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SYNTHESIS OF AROMATIC DERIVATIVES OF 1,5-BENZODIAZEPINE IN THE REACTION OF 4-NITRO-o-PHENYLENEDIAMINE WITH CHALCONE DIBROMIDES

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The reaction of 4-nitro-o-phenylenediamine with 4-nitro-4'-R-chalcone dibromides affords the corresponding β-(2-amino-4-nitroanilino)chalcones; x-ray diffraction data indicate that these are the Z-isomers. Experiments have been performed to determine the conditions required for cyclization of these compounds into 2,4-diaryl-7(8)-nitro-1,5-benzodiazepines. In the solid phase or in ethanol solutions, these latter compounds exist primarily in the 3H tautomeric form; but in DMSO solutions, the 1H form predominates.

It was shown in [1] that the interaction of 4-nitro-o-phenylenediamine (I) with 3-(p-nitrophenyl)-1-phenyl-2,3-dibromopropenone (IIa) in the presence of a basic catalyst leads to the formation of the photochromic 1,1a-dihydroazirino[1,2-a]quinoxaline (IIIa) and β-(2-amino-4-nitroanilino)-4-nitrochalcone (IVa). The ratio of these two reaction products depends greatly on the solvent that is used, the length of time the reaction mixture is refluxed, and the content of catalyst in the mixture. The highest yields of IIIa are obtained by refluxing the mixture for 1 h in methanol and then holding at room temperature for one day, with N,N-dimethylbenzylamine as a catalyst [2].

Here we are reporting on work aimed at determining the optimal conditions for the formation of β-aminochalcones (IVa-g), which could then be used to synthesize the corresponding benzodiazepines (Va-g). It was established that the formation of compounds IVa-g is favored by the following: The presence of a nitro group in the benzylidene fragment of the haloketones IIa-g, a twofold to threefold molar excess of triethylamine relative to the original chalcone dibromide, and refluxing the reaction mixture for 4-4.5 h.

Prolonged heating and excess triethylamine accelerate the dehydrobromination of the intermediate bromoketones (VIa-g), which leads to the enaminoketones IVa-g. Under milder conditions, the intermediates VI undergo γ-elimination of HBr, resulting in the formation of the products III, which contain a three-membered aziridine ring. It may be that the original dibromides II are first dehydrobrominated, thus being converted to unsaturated bromides 4-$NO_2C_6H_4CH{=}CBrCOAr$ (VII). Addition of compound I to these unsaturated bromides also leads to the formation of the indicated intermediates VI. The view that bromoolefins VII are formed is supported by the fact that the ratio of reaction products IIIa and IVa is practically independent of whether the initial reactant is the dibromide IIa or the isomeric cis(trans)-bromoolefins VIIa, obtained previously from the IIa (see Experimental section). These bromoolefins were synthesized by dehydrobromination of the dibromide IIa by a procedure given in [3].

Under the conditions described above, dihydroazirinoquinoxalines III were recovered only in the case of the dibromides IIa, b, d, g, and these with yields generally no greater than 10%. Compounds IIIa, b, d, g are yellowish green crystalline substances that change in color upon exposure to light. The existence of reversible photochromism can be considered as an analytical indicator of these products. We also used IR and UV spectra for identification (see Table 1).

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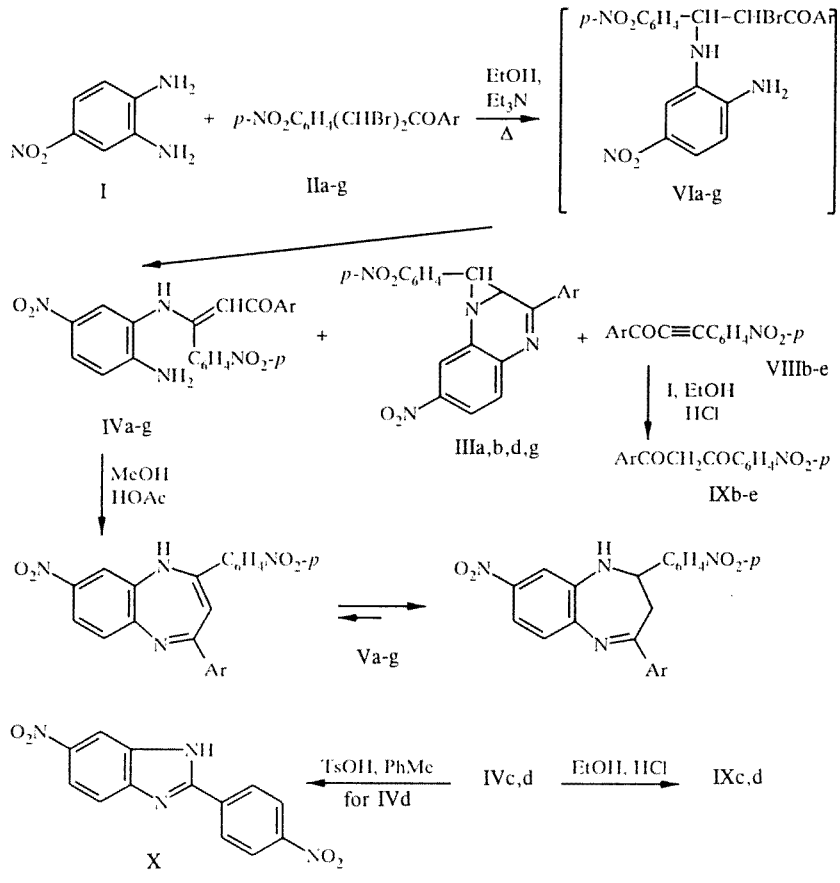

IIa-g, IIIa, b, d, g, IV-Va-g, VIII-IXb-e, and Xa-f Ar = C_6H_4R-p, with R as follows: a) H; b) CH_3; c) Cl; d) Br; e) C_6H_5; f) NO_2; g) Ar = 2-thienyl.

The synthesized β-aminochalcones IVa-g were identified by their spectra. In the IR spectra of these compounds bands of stretching vibrations of the bound carbonyl group are observed in the 1625-1641 cm^{-1} interval. In the 3338-3473 cm^{-1} interval there are two bands; the low-frequency band has a high intensity and apparently represents a superposition of bands of the imino group and symmetric vibrations of the primary amine group.

In the PMR spectra of compound IVa (in DMSO-d_6) we find strong signals of the NH_2 group at 7.0 ppm (2H, s), the fragment =CHC(=O) at 6.4 ppm (1H, s), and aryl substituents at 8.20-8.22 (2H, d), 7.99-8.02 (2H, d), 7.71-7.74 (6H, m), 7.31-7.32 (1H, d), and 6.73-6.76 ppm (1H, d), and also a signal of a proton of the chelate ring at 11.92 ppm (1H, s). In all cases, we observed the formation of only one form of the chalcones IVa-g; according to data obtained on IVa by x-ray structure analysis, this is the Z-isomer.

The structure of compounds IVa,g was also confirmed by mass spectra (see Experimental section), and in the case of the chalcone IVa by x-ray structure analysis as well (see below).

Along with the dihydroazirinoquinoxalines IIIa,b,d,g and β-aminochalcones IVa-g, we found in the reaction products from a number of experiments the acetylenic ketones (VIIIb-e). It was noted that the yields of these latter compounds increase with increasing quantity of added triethylamine. For example, with a fivefold excess of amine relative to the ketone IIb, the yield of compound VIIIb was 58%, in comparison with 18% under the usual conditions. The ketones VIIIb-e are identical in their characteristics (melting point and IR spectrum) with those described previously in [4].

The final products of interaction of compounds VIIIb-e with the diamine I in ethanol in the presence of catalytic quantities of HCl proved to be the corresponding β-diketones (IXb-e). They were identified by means of their UV spectra (see Experimental section). These are evidently formed by hydrolysis of the intermediate β-aminochalcones IVb-e. Evidence for this sequence of stages may be found in the following experimental facts: Compounds IVc,d, upon heating in ethanol with the addition of catalytic quantities of HCl, are converted to the diketones IXc,d. Under more severe conditions, when compound

TABLE 1. Characteristics of Synthesized Compounds IIIb,d,g, IVa-g, and Va-g

Compound	mp, °C	Empirical formula	N, %		UV spectrum, λ_{max} (and $\varepsilon \cdot 10^{-3}$)	IR spectrum*	Yield, %
			found	calculated			
IIIb	187	$C_{22}H_{16}N_4O_4$	13,8	14,0	253(24,7), 350(14,8)	1610, 1510, 1343	< 10
IIId	241...243	$C_{21}H_{13}BrN_4O_4$	11,5	12,0	257(28,0), 347(17,2)	1602, 1520, 1347	< 10
IIIg	203...204	$C_{19}H_{12}N_4O_4S$	14,0	14,3	255(27,2), 352(15,3)	1608, 1517, 1340	25
IVa	220...221	$C_{21}H_{16}N_4O_5$	14,1	13,5	274(20,1), 367(22,3)	1635, 3364, 3473	45
IVb	202...203	$C_{22}H_{18}N_4O_5$	13,0	13,4	272(23,3), 364(20,8)	1641, 3345, 3440	39
IVc	237	$C_{21}H_{15}ClN_4O_5$	12,9	12,8	271(18,9), 365(23,4)	1639, 3339, 3452	35
IVd	238...240	$C_{21}H_{15}BrN_4O_5$	11,2	11,6	273(19,8), 367(22,7)	1640, 3340, 3460	32
IVe	240...241	$C_{27}H_{20}N_4O_5$	11,8	11,7	286 sh, 341(24,0)	1627, 3347, 3448	50
IVf	243...244	$C_{21}H_{15}N_5O_7$	15,9	15,6	271(23,1), 367(21,5)	1625, 3370, 3467	40
IVg	230...231	$C_{19}H_{14}N_4O_5S$	13,6	13,7	275(17,3), 368(22,2)	1640, 3338, 3435	25
Va	256...257	$C_{21}H_{14}N_4O_4$	14,1	14,5	225 sh, 263 sh, 297(28,0)	1600, 1507, 1342	95
Vb	265...266	$C_{22}H_{16}N_4O_4$	14,2	14,0	228 sh, 265 sh, 295(30,2)	1608, 1513, 1347	70
Vc	290...291	$C_{21}H_{13}ClN_4O_4$	13,1	13,3	223 sh, 266 sh, 297(30,4)	1602, 1512, 1340	95
Vd	297...299	$C_{21}H_{13}BrN_4O_4$	12,2	12,0	223 sh, 267 sh, 297(36,9)	1598, 1514, 1341	81
Ve	229...230	$C_{27}H_{18}N_4O_4$	11,8	12,1	230 sh, 248 sh, 320(29,8)	1596, 1506, 1343	49
Vf	295...296	$C_{21}H_{13}N_5O_6$	16,0	16,2	230 sh, 277 sh, 300(32,2)	1601, 1518, 1340	90
Vg	261...262	$C_{19}H_{12}N_4O_4S$	14,0	14,3	228 sh, 265 sh, 296(30,7)	1605, 1513, 1349	72

*$\nu_{C=N}$, ν^s, NO2, ν^{as}NO2 (IIIb,d,g and Va-g); or $\nu_{C=O}$, ν_{N-H} (or ν^sNH), ν^{as}NH (IVa-g).

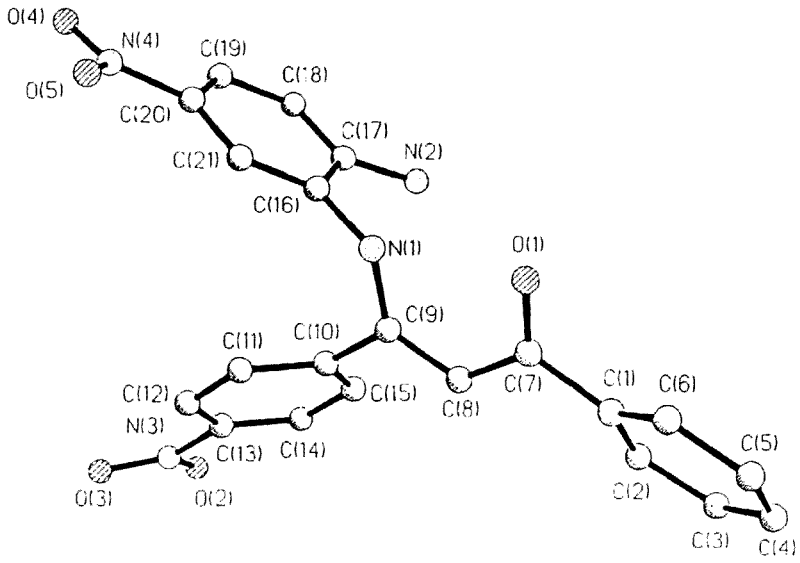

Fig. 1. Structure of molecule of 3-(2-amino-4-nitroanilino)-3-(p-nitrophenyl)-1-phenylpropenone.

IVd in toluene is refluxed in the presence of p-TsOH, 6-nitro-2-(p-nitrophenyl)benzimidazole X is formed; this was identified by its mass spectrum (see Experimental section).

The desired products, the 2,4-diaryl-1,5-benzodiazepines Va-g, were obtained by cyclization of the enaminoketones IVa-g in a 4:1 mixture of acetic acid and methanol. We used as a qualitative indication of diazepine ring formation a test for the formation of the diazatropylium cation [5]. In the IR spectra of compounds Va-g (Table 1) there are bands of stretching vibrations of the azomethine group in the 1595-1608 cm^{-1} region, and also broad bands of symmetric and asymmetric vibrations of the nitro group in the 1340-1349 and 1506-1518 cm^{-1} regions, respectively. Bands of stretching vibrations of the secondary amino group in the 3200-3500 cm^{-1} interval were not observed.

In the electronic absorption spectra of the benzodiazepines Va-g, measured in ethanol (Table 1), a broad, unstructured band is observed in the 295-297 nm region, also several inflections in the short-wave region. The positions of the absorption bands and the high intensity of the long-wave absorption indicate that compounds Va-g in methanol exist primarily in the dianil form [6].

At the same time, the PMR spectra of the diazepines Va,c (measured in DMSO-d_6) provide evidence more in favor of the 1H tautomeric form, since these spectra do not contain any signals of methylene-group protons. The signals in these spectra were assigned on the basis of data reported in [7] on the PMR spectrum of 2-(4-nitrophenyl)-8-hydroxy-4-phenyl-1H-pyrimido[4,5-d]-1,5-diazepine, in which the region of the aromatic protons is considerably simpler. Thus, in the spectra of compounds Va,c in the weak field (8.38-8.41 ppm), there is a multiplet signal of protons of the 8-nitro-o-phenylenediamine fragment (3H); the signals of the o-protons of the p-nitrophenyl substituent are found in the 8.29-8.33 region (2H, m), and the signals of the m-protons and the =CH fragment of the diazepine ring are found in the 8.17-8.20 ppm region (3H, m). The protons of the phenyl substituent in the diazepine Va are represented by a doublet (2H) and a multiplet (3H) at 7.80 and 7.52-7.54 ppm; two doublets of the protons of the chlorophenyl radical of the diazepine Vc are manifested in the 7.78 and 7.56 ppm regions, respectively. In the spectra of compounds Va,c, measured in DMSO-d_6, we were unable to detect any signals from protons of the NH group.

The diazepine structure of compound Vc is further supported by its mass spectrum (see Experimental section), in which peaks of a molecular ion with *m/z* 420(422) are clearly manifested. The channels of fragmentation include successive splitting out of radicals bound to the aromatic ring, and also detachment of acetylene and chloroacetylene fragments.

Thus, the data obtained in this work provide unambiguous support for the cyclic structure of compounds Va-g.

TABLE 2. Coordinates of Nonhydrogen Atoms ($\times 10^4$) and Hydrogen Atoms ($\times 10^3$) in Molecule of Compound IVa

Atom	x	y	z
$O_{(1)}$	-5010(3)	-4814(2)	3723(2)
$O_{(2)}$	3828(3)	982(2)	400(2)
$O_{(3)}$	998(3)	1995(2)	568(2)
$O_{(4)}$	-3157(3)	-442(2)	6826(2)
$O_{(5)}$	-5986(3)	-784(2)	6130(2)
$N_{(1)}$	-3200(3)	-3114(2)	3996(2)
$N_{(2)}$	1103(3)	-3812(2)	4793(2)
$N_{(3)}$	1976(3)	1081(2)	719(2)
$N_{(4)}$	-4026(4)	-893(2)	6296(2)
$C_{(1)}$	-4204(4)	-5200(2)	2104(2)
$C_{(2)}$	-2472(4)	-5310(2)	1422(2)
$C_{(3)}$	-2550(4)	-6011(2)	857(2)
$C_{(4)}$	-4359(4)	-6581(2)	927(2)
$C_{(5)}$	-6076(4)	-6462(2)	1580(2)
$C_{(6)}$	-6001(4)	-5792(2)	2186(2)
$C_{(7)}$	-4099(4)	-4503(2)	2783(2)
$C_{(8)}$	-2940(4)	-3514(2)	2338(2)
$C_{(9)}$	-2517(4)	-2875(2)	2912(2)
$C_{(10)}$	-1291(4)	-1853(2)	2373(2)
$C_{(11)}$	-2221(4)	-806(2)	2304(2)
$C_{(12)}$	-1153(4)	149(2)	1767(2)
$C_{(13)}$	845(4)	52(2)	1302(2)
$C_{(14)}$	1839(4)	-967(2)	1358(2)
$C_{(15)}$	750(4)	-1926(2)	1897(2)
$C_{(16)}$	-2284(4)	-2687(2)	4728(2)
$C_{(17)}$	-119(4)	-3040(2)	5106(2)
$C_{(18)}$	730(4)	-2615(2)	5823(2)
$C_{(19)}$	-511(4)	-1887(2)	6183(2)
$C_{(20)}$	-2653(4)	-1596(2)	5847(2)
$C_{(21)}$	-3541(4)	-1976(2)	5116(2)
$H_{(1n1)}$	-394(1)	-377(1)	428(1)
$H_{(1n2)}$	63(1)	-383(1)	421(1)
$H_{(2n2)}$	246(1)	-403(1)	511(1)
$H_{(3)}$	-132(1)	-609(1)	46(1)
$H_{(4)}$	-418(1)	-705(1)	48(1)
$H_{(5)}$	-745(1)	-689(1)	169(1)
$H_{(6)}$	-721(1)	-570(1)	265(1)
$H_{(8)}$	-250(1)	-325(1)	158(1)
$H_{(11)}$	-369(1)	-79(1)	266(1)
$H_{(12)}$	-182(1)	88(1)	169(1)
$H_{(14)}$	330(1)	-94(1)	100(1)
$H_{(15)}$	133(1)	-263(1)	193(1)
$H_{(17)}$	-117(1)	-491(1)	141(1)
$H_{(18)}$	228(1)	-288(1)	612(1)
$H_{(19)}$	5(1)	-160(1)	666(1)
$H_{(21)}$	-504(1)	-177(1)	487(1)

The question of the direction of interaction of 4-nitro-o-phenylenediamine with chalcone dibromides was resolved in the example of compound IVa by means of x-ray structure analysis (see Fig. 1 and Tables 2-4). According to these data, the more basic amino group of compound I enters into a reaction of nucleophilic addition at the double bond of the bromoolefin VIa. This view is also supported by data cited above for the diazepines Va,c regarding the chemical shifts of the protons of the 7(8)-nitro-o-phenylenediamine fragment [8].

In [2], where derivatives of azirinoquinoxaline were described, dipole moments were calculated and used as a basis for postulating an alternative direction of interaction of the diamine I with chalcone dibromides. Since the process of forming

TABLE 3. Bond Lengths (Å) in Molecule of Compound IVa

Bond	l	Bond	l	Bond	l
$O_{(1)}-C_{(7)}$	1,250(3)	$C_{(1)}-C_{(6)}$	1,383(4)	$C_{(11)}-C_{(12)}$	1,371(3)
$O_{(2)}-N_{(3)}$	1,213(3)	$C_{(1)}-C_{(7)}$	1,490(4)	$C_{(12)}-C_{(13)}$	1,368(3)
$O_{(3)}-N_{(3)}$	1,221(3)	$C_{(2)}-C_{(3)}$	1,374(5)	$C_{(13)}-C_{(14)}$	1,375(4)
$O_{(4)}-N_{(4)}$	1,225(4)	$C_{(3)}-C_{(4)}$	1,375(4)	$C_{(14)}-C_{(15)}$	1,382(3)
$O_{(5)}-N_{(4)}$	1,221(3)	$C_{(4)}-C_{(5)}$	1,366(4)	$C_{(16)}-C_{(17)}$	1,411(3)
$N_{(1)}-C_{(9)}$	1,358(4)	$C_{(5)}-C_{(6)}$	1,382(5)	$C_{(16)}-C_{(21)}$	1,377(4)
$N_{(1)}-C_{(16)}$	1,426(4)	$C_{(7)}-C_{(8)}$	1,426(4)	$C_{(17)}-C_{(18)}$	1,388(5)
$N_{(2)}-C_{(17)}$	1,372(4)	$C_{(8)}-C_{(9)}$	1,367(5)	$C_{(18)}-C_{(19)}$	1,369(4)
$N_{(3)}-C_{(13)}$	1,471(3)	$C_{(9)}-C_{(10)}$	1,492(3)	$C_{(19)}-C_{(20)}$	1,377(3)
$N_{(4)}-C_{(20)}$	1,452(4)	$C_{(10)}-C_{(11)}$	1,390(4)	$C_{(20)}-C_{(21)}$	1,376(4)
$C_{(1)}-C_{(2)}$	1,393(4)	$C_{(10)}-C_{(15)}$	1,392(3)		

TABLE 4. Bond Angles (deg) in Molecule of Compound IVa

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

the aziridine ring and forming the enamines proceeds through the intermediate VI, the structure of the products obtained in [2] requires a better definition.

According to the data obtained by x-ray structure analysis, in the molecule of the aminochalcone IVa, the enone fragment has the (S)-cis conformation, with the $O_{(1)}-C_{(7)}-C_{(8)}-C_{(9)}$ torsion angle 6.7(4)°. The phenyl and nitrophenyl substituents are rotated 33.7(3)° and 55.2(3)°, respectively, relative to the mean square plane $O_{(1)}$, $C_{(7)}$, $C_{(8)}$, $C_{(9)}$, $N_{(1)}$. Such a conformation of these aromatic rings is due to intramolecular shortening of the contacts $C_{(11)}\ldots N_{(1)}$ 3.02(1) Å, in comparison with a 3.21(1) Å sum of the van der Waals radii [9], also $C_{(11)}\ldots C_{(16)}$ 3.13(1) Å (3.42 Å), $C_{(8)}\ldots C_{(15)}$ 3.09(1) Å, $H_{(2)}\ldots C_{(8)}$ 2.67(1) Å (2.87 Å), $C_{(6)}\ldots O_{(1)}$ 2.85(1) Å (3.00 Å) (in each case, the sum of the van der Waals radii is shown in parentheses). The nitrophenyl fragment is turned very nearly perpendicular to the $N_{(1)}-C_{(9)}$ bond; the torsion angle $C_{(9)}-N_{(1)}-C_{(16)}-C_{(2)}$ is equal to 116.4(2) Å as a consequence of unfavorable nonvalence interactions between the atoms $N_{(1)}-H_{(1N2)}$ [distance 2.44(1)Å] and $C_{(9)}\ldots H_{(1N2)}$ [2.50(1) Å]. The $N_{(1)}$ and $N_{(2)}$ nitrogen atoms have a plane-trigonal configuration (sum of bond angles 360° − 3.2°, and 360° − 2.6°). The shortened intramolecular contacts $C_{(8)}\ldots H_{(1N1)}$ 2.47(1) Å, $C_{(7)}\ldots H_{(1N1)}$ 2.48(1) Å, $N_{(1)}\ldots O_{(1)}$ 2.76(1) Å, $C_{(7)}\ldots N_{(1)}$ 2.91(1) Å, $C_{(9)}\ldots O_{(1)}$ 2.88(1) Å are probably responsible for the increase of the bond angles $C_{(7)}-C_{(8)}-C_{(9)}$ and $N_{(1)}-C_{(9)}-C_{(8)}$ to 124.5(2)° and 122.7(2)°, respectively. The nitro groups are practically coplanar with the benzene rings; the torsion angle $O_{(2)}-N_{(3)}-C_{(13)}-C_{(14)}$ is 9.7(3)°, and the angle $O_{(4)}-N_{(4)}-C_{(20)}-C_{(19)}$ is 6.6(4)°.

In the crystal, the molecules form centrosymmetric dimers through intramolecular hydrogen bonds $H_{(2N2)}...O_{(1')}$ [O...H 2.22(1) Å, N–H...O 129.6°]. We also found a shortened intermolecular contact 2.79(1) Å between the $C_{(7)}$ atom and the $H_{(2N2)}$ atom of the molecule, bound with the base molecule by the symmetric transformation $-x, -1 - y, 1 - z$.

EXPERIMENTAL

X-ray Structure Analysis of Compound IVa. The crystals are triclinic; at 20°C, $a = 6.169(2)$, $b = 12.922(3)$, $c = 12.930(4)$ Å, $\alpha = 6.75(2)°$, $\beta = 87.86(2)°$, $\gamma = 84.65(2)°$, $Z = 2$, $V = 942.9(6)$ Å^3, $d_{calc} = 1.259$ g/cm^3, space group P1. The parameters of the cell and the intensities of 1562 independent reflections with $F > 6\sigma(F)$ were measured in a Siemens P3/PC automatic four-circle diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$ scanning, $2\gamma_{max} = 50°$).

The structure was deciphered by the direct method, using the SHELXTL PLUS program set. The positions of the hydrogen atoms were determined from a difference synthesis of electron density. Refinement in the anisotropic approximation (isotropic for the hydrogen atoms) was carried to $R = 0.039$ ($R_w = 0.037$, $S = 1.67$).

The IR spectra were recorded on an IR-75 spectrometer in KBr tablets; the electronic absorption spectra were recorded on a Specord UV-Vis instrument in ethanol with a $1.5 \cdot 10^{-5}$ M concentration of the substance. The PMR spectra were recorded in Bruker AC-200 and Varian VXR-200 Gemini instruments in DMSO-d_6, internal standard TMS. The mass spectra were obtained in a Finnigan MAT 4615P instrument under standard conditions. The purities of the products were monitored by means of TLC on Silufol UV-254 plates, with chloroform as the solvent.

Elemental analyses of the synthesized compounds for nitrogen matched the calculated values (see Table 1).

β-(2-Amino-4-nitroanilino)-4-nitro-4′-R-chalcones (IVa-g); 4-Nitro-1-(p-nitrophenyl)-8-(p-R-phenyl)-1,8a-dihydroazirino[1,2-a]quinoxalines (IIIa,b,d,g); and 1-(p-R-Phenyl)-3-(p-nitrophenyl)-2-propyn-1-ones (VIIIb-e).

A. A mixture of 0.41 g (2.7 mmoles) of the diamine I, 1.2 g (2.9 mmoles) of chalcone dibromide IIa, and 2.0 ml of Et_3N in 60 ml of ethanol was refluxed for 4 h. The solvent was removed in a rotary evaporator, and the residue was crystallized from a 1:3 mixture of chloroform and methanol, obtaining compound IVa. After one day, 0.6 g of the known photochromic product IIIa [2] was recovered from the mother liquor. Analogously, starting with the dibromides IIb-g, the products IVb-g and IIIb,d,g were obtained. Upon evaporation of the mother liquor down to 1/3 of the original volume, the ketones VIIIb-e were recovered.

Compound IVa. Mass spectrum, *m/z* (and *I*, %): 404(33), 403(12), 386(74), 385(28), 339(10), 299(22), 282(32), 193(9), 164(10), 120(8), 105(100), 77(55).

Compound IVg. Mass spectrum, *m/z* (and *I*, %): 410(10), 352(58), 299(19), 285(14), 284(27), 254(8), 238(9), 208(7), 192(13), 180(5), 164(20), 126(25), 110(100), 102(6), 90(7), 76(5).

Compound VIIIb. Yield 18%, mp 165°C (literature mp [4] 165°C). IR spectrum: 1630, 2215 cm^{-1}.

Compound VIIIc. Yield 25%, mp 172-173°C (literature mp [4] 172°C). IR spectrum: 1627, 2215 cm^{-1}.

Compound VIIId. Yield 20%, mp 177-178°C (literature mp [4] 177-178°C). IR spectrum: 1628, 2218 cm^{-1}.

Compound VIIIe. Yield 20%, mp 196-197°C (literature mp [4] 197-198°C). IR spectrum: 1635, 2210 cm^{-1}.

B. A mixture of 0.3 g (2.0 mmoles) of the diamine I and 0.66 g (2.0 mmoles) of the cis-bromoolefin VIIa in 40 ml of ethanol was refluxed for 3.5-4 h. The solvent was removed in a rotary evaporator, and the residue was crystallized from a 1:3 mixture of chloroform and methanol, obtaining 0.32 g (40%) of the chalcone IVa. From the mother liquor, 0.04 g of compound IIIa was recovered.

The same compounds were obtained when using the trans isomer of VIIa; the reaction was completed in 3 h (monitored by TLC).

C. A mixture of 0.69 g (4.5 mmoles) of the diamine I, 2.0 g (4.5 mmoles) of the dibromide IIb, and 3.5 ml of Et_3N in 40 ml of ethanol was refluxed for 2 h. The reaction mixture was allowed to stand for one day, and the resulting precipitate was crystallized from methanol, obtaining 0.74 g (58%) of compound VIIIb, identical to the above-described sample of VIIIb with respect to melting point and IR spectrum.

1-(p-R-Phenyl)-3-(p-nitrophenyl)-1,3-propanediones (IXb-e).

D. A solution of 0.6 g (1.4 mmoles) of the enaminoketone IVc in 40 ml of ethanol, containing 3 drops of concentrated HCl, was refluxed for 30 min. The precipitate that formed upon cooling was filtered off, obtaining 0.2 g (42%) of compound IXc, mp 170°C (from ethanol) (literature mp [10] 170°C).

Analogously, from 0.1 g (0.2 mmole) of the enaminoketone IVd in 15 ml of ethanol, obtained 0.04 g (57%) of compound IXd, mp 170-171°C (from ethanol).

E. A solution of 0.1 g (0.3 mmole) of the ketone VIIId and 0.05 g (0.3 mmole) of the diamine I in 20 ml of ethanol, containing 2 drops of concentrated HCl, was refluxed for 1 h. The precipitate was filtered off, obtaining 0.04 g (38%) of the diketone IXd, identical to the sample of IXd described above.

Analogously, starting with the ketones VIIIb,c,e, obtained compounds IXb,c,e.

Compound IXb. Yield 45%, mp 162-163°C (literature mp [10] 161-162°C). UV spectrum: 265, 355 nm (EtOH).

Compound IXc. Yield 40%, mp 170°C (literature mp [10] 170°C).

Compound IXd. Yield 38%, mp 170-171°C. UV spectrum: 265, 358 nm (EtOH).

Compound IXe. Yield 50%, mp 180-182°C. UV spectrum: 279, 365 nm (EtOH).

5(6)-Nitro-2-(p-nitrophenyl)benzimidazole (X). A solution of 0.48 g (1.0 mmole) of the enaminoketone IVd and 10 mg of p-toluenesulfonic acid in 20 ml of toluene was refluxed for 2 h. The solvent was evaporated, and the residue was recrystallized from methanol, obtaining 0.16 g (55%) of compound X, mp 275-276°C (literature mp [11] 276-277°C). Mass spectrum, *m/z* (and *I*, %): 284(12), 283(97), 282(100), 268(43), 236(14), 192(18), 161(25), 150(11), 119(63), 91(43), 69(54).

7-Nitro-4-(p-nitrophenyl)-2-phenylbenzo[b]-1,5-diazepine (VIa). A mixture of 0.81 g (2.0 mmoles) of compound IVa and 60 ml of acetic acid in 15 ml of methanol was refluxed for 20 min. During this time of refluxing, the solution became clear, and a light yellow crystalline precipitate of compound Va was formed. Mass spectrum, *m/z* (and *I*, %): 422(27), 420(80), 346(12), 345(68), 373(22), 339(32), 327(13), 292(8), 227(8), 210(15), 190(22), 139(32), 137(100), 111(8), 102(71).

Analogously, from ketones IVc-g, obtained compounds Vc-g (Table 1).

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