258 (48.3); 268 (40.5); 269 (30.7); 270 (52.1); 281 (34.8); 282 (39.0); 283 (34.2); 284 (31.4); 286 (34.2); 309 (51.8); 310 (36.5); 311 (50.3); 312 (32.9); 313 (58.5); 314 (75.6); 339 (84.6); 340 (56.1); 342 (100.0); 343 (46.1); 383 (73.2); 385 (93.8); 386 (30.0). Found: C 62.3; H 6.2; N 10.9%. $C_{20}H_{23}N_3O_5$. Calculated: C 62.3; H 6.0; N 10.9%.

Compound IXc, with mp 173-174°C, was similarly obtained in 26% yield from isobutyl acetoacetate. PMR spectrum ($CDCl_3$): 3.44 (s, NCH_3); 2.22 (d, 2-CH_3); 2.76 (s, 5-CH_3); 0.99 (s), 1.11 (s), 1.8-2.1, 3.6-4.4 [m, 3-$COOCH_2CH(CH_3)_2$, 6-$COOCH_2CH(CH_3)_2$]; 5.30 (dq, 3a-H); 6.21 (d, 11a-H); 6.44 (d, 8-H); 6.74 ppm (d, 9-H). Found: C 65.2; H 7.2; N 9.4%. $C_{24}H_{31}N_3O_5$. Calculated: C 65.3; H 7.1; N 9.5%.

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CYCLIZATION OF N-ALKYLAZINIUM CATIONS WITH BISNUCLEOPHILES. 5.* CYCLIC ADDUCTS AND RECYCLIZATION PRODUCTS IN THE REACTIONS OF BENZODIAZINIUM CATIONS WITH IMIDO ESTERS

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The reaction of imido esters that contain an active methylene group with four isomeric benzodiazinium cations, viz., the 1-methylquinoxalinium, 2-methylcinnolinium, 3-methylquinazolinium, and 2-methylphthalazinium cations, was investigated. The 1-methylquinoxalinium cation reacts with imido esters via a scheme involving anionic [3⁻ +2]-cycloaddition to form tetrahydropyrrolo[2,3-b]quinoxalines. The 2-methylcinnolinium cation forms an adduct with an annelated pyrrole ring. Under the influence of imido esters, the 3-methylquinazolinium cation undergoes recyclization to a 2,3-disubstituted quinoline. The 2-methylphthalazinium cation is inert in this reaction.

The research of Strauss on reactions involving so-called "meta bridging" of polynitroaromatic compounds with bisnucleophilic reagents, which leads to complex polycyclic systems in one step [2-6], compelled us to investigate the possibility of the participation of highly π-deficient N-alkylazinium cations in such cyclizations. The observed ortho cyclization of quinoxalinium salts (I) with enamines of ketones [7] has been extended to other 1,3-bisnucleophilic reagents, viz., β-diketons and their esters [8] and amide [9], as well as to other azinium cations that contain a pyrazine fragment [1]. The formation of a five-membered ring, which leads to [2,3-b]-annelated tetrahydropyrazines, was observed in all of these reactions [1,7-9].

In the present research we investigated the reactions of yet another type of bisnucleophilic reagent, viz., CH-active imido esters, with four isomeric benzodiazepinium cations, viz., 1-methylquinoxalinium (I), 2-methylcinnolinium (II), 3-methylquinazolinium (III), and 2-methylphthalazinium (IV) cations. If one starts from the analogies with the reactions of aromatic polynitro compounds, due to the different orientations of the aza groups in this

*See [1] for Communication 4.

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