dry residue was washed with 10 ml of warm toluene, dried under vacuum, and purified by sublimation. We obtained 0.68 g (47.8%) of hydroxytriazaadamantane II, mp 262-263°C. IR spectrum: 2500-3160, 1315, and 1135 cm^{-1} (OH). PMR spectrum ($CDCl_3$): 2.1 (1H, broadened signal, C–OH); 2.71 (6H, singlet, N–CH_2–C); 3.47 and 3.95 ppm (6H, 2 doublets, N–CH_2–N, ^2J = 13.5 Hz). Found: mol. wt. 155. Calculated: mol. wt. 155.

Kinetic Measurements. The rate of hydrolysis of bromotriazaadamantane I was monitored according to the increase of the concentration of Br^- ions. A concentration cell consisting of a silver bromide electrode (in the reaction solution) and a saturated silver chloride electrode (reference electrode) was used for the measurement. A graph of the relation of the emf of the cell to the concentration of Br^- ions was plotted. In this case, it was impossible to monitor the reaction rate according to the pH change because the hydrolysis product, triazaadamantane II, is more basic (pK 8.50) than the starting bromotriazaadamantane I (pK 10.11); therefore, the concentration of H^+ ions decreased during the reaction, i.e., could not be used to plot concentration–time relations.

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RECYCLIZATION OF INDOLO[2,3-c]PYRYLIUM SALTS BY REACTION WITH SECONDARY AMINES

V. I. Dulenko, A. V. Kibal'nyi,
Yu. A. Nikolyukin, V. I. Luk'yanenko,*
A. V. Goncharov, S. A. Sidorova,
D. S. Yufit, and Yu. T. Struchkov

UDC 547.759.3'816.07:548.737

1-R-3-methylindolo[2,3-c]pyrylium salts react with cyclic secondary amines (morpholine, piperidine, and N-methylpiperazine) to give, depending on the structure of the alkyl substituent R, either 1- (when R = Me) or 3-aminocarbazoles (when R = i-Pr), or mixtures of both (when R = Et). The position of the amino-substituent in 1-morpholino-3,9-dimethylcarbazole has been established by x-ray diffraction examination.

The conversion of pyrylium salts into N,N-dialkylanilines was first reported by Diels and Alder in 1927, as exemplified by the reaction of 2-methylpyrylium salts bearing various substituents in the 2- and 4-positions with secondary amines (dimethylamine and piperidine) [1]. This reaction was subsequently used for the development of novel syntheses of dialkylamino-derivatives of naphthalene [2], benzo[b]thiophene [3], benzo[b]selenophene [3], dibenzofuran [4], dibenzothiophene [4], and isomeric thiobenzo[b]thiophenes [5]. The postulated reaction mechanism involves addition of the amine at one of the α-positions of the pyrylium ring, electrocyclic cleavage of the resulting intermediate, and aldol condensation of the cleavage products to give a new aromatic ring [6].

This communication reports the reactions of secondary amines with the indolo[2,3-c]pyrylium salts (Ia-c) to give the aminocarbazoles (IIa-f), (IIIa-f), or their mixtures (Table 1).

*Deceased.

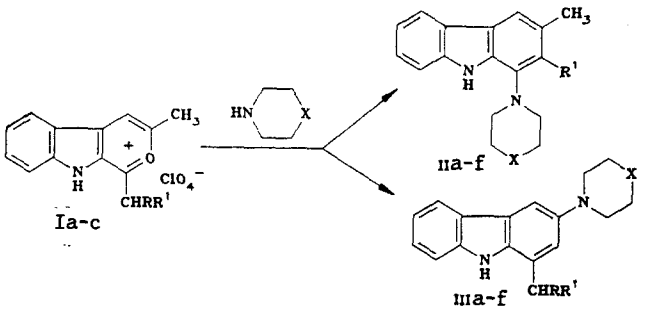
Institute of Physical Organic and Coal Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk 340114. P. I. Lebedev-Polyanskii Vladimir State Pedagogical Institute, Vladimir 600024.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 546-551, April, 1990. Original article submitted November 1, 1988.

TABLE 1. Properties of Compounds Obtained

Compound	Empirical formula	mp, °C* (ethanol)	R_f	Yield, %**
Ib	$C_{14}H_{14}ClNO_5$	200...201	—	71
Ic	$C_{15}H_{16}ClNO_5$	200...201	—	68
IIa	$C_{17}H_{18}N_2O$	213...215	0,64	75
IIb	$C_{18}H_{20}N_2O$	279...280	0,42	60
IIc	$C_{18}H_{20}N_2$	90...92	0,61	72
IId	$C_{19}H_{22}N_2 \cdot HCl$	295...297	0,86	60
IIe	$C_{18}H_{21}N_3 \cdot 2HCl$	305...306	0,15	31
IIf	$C_{19}H_{23}N_3 \cdot C_6H_3N_3O_7$	204...205	0,65	55
IIIa	$C_{18}H_{20}N_2O$	179...180	0,23	15
IIIb	$C_{19}H_{22}N_2O$	188...190	0,84	82
IIIc	$C_{19}H_{22}N_2 \cdot HCl$	306...308	0,57	18
IIId	$C_{20}H_{24}N_2$	129...131	—	68
IIIe	$C_{19}H_{23}N_3 \cdot C_6H_3N_3O_7$	198...200	0,18	12
IIIf	$C_{20}H_{25}N_3$	116...117	0,48	62
V	$C_{18}H_{20}N_2O$	125...126	0,89	66

*Compounds (IIa, b) were recrystallized from toluene, (IIId) and (V) from hexane, (IIIe) from propan-2-ol, and (IIIf) from a 1:4 mixture of benzene and isooctane.
**The yields of (IIIb, d, f) and (IIIa, c, e) were found from the PMR spectra.



Ia R=R¹=H; b R=H, R¹=CH₃; c R=R¹=CH₃; II a R¹=H, X=O; b R¹=CH₃, X=O; c R¹=H, X=CH₂; d R¹=CH₃, X=CH₂; e R¹=H, X=NCH₃; f R¹=CH₃, X=NCH₃; III a R=H, R¹=CH₃, X=O; b R=R¹=CH₃, X=O; c R=H, R¹=CH₃, X=CH₂; d R=R¹=CH₃, X=CH₂; e R=H, R¹=CH₃, X=NCH₃; f R=R¹=CH₃, X=NCH₃

The two different routes for this reaction arise as a result of the possibility of nucleophilic addition of the secondary amine at either of the α-positions in the pyrylium ring in (Ia-c).

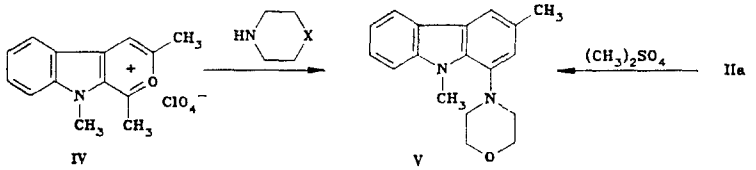
Treatment of the perchlorate (Ic) (with an isopropyl group in the 1-position) with secondary amines (morpholine, piperidine, or N-methylpiperazine), affords 60-80% yields of the carbazoles (IIIb, d, f) with an amino-group in the 3-position. In this instance, no 1-derivatives (II) were formed as a result of the inability of the isopropyl group to participate in the final step of the reaction (aldol condensation). According to their PMR spectra and TLC, the 1,3-dimethyl salt (Ia) also reacted with the above amines to give aminocarbazoles of a single type. It was not, however, possible to assign the products structures (II) or (III) unambiguously from their spectra. On the other hand, 1-ethyl-3-methylindolo[2,3-c]pyrylium perchlorate (Ib) gave mixtures of aminocarbazoles, which were separable by column chromatography on alumina or by crystallization of their hydrochlorides or picrates. The separated compounds were readily identifiable by their PMR spectra, which in the case of the 1-aminocarbazoles (IIb, d, f) showed two singlets for the methyl protons, whereas the 3-aminocarbazoles (IIIa, b, e) gave rise to signals for the ethyl protons. The amount of 1-isomer, as found from the integral intensities of the PMR spectra of the mixtures obtained, was 4-5 times greater than that of the 3-isomer (Table 2). This shows that the salt (Ib) is attacked by secondary amines preferentially at the 1-position. With this in mind, the recyclization products of the dimethyl salt (Ia) are to be regarded as the 1-isomers (IIa, b, e).

TABLE 2. PMR Spectra of Compounds Obtained

Compound	Chemical shifts, δ, ppm (J, Hz)*
Ib	1,58 (3H, t, J=7,5; 1-β-CH_3); 2,91 (3H, s, 3-CH_3); 3,48 (2H, q, J=7,5; 1-α-CH_2); 7,26...8,30 (5H, m, H_{arom})
Ic	1,67 (6H, d, J=7; 1-β,β-CH_3); 3,00 (3H, s, 3-CH_3); 4,07 (1H, q, J=7; 1-α-CH); 7,38...8,45 (5H, m, H_{arom})
IIa	2,42 (3H, s, 3-CH_3); 2,97...3,18 (4H, m, 1-β,β-CH_2); 3,80...4,01 (4H, m, 1-α,α-CH_2); 6,83...8,12 (7H, m, H arom NH)
IIb	2,34 (3H, s, 3-CH_3); 2,40 (3H, s, 2-CH_3); 3,41...3,75 (4H, m, 1-β,β-CH_2); 4,00...4,50 (4H, m, 1-α,α-CH_2); 6,78...7,62 (5H, m, H_{arom})
IIc	1,74...2,21 (6H, m, 1-β,β,γ-CH_2); 2,43 (3H, s, 3-CH_3); 3,30...4,04 (4H, m, 1-α,α-CH_2); 6,91...7,94 (6H, m, H_{arom})
IId	1,37...1,77 (6H, m, 1-β,β,γ-CH_2); 2,36 (6H, s, 2- and 3-CH_3); 2,90...3,70 (4H, m, 1-α,α-CH_2); 7,00...8,17 (5H, m, H_{arom})
IIe	2,51 (3H, s, 3-CH_3); 3,29 (3H, s, N—CH_3); 3,93...5,01 (8H, m, 1-α,α,β,β-CH_2); 7,13...8,13 (6H, m, H_{arom})
IIf	2,50 (3H, s, 3-CH_3); 2,62 (3H, s 2-CH_3); 3,30 (3H, s, N—CH_3); 4,05...4,53 (8H, m, 1-α,α,β,β-CH_2); 7,15...8,13 (5H, m, H_{arom}); 8,87 (2H, s, arom. protons of picric acid)
IIIa	1,38 (3H, t, J=7,5; 1-β-CH_3); 2,95 (2H, q, J=7,5; 1-α-CH_2); 3,68...4,58 (8H, m, 3-α,α,β,β-CH_2); 7,07...8,13 (6H, m, H_{arom})
IIIb	1,40 (6H, d, J=7; 1-β,β-CH_3); 3,22...3,68 (1H, q, J=7; 1-α-CH); 3,83...4,70 (8H, m, 3-α,α,β,β-CH_2); 7,16...8,32 (6H, m, H_{arom}.)
IIIc	1,39 (3H, t, J=7,5; 1-β-CH_3); 1,93...2,30 (6H, m, 3-β,β,γ-CH_2); 2,92 (2H, q, J=7,5; 1-α-CH_2); 3,42...3,85 (4H, m, 3-α,α-CH_2); 7,12...8,07 (6H, m, H_{arom}.)
IIId	1,75...2,25 (6H, m, 3-β,β,γ-CH_2); 1,44 (6H, d, J=7; 1-β,β-CH_3); 3,20...3,86 (5H, m, 1-α-CH and 3-α,α-CH_2); 7,15...8,30 (6H, m, H_{arom}.)
IIIe	1,46 (3H, t, J=7,5; 1-β-CH_3); 3,07 (2H, q, J=7,5; 1-α-CH_2); 3,30 (3H, m, N—CH_3); 4,05...4,47 (8H, m, 3-α,α,β,β-CH_2); 7,22...8,20 (6H, m, H_{arom}.) 9,00 (2H, s, arom. protons of picric acid)
IIIf	1,29 (6H, d, J=7,5; 1-β,β-CH_3); 2,28 (3H, s, 3-N—CH_3); 2,46...2,67 (4H, m, 3-β,β-CH_2); 2,87...3,28 (5H, m, 1-α-CH and 3-α,α-CH_2); 6,92...8,03 (7H, m, H_{arom}.)
V	2,55 (3H, s, 3-CH_3); 3,91...4,19 (4H, m, 1-β,β-CH_2); 4,05 (3H, s, 9-CH_3); 4,25...4,55 (4H, m, 1-α,α-CH_2); 7,06...8,10 (6H, m, H_{arom}.)

*The spectra of (Ib, c), (IIa-e), and (V) were obtained in CF_3COOH, (IIa) and (IIIf) in $CDCl_3$, and (IId) in deuteropyridine.

In order to assess the effect of a substituent at the indole nitrogen on the course of the reaction, recyclization of the salt (IV) was carried out with morpholine. The resulting aminocarbazole was identical to the product of methylation of the carbazole (IIa), enabling it to be assigned the structure of the 1-isomer (V).



The position of the amino-group in the carbazoles (IIa, c, e) and (V) was established unambiguously by x-ray diffraction examination of the carbazole (V), confirming their assignment to the 1-isomer series.

The small number of reflections was probably due to the poor quality of the crystal, resulting in low precision of measurement of the bond lengths and valence angles in the (V) molecule), so that these geometric parameters are not discussed in detail (Tables 3 and 4). It is, however, worthy of note that the mean values of these bonds and valence angles (Fig. 1) are in general agreement with those found for other carbazoles [7, 8].

The five-membered (A) and six-membered (B, C) rings are planar to within 0.01 and 0.02 Å respectively. The methyl group attached to nitrogen departs from the plane of ring A by 0.1 Å. Both the six-membered rings B and C in (V) are deflected from the central five-membered ring A on the same side, their mean square planes forming dihedral angles of 2.4° with the plane of ring A. Such small, but appreciable flexions are also present in N-methylcarbazole [7].

TABLE 3. Valence Angles

Angle	ω°	Angle	ω°
$C_{(1)}$—$N_{(1)}$—$C_{(16)}$	115(1)	$C_{(13)}$—$N_{(9)}$—$C_{(14)}$	118(1)
$C_{(1)}$—$N_{(1)}$—$C_{(19)}$	119(1)	$C_{(10)}$—$N_{(9)}$—$C_{(14)}$	133(1)
$C_{(19)}$—$N_{(1)}$—$C_{(16)}$	107(1)	$N_{(9)}$—$C_{(10)}$—$C_{(11)}$	113(1)
$C_{(18)}$—$O_{(1)}$—$C_{(17)}$	114(1)	$N_{(9)}$—$C_{(10)}$—$C_{(1)}$	129(1)
$C_{(10)}$—$C_{(1)}$—$C_{(2)}$	118(1)	$C_{(1)}$—$C_{(10)}$—$C_{(11)}$	118(1)
$C_{(10)}$—$C_{(1)}$—$N_{(1)}$	122(1)	$C_{(10)}$—$C_{(11)}$—$C_{(12)}$	105(1)
$N_{(1)}$—$C_{(1)}$—$C_{(2)}$	119(1)	$C_{(10)}$—$C_{(11)}$—$C_{(4)}$	119(1)
$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	123(1)	$C_{(4)}$—$C_{(11)}$—$C_{(12)}$	135(1)
$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	120(1)	$C_{(11)}$—$C_{(12)}$—$C_{(13)}$	108(1)
$C_{(2)}$—$C_{(3)}$—$C_{(15)}$	117(1)	$C_{(11)}$—$C_{(12)}$—$C_{(5)}$	132(1)
$C_{(4)}$—$C_{(3)}$—$C_{(15)}$	123(1)	$C_{(13)}$—$C_{(12)}$—$C_{(5)}$	119(1)
$C_{(3)}$—$C_{(4)}$—$C_{(11)}$	122(1)	$C_{(12)}$—$C_{(13)}$—$N_{(9)}$	105(1)
$C_{(12)}$—$C_{(5)}$—$C_{(6)}$	117(1)	$C_{(8)}$—$C_{(13)}$—$C_{(12)}$	124(1)
$C_{(5)}$—$C_{(6)}$—$C_{(7)}$	124(1)	$C_{(8)}$—$C_{(13)}$—$N_{(9)}$	118(1)
$C_{(6)}$—$C_{(7)}$—$C_{(8)}$	116(1)	$N_{(1)}$—$C_{(16)}$—$C_{(17)}$	111(1)
$C_{(7)}$—$C_{(8)}$—$C_{(13)}$	120(1)	$C_{(16)}$—$C_{(17)}$—$O_{(1)}$	108(1)
$C_{(13}$—$N_{(9)}$—$C_{(10)}$	109(1)	$C_{(1)}$—$C_{(18)}$—$C_{(19)}$	109(1)
		$C_{(18)}$—$C_{(19)}$—$N_{(1)}$	110(1)

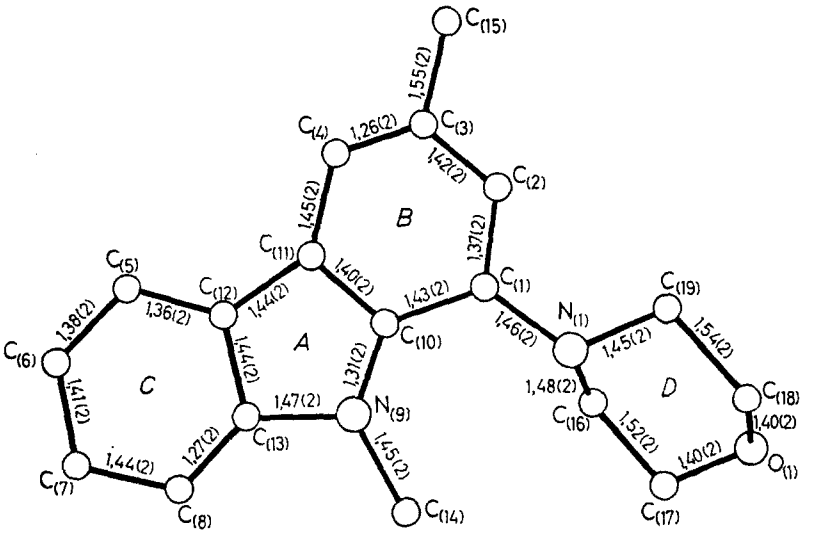
TABLE 4. Atom Coordinates ($\times 10^4$, for Coordinates y $\times 10^3$)*

Atom	x	y	z
$O_{(1)}$	1652(5)	229(1)	9803(5)
$N_{(1)}$	1568(6)	−180(1)	7984(4)
$C_{(1)}$	851(7)	−199(1)	8890(6)
$C_{(2)}$	272(8)	−290(2)	9176(6)
$C_{(3)}$	−178(8)	−423(2)	8932(6)
$C_{(4)}$	−6(8)	−471(2)	8442(6)
$C_{(5)}$	738(9)	−511(2)	7126(6)
$C_{(6)}$	1146(96)	−488(2)	6626(6)
$C_{(7)}$	1763(9)	−366(2)	6536(6)
$C_{(8)}$	1931(8)	−256(2)	7001(6)
$N_{(9)}$	1269(6)	−60(1)	9172(4)
$C_{(10)}$	1054(7)	250(2)	8337(5)
$C_{(11)}$	605(7)	−384(1)	8104(5)
$C_{(12)}$	890(8)	−397(2)	7535(7)
$C_{(13)}$	1524(7)	−272(2)	7452(6)
$C_{(14)}$	2187(9)	−50(2)	8046(7)
$C_{(15)}$	−831(9)	−513(2)	9302(7)
$C_{(16)}$	923(8)	108(2)	9049(5)
$C_{(17)}$	1514(8)	246(2)	9229(6)
$C_{(18)}$	1993(8)	74(2)	9955(6)
$C_{(19)}$	1406(8)	−68(2)	9769(6)

*The anisotropic temperature factors may be obtained from the authors.

The heterocycle D has the chair conformation. The modified Kremer—Pople parameters [9] are Q = 1.57 Å, θ = 171.2°, and ψ = 139.6°. Atoms $N_{(1)}$ and $O_{(1)}$ stand out from the plane $C_{(16)}C_{(17)}C_{(18)}C_{(19)}$ by 0.7 and 0.6 Å respectively. The mean square plane of the morpholine ring forms a dihedral angle of 122° with the plane of the six-membered ring B.

There were no shortened intermolecular components in the structure.



Molecular structure of (V).

EXPERIMENTAL

PMR spectra were obtained on a Tesla BS-467 (60 MHz) instrument, internal standard TMS. The purity of the carbazoles obtained was checked by TLC on Silufol UV-254 plates in the systems: benzene—propan-2-ol, 3:1 (for IIa, b), (IIIa), and (V)), benzene—propan-2-ol—pyridine, 5:5:5:1 (sic – translator) (for (IIc-e) and (IIIb, c, f)), and ethanol—pyridine, 20:1 (for (IIf) and (IIIe)).

The perchlorates (Ia) and (IV) have been reported [10, 11], and the salts (Ib) and (Ic) were obtained similarly.

The properties of the compounds obtained are shown in Tables 1 and 2. The elemental analyses for C, H, Cl, and N for compounds (Ib, c), (IIa-f), (IIIa-f), and (V) were in agreement with the calculated values.

1-Morpholino-3-methylcarbazole (IIa). A mixture of 2.98 g (0.01 mole) of the perchlorate (Ia) and 43.6 g (0.5 mole) morpholine was boiled for 4 h. Excess morpholine was then distilled off, and the residue treated with 50 ml of water. The solid which separated was filtered off, washed with water, and dried to give 2 g (75%) of product.

Similarly, from (Ia) and piperidine there was obtained the aminocarbazole (IIc), and from (Ic) and morpholine, piperidine, and N-methylpiperazine were obtained from the aminocarbazoles (IIIb), (IIId), and (IIIf) respectively.

1-Morpholino-3,9-dimethylcarbazole (V). A mixture of 3.1 g (0.01 mole) of the perchlorate (IV) and 43.6 g (0.5 mole) of morpholine was boiled for 4 h, and the excess morpholine distilled off. The residue was dissolved in 150 ml of benzene, washed with 3% sodium hydroxide followed by water until neutral, and dried over potassium carbonate. The benzene was distilled off, and the residue recrystallized from hexane to give 1.85 g (66%) of product.

1-(N-Methylpiperazino)-3-methylcarbazole (IIe) was obtained similarly from 0.01 mole of the perchlorate (Ia) and 0.5 mole of N-methylpiperazine. The residue following removal of the benzene was dissolved in 10 ml of ethanol and treated with ethereal hydrogen chloride to pH 2. The precipitated (IIe) dihydrochloride was filtered off, washed with ether, and dried to give 1.1 g (31%) of product.

Recyclization of the perchlorate (Ib) (0.01 mole) with morpholine, piperidine, and N-methylpiperazine was carried out as described above for the aminocarbazole (V), giving mixtures of aminocarbazoles (IIb) and (IIIa), (IId) and (IIIc), and (IIf) and (IIIe) respectively.

Separation of Aminocarbazoles (IIb) and (IIIa). The mixture of aminocarbazoles (2.1 g) was dissolved in 20 ml of dichloromethane, and chromatographed on a column (diameter 3 cm) of neutral alumina L 40/250 (CHEMAPOL). Elution with dichloromethane gave 1.2 g (43%) of the isomer (IIb), and then with benzene, 0.3 g (11%) of isomer (IIIa).

Separation of Aminocarbazoles (IId) and (IIIc). The mixture of aminocarbazoles (2.2 g) was dissolved in 30 ml of ethanol, 100 ml of 5% hydrochloric acid added, and the mixture heated at 70°C until a clear solution was obtained. The (IId) hydrochloride separated on slow cooling, and was filtered off and dried (1.2 g, 38%). The filtrate was evaporated under reduced pressure, and the residue recrystallized from propan-2-ol to give 0.38 g (12%) of (IIIc).

Separation of Aminocarbazoles (IIf) and (IIIe). The mixture of aminocarbazoles (2 g) was dissolved in 50 ml of ether, and a solution of 5.7 g (0.025 mole) of picric acid in 100 ml of ether added. The solid which separated was filtered off, washed with ether, and dried in vacuo to give 3.5 g (67%) of a mixture of picrates of (IIf) and (IIIe), mp 190-200°C (decomp.). The mixed picrates (1.5 g) were stirred with 50 ml of methanol at 20°C for 3 h. The insoluble residue was filtered off, washed with a small amount of methanol, and recrystallized from water to give 0.15 g (10%) of (IIIe) picrate. The methanolic filtrate was evaporated under reduced pressure, and the residue crystallized from ethanol to give 0.3 g (20%) of (IIf) picrate. Chromatography of these compounds on Silufol UV-254 plates in the system ethanol—pyridine (20:1) resulted in dissociation of the picrates to give the free bases, which showed characteristic blue fluorescence under UV, and picric acid (R_f 0.82, yellow spot in ordinary light).

Methylation of 1-Morpholino-3-methylcarbazole (IIa) and X-Ray Diffraction Examination of 1-Morpholino-3,9-dimethylcarbazole (V). To a solution of 2.66 g (0.01 mole) of the carbazole (IIa) in 20 ml of benzene was added 10 ml of a 50% solution of sodium hydroxide, followed by 0.14 g (0.5 mmole) of triethylbenzylammonium bromide. A solution of 1.5 g (0.012 mole) of dimethyl sulfate in 10 ml of benzene was then added with vigorous stirring over 30 min, and the mixture stirred for 2 h at 20°C and 30 min at 50°C. The mixture was cooled, extracted with benzene (3 × 50 ml), the extract washed with water until neutral, dried over potassium carbonate, and evaporated. The residue was recrystallized twice from hexane, to give 2.5 g (89%) of the carbazole (V), mp 125-126°C. The analytical and spectral properties of the product were identical with those of the product of recyclization of the perchlorate (IV) with morpholine.

The crystals of (V) were rhombic, with (at 20°C) a = 16.216(2), b = 7.9542(9), c = 23.965(3) Å, space group Pbca. The elementary cell parameters and the intensities of 647 independent reflections, 552 of which had $I \geq 2\sigma$, used in the subsequent calculations, were obtained on a Hilger-Watts automatic four-circle diffracometer (λ_{MoK_α}, graphite monochromator, $\theta/2\theta$ scanning, $\theta \leq 24°$). The structure was calculated directly using the MULTAN program, and refined by least squares in isotropic approximation for all the nonhydrogen atoms. All the hydrogen atoms save two, located from the difference series, were placed in the calculated positions with $B_{iso} = 6$ Å^2, and were not refined. The final values of the divergence factors were R = 0.081 and $R_w = 0.065$. All calculations were carried out on an Eclipse/200 computer using the INEXTL programs [12].

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INVESTIGATION OF AZOLES AND AZINES.

75.* STRUCTURE OF 2-ARYL-1,3-OXAZINE-4,6-DIONES IN THE GAS PHASE

V. É. Zakhs, I. V. Viktorovskii, and B. A. Ivin

UDC 547.867.2:541.623:543.51'

The mass-spectrometric fragmentation of a number of potentially tautomeric 2-aryl-1,3-oxazine-4,6-diones and model substances that fix the possible tautomeric forms was studied. The characteristic fragmentation pathways that are peculiar to one or another tautomer and the characteristic ions that make it possible to identify them in tautomeric mixtures were ascertained. It is shown that in the gas phase 2-aryl-1,3-oxazine-4,6-diones exist in mixtures of 4-hydroxy, 6-oxo, dipolar-ionic, and dicarbonyl forms; the amounts of the latter two forms increase with intensification of the electron-acceptor properties of the substituent in the para position of the benzene ring.

Inasmuch as they are trans-fixed β-dicarbonyl compounds, 2-aryl-1,3-oxazine-4,6-diones I can exist in four tautomeric forms:

*See [1] for Communication 74.

Leningrad Institute of Pharmaceutical Chemistry, Leningrad 197022. All-Union Scientific-Research Technological Institute of Antibiotics and Enzymes for Medical Use, Leningrad 198020.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 552-556, April, 1990. Original article submitted December 16, 1987; revision submitted May 3, 1989.

0009-3122/90/2604-0472$12.50